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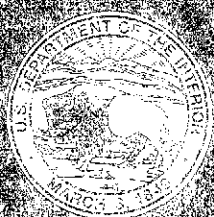
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Cyanide Chemistry: Flotation, Metals Processing and Waste Treatment



UNITED STATES DEPARTMENT OF THE INTERIOR

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Information Circular 9429

Cyanide Chemistry—Precious Metals Processing and Waste Treatment

By Charles M. Flynn, Jr., and Sandra McGill Haslem

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Bruce Babbitt, Secretary**

**BUREAU OF MINES
Rhea Lydia Graham, Director**

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CONTENTS

	<i>Page</i>
Abstract	1
Chapter 1.—General introduction	2
Introduction	2
Purpose of this publication	2
Content and organization of this publication	2
Data not included in this publication	3
References	3
Chapter 2.—Nomenclature	5
Introduction	5
Forms of cyanide	5
Free cyanide	5
Complexed cyanide	5
Species derived from cyanide	6
Auxiliary species	14
Metal species	14
References	14
Chapter 3.—Survey of cyanides of the elements	16
Introduction	16
Survey of cyanides of the elements	16
Alkali and alkaline earth metals	16
Lanthanide and actinide metals	16
Transition metals	16
Posttransition metals	16
Boron group	16
Carbon group	18
Nitrogen group	18
Oxygen group	18
Halogen group	18
Rare gas group	18
References	18
Chapter 4.—Chemical equilibria	19
Introduction	19
Fundamental thermodynamic equations	19
Individual species	19
Chemical reactions	19
Redox reactions	20
Activity, activity coefficients, and equilibrium constants	20
Data and sources	21
Data requirements	21
Summary of data tables	22
Additional details concerning data for metal species	22
Equilibrium predominance area diagrams	24
Variables in EPAD for aqueous systems	24
Solution species	24
Solid phases	24
Gaseous species	24
Construction of EPAD	24
Reliability of EPAD	25
Information obtainable by inspection of log K data	25
Example 1: polyprotic acid	25
Example 2: hydrolyzable metal ion	26
Example 3: metal complex formation	27

CONTENTS—Continued

	<i>Page</i>
Example 4: metal complex formation with disproportionation	28
Example 5: metal complex formation with a hydrolyzable metal ion and a ligand derived from a weak acid	28
Example 6: generation of additional EPAD	31
References	32
Chapter 5.—Ultraviolet and visible spectra	33
Introduction	33
Absorption of light by chemical species	33
Data presentation	33
Free cyanide and derived species	34
Metal cyanide species	34
Auxiliary species	34
References	40
Chapter 6.—Infrared spectra	43
Introduction	43
Free cyanide and derived species	43
Metal cyanide species	43
Metal thiocyanate species	43
References	43
Chapter 7.—Reactions of free cyanide and derived species	46
Introduction	46
General remarks	46
Reaction rate fundamentals	46
Classification of types of reactions	47
Data organization and presentation	48
Oxidation reactions	49
Oxidation of cyanide to cyanate	49
Oxidation of cyanide to cyanogen	52
Oxidation of cyanide to thiocyanate	52
Oxidation of thiocyanate	53
Other oxidants; mechanism of thiocyanate oxidations	54
Oxidation of cyanate	54
Addition, exchange, and substitution reactions of carbon(II) species	55
Addition reactions	55
Exchange reactions involving ammonia and sulfide	55
Hydrolysis reactions	56
Addition, exchange, and substitution reactions of carbon(III) species	57
Addition reactions	57
Exchange reactions involving ammonia and sulfide	58
Hydrolysis reactions	59
Addition, exchange, and substitution reactions of carbon(IV) species	60
Reactions of cyanogen halides	60
Other addition reactions of carbon(IV) species	62
Exchange reactions involving ammonia and sulfide	63
Hydrolysis reactions	63
Summary of reactions of free cyanide and derived species	65
Redox reactions	65
Water addition and hydrolysis reactions	65
Other reactions	65
Selenium in cyanide process solutions	67
Cyanide degradation in industrial processes	67
References	68

CONTENTS—Continued

	<i>Page</i>
Chapter 8.—Reactions of metal cyanide species	71
Introduction	71
Overview and classification of metal cyanide species	71
Zinc, cadmium, and mercury	71
Copper, silver, and gold	72
Nickel	73
Cobalt	74
Iron	74
Manganese	76
Chromium	77
Vanadium	77
Titanium	78
Summary of metal cyanide destruction reactions	78
Nonoxidative reactions	78
Oxidative reactions	78
Possible formation of fulminates	78
Cementation of metals from cyanide solutions	79
Reaction of metal cyanide species with sulfur or polysulfides	80
Occurrence of other metal complexes in cyanide process solutions	81
References	84
Chapter 9.—Photochemistry of metal cyanide species	87
Introduction	87
Principles of photochemistry	87
Cobalt	88
Iron	88
Chromium	90
Summary of photochemistry of metal cyanide complexes	90
Photocatalytic oxygen oxidation of free cyanide	90
References	90
Chapter 10.—Mixtures of metal cyanide species	92
Introduction	92
Reactions between dissolved metal cyanide species	92
Reactions between anionic metal cyanide species and metal cations	93
Reactions between metal cyanide species and metal cations or oxide species	93
References	102
Chapter 11.—Solution of chemical equilibrium problems	104
Introduction	104
Examples of the use of equilibrium predominance area diagrams	104
Example 1: cyanide safety	104
Example 2: cyanide and carbonates	104
Example 3: cyanide and carbon dioxide	105
Example 4: zinc species in cyanide solutions	105
Example 5: precipitation of zinc cyanide in cyanide systems	105
Example 6: recovery of zinc as zinc cyanide	106
Example 7: decomposition of zinc cyanide species	106
Example 8: mixed metals in cyanide systems—zinc and iron	106
Example 9: pZn-pH diagrams	107
Example 10: reduction of zinc in cyanide solutions	107
Examples of equilibrium constant calculations	108
Example 1: cementation	108
Example 2: gold leaching	108

CONTENTS—Continued

	<i>Page</i>
Example 3: silver versus zinc cyanide species	109
Example 4: regeneration of cyanide from zinc-containing solutions	109
References	109
Chapter 12.—Solution of reaction rate problems	110
Introduction	110
Dependence of reaction rates on pH	110
First-order reactions	111
Second-order reactions	111
Effect of temperature on reaction rates	113
Acknowledgments	114
Glossary	115
Appendix A.—Ionic strength	117
Appendix B.—Thermodynamic data for free cyanide and derived species	118
Appendix C.—Thermodynamic data for auxiliary species	127
Appendix D.—Thermodynamic data for metal species	134
Appendix E.—Equilibrium predominance area diagrams	179
Appendix F.—Rate data for reactions of free cyanide and derived species	265

ILLUSTRATIONS

2-1. Equilibrium distribution diagram for free cyanide versus pH at 25° C and zero ionic strength	5
3-1. Survey of cyanides of the elements	17
7-1. Oxidation of free cyanide	49
7-2. Eh-pH diagrams for oxidants	50
7-3. Log rate constant (log <i>k</i>) versus pH for reaction of cyanide with thiosulfate	53
7-4. Log <i>k</i> versus pH for reaction of thiocyanate with hydrogen peroxide	53
7-5. Addition reactions of free cyanide	56
7-6. Hydrolysis reactions of carbon(II) species	56
7-7. Log <i>k</i> versus pH for addition of water to cyanide	56
7-8. Log <i>k</i> versus pH for hydrolysis of formamide	57
7-9. Addition reactions of cyanogen	57
7-10. Log <i>k</i> versus pH for addition of water to cyanogen	58
7-11. Log <i>k</i> versus pH for disproportionation of cyanoformamide	58
7-12. Reactions of carbon(III) species {NCCXY}	59
7-13. Hydrolysis reactions of carbon(III) species with four nitrogen or sulfur atoms	59
7-14. Hydrolysis reactions of carbon(III) species with three nitrogen or sulfur atoms	60
7-15. Hydrolysis reactions of carbon(III) species with two nitrogen or sulfur atoms	60
7-16. Log <i>k</i> versus pH for hydrolysis of oxamide	61
7-17. Log <i>k</i> versus pH for hydrolysis of oxamic acid	61
7-18. Substitution reactions of cyanogen chloride and subsequent addition reactions	61
7-19. Log <i>k</i> versus pH for hydrolysis of cyanogen chloride	61
7-20. Log <i>k</i> versus pH for addition of water to cyanamide	62
7-21. Log <i>k</i> versus pH for addition of water to cyanate	63
7-22. Hydrolysis reactions of carbon(IV) species	64
7-23. Log <i>k</i> versus pH for hydrolysis of guanidinium ion	64
7-24. Log <i>k</i> versus pH for decomposition of thiourea	64
7-25. Log <i>k</i> versus pH for hydrolysis of urea	65
8-1. Formation of aquodecacyanoferrate and decacyanoferrate species	76
8-2. Formation of undecacyanoferrate species	76
9-1. Photochemical decomposition of hexacyanoferrates	89
10-1. Plots of (log <i>K</i> *)/ <i>n</i> for metal cyanide species	97

ILLUSTRATIONS—Continued

	<i>Page</i>
E-1. pL-pH diagram for free cyanide	181
E-2. pL-pH diagram for free carbonic acid	181
E-3. Eh-pH diagram for free cyanate and cyanide	182
E-4. Eh-pH diagram for sulfur	182
E-5. Eh-pH diagram for sulfur with pCN = 5.0	183
E-6. Eh-pH diagram for sulfur with pCN = 2.0	183
E-7. Eh-pH diagram for selenium	184
E-8. Eh-pH diagram for selenium with pCN = 5.0	184
E-9. Eh-pH diagram for selenium with pCN = 2.0	185
E-10. pZn-pH diagram with no ligands	185
E-11. pZn-pH diagram for pCN = 5.0	186
E-12. pZn-pH diagram for pCN = 4.0	186
E-13. pZn-pH diagram for pCN = 3.0	187
E-14. pZn-pH diagram for pCN = 2.0	187
E-15. pZn-pH diagram for pCO ₃ = 3.0	188
E-16. pZn-pH diagram for pCN = 5.0 and pCO ₃ = 3.0	188
E-17. pZn-pH diagram for pCN = 5.0 and p[Fe(CN) ₆ ⁴⁻] = 4.0	189
E-18. pZn-pH diagram for pCN = 2.0 and pSH = 6.0	189
E-19. pCN-pH diagram for zinc solution species	190
E-20. pCN-pH diagram for pZn = 5.0	190
E-21. pCN-pH diagram for pZn = 4.0	191
E-22. pCN-pH diagram for pZn = 3.0	191
E-23. pCN-pH diagram for pZn = 2.0	192
E-24. pCN-pH diagram for pZn = 4.0 and p[Fe(CN) ₆ ⁴⁻] = 4.0	192
E-25. pZn-pCN diagram for pH = 12.0	193
E-26. pZn-pCN diagram for pH = 11.0	193
E-27. pZn-pCN diagram for pH = 10.0	194
E-28. pZn-pCN diagram for pH = 9.0	194
E-29. pZn-pCN diagram for pH = 8.0	195
E-30. pZn-pCN diagram for pH = 7.0	195
E-31. Eh-pH diagram for pZn = 2.0 and pCN = 2.0	196
E-32. pCd-pH diagram with no ligands	196
E-33. pCd-pH diagram for pCN = 5.0	197
E-34. pCd-pH diagram for pCN = 4.0	197
E-35. pCd-pH diagram for pCN = 3.0	198
E-36. pCd-pH diagram for pCN = 2.0	198
E-37. pCd-pH diagram for pCO ₃ = 3.0	199
E-38. pCd-pH diagram for pCN = 5.0 and pCO ₃ = 3.0	199
E-39. pCd-pH diagram for pCN = 5.0 and p[Fe(CN) ₆ ⁴⁻] = 4.0	200
E-40. pCd-pH diagram for pCN = 2.0 and pSH = 6.0	200
E-41. pCN-pH diagram for cadmium solution species	201
E-42. pCN-pH diagram for pCd = 5.0	201
E-43. pCN-pH diagram for pCd = 4.0	202
E-44. pCN-pH diagram for pCd = 3.0	202
E-45. pCN-pH diagram for pCd = 2.0	203
E-46. pCN-pH diagram for pCd = 4.0 and p[Fe(CN) ₆ ⁴⁻] = 4.0	203
E-47. pCd-pCN diagram for pH = 12.0	204
E-48. pCd-pCN diagram for pH = 11.0	204
E-49. pCd-pCN diagram for pH = 10.0	205
E-50. pCd-pCN diagram for pH = 9.0	205
E-51. pCd-pCN diagram for pH = 8.0	206

ILLUSTRATIONS—Continued

Page

E-52.	pCd-pCN diagram for pH = 7.0	206
E-53.	Eh-pH diagram for pCd = 2.0 and pCN = 2.0	207
E-54.	pHg-pH diagram for pCN = 5.0	207
E-55.	pHg-pH diagram for pCN = 4.0	208
E-56.	pHg-pH diagram for pCN = 3.0	208
E-57.	pHg-pH diagram for pCN = 2.0	209
E-58.	pHg-pH diagram for pCN = 5.0 and pCl = 3.0	209
E-59.	pHg-pH diagram for pCN = 5.0 and pSCN = 4.0	210
E-60.	pHg-pH diagram for pCN = 5.0 and pS ₂ O ₃ = 4.0	210
E-61.	pHg-pH diagram for pCN = 2.0 and pSH = 6.0	211
E-62.	pCN-pH diagram for mercury solution species	211
E-63.	pCN-pH diagram for pHg = 3.0	212
E-64.	pCN-pH diagram for pHg = 2.0	212
E-65.	pCN-pH diagram for mercury solution species with pCl = 3.0	213
E-66.	pCN-pH diagram for mercury solution species with pSCN = 4.0	213
E-67.	pCN-pH diagram for mercury solution species with pS ₂ O ₃ = 4.0	214
E-68.	pHg-pCN diagram for pH = 12.0	214
E-69.	pHg-pCN diagram for pH = 11.0	215
E-70.	pHg-pCN diagram for pH = 10.0	215
E-71.	pHg-pCN diagram for pH = 9.0	216
E-72.	pHg-pCN diagram for pH = 8.0	216
E-73.	pHg-pCN diagram for pH = 7.0	217
E-74.	Eh-pH diagram for pHg = 2.0 and pCN = 2.0	217
E-75.	pCu(I)-pH diagram for pCN = 5.0	218
E-76.	pCu(I)-pH diagram for pCN = 4.0	218
E-77.	pCu(I)-pH diagram for pCN = 3.0	219
E-78.	pCu(I)-pH diagram for pCN = 2.0	219
E-79.	pCu(I)-pH diagram for pCN = 5.0 and pSCN = 4.0	220
E-80.	pCu(I)-pH diagram for pCN = 5.0 and pS ₂ O ₃ = 4.0	220
E-81.	pCu(I)-pH diagram for pCN = 2.0 and pSH = 6.0	221
E-82.	pCN-pH diagram for copper(I) solution species	221
E-83.	pCN-pH diagram for pCu(I) = 5.0	222
E-84.	pCN-pH diagram for pCu(I) = 4.0	222
E-85.	pCN-pH diagram for pCu(I) = 3.0	223
E-86.	pCN-pH diagram for pCu(I) = 2.0	223
E-87.	pCN-pH diagram for copper(I) solution species with pSCN = 4.0	224
E-88.	pCN-pH diagram for copper(I) solution species with pS ₂ O ₃ = 4.0	224
E-89.	pCu(I)-pCN diagram for pH = 12.0	225
E-90.	pCu(I)-pCN diagram for pH = 11.0	225
E-91.	pCu(I)-pCN diagram for pH = 10.0	226
E-92.	pCu(I)-pCN diagram for pH = 9.0	226
E-93.	pCu(I)-pCN diagram for pH = 8.0	227
E-94.	pCu(I)-pCN diagram for pH = 7.0	227
E-95.	pCu(II)-pH diagram with no ligands	228
E-96.	pCu(II)-pH diagram for pCO ₃ = 3.0	228
E-97.	pCu(II)-pH diagram for pCN = 5.0 and p[Fe(CN) ₆ ⁴⁻] = 4.0	229
E-98.	Eh-pH diagram for pCu(II) = 2.0 and pCN = 2.0	229
E-99.	Eh-pH diagram for pCu(II) = 2.0 and pCN = 5.0	230
E-100.	Eh-pH diagram for pCu(II) = 4.0 and pCN = 5.0	230
E-101.	pAg-pH diagram for pCN = 5.0	231
E-102.	pAg-pH diagram for pCN = 4.0	231

ILLUSTRATIONS—Continued

	<i>Page</i>
E-103. pAg-pH diagram for pCN = 3.0	232
E-104. pAg-pH diagram for pCN = 2.0	232
E-105. pAg-pH diagram for pCN = 5.0 and pCl = 3.0	233
E-106. pAg-pH diagram for pCN = 5.0 and pSCN = 4.0	233
E-107. pAg-pH diagram for pCN = 5.0 and pS ₂ O ₃ = 4.0	234
E-108. pAg-pH diagram for pCN = 2.0 and pSH = 6.0	234
E-109. pCN-pH diagram for silver solution species	235
E-110. pCN-pH diagram for pAg = 5.0	235
E-111. pCN-pH diagram for pAg = 4.0	236
E-112. pCN-pH diagram for pAg = 3.0	236
E-113. pCN-pH diagram for pAg = 2.0	237
E-114. pCN-pH diagram for silver solution species with pCl = 3.0	237
E-115. pCN-pH diagram for silver solution species with pSCN = 4.0	238
E-116. pCN-pH diagram for silver solution species with pS ₂ O ₃ = 4.0	238
E-117. pAg-pCN diagram for pH = 11.0	239
E-118. pAg-pCN diagram for pH = 9.0	239
E-119. pAg-pCN diagram for pH = 8.0	240
E-120. pAg-pCN diagram for pH = 7.0	240
E-121. Eh-pH diagram for pAg = 2.0 and pCN = 2.0	241
E-122. pAu(I)-pH diagram for pCN = 5.0	241
E-123. pAu(I)-pH diagram for pCN = 4.0	242
E-124. pAu(I)-pH diagram for pCN = 3.0	242
E-125. pAu(I)-pH diagram for pCN = 2.0	243
E-126. pAu(I)-pH diagram for pCN = 5.0 and pSCN = 4.0	243
E-127. pAu(I)-pH diagram for pCN = 5.0 and pS ₂ O ₃ = 4.0	244
E-128. pCN-pH diagram for gold(I) solution species	244
E-129. pCN-pH diagram for pAu(I) = 5.0	245
E-130. pCN-pH diagram for pAu(I) = 4.0	245
E-131. pCN-pH diagram for pAu(I) = 3.0	246
E-132. pCN-pH diagram for pAu(I) = 2.0	246
E-133. pCN-pH diagram for gold(I) solution species with pCl = 3.0	247
E-134. pCN-pH diagram for gold(I) solution species with pSCN = 4.0	247
E-135. pCN-pH diagram for gold(I) solution species with pS ₂ O ₃ = 4.0	248
E-136. pAu(I)-pCN diagram for pH = 11.0	248
E-137. pAu(I)-pCN diagram for pH = 9.0	249
E-138. pAu(I)-pCN diagram for pH = 8.0	249
E-139. pAu(I)-pCN diagram for pH = 7.0	250
E-140. Eh-pH diagram for pAu = 2.0 and pCN = 2.0	250
E-141. pNi-pH diagram with no ligands	251
E-142. pNi-pH diagram for pCN = 5.0	251
E-143. pNi-pH diagram for pCN = 4.0	252
E-144. pNi-pH diagram for pCN = 3.0	252
E-145. pNi-pH diagram for pCN = 2.0	253
E-146. pNi-pH diagram for pCO ₃ = 3.0	253
E-147. pNi-pH diagram for pCN = 5.0 and pCO ₃ = 3.0	254
E-148. pNi-pH diagram for pCN = 5.0 and p[Fe(CN) ₆ ⁴⁻] = 4.0	254
E-149. pNi-pH diagram for pCN = 2.0 and pS = 6.0	255
E-150. pCN-pH diagram for nickel solution species	255
E-151. pCN-pH diagram for pNi = 5.0	256
E-152. pCN-pH diagram for pNi = 4.0	256
E-153. pCN-pH diagram for pNi = 3.0	257

ILLUSTRATIONS—Continued

	<i>Page</i>
E-154. pCN-pH diagram for pNi = 2.0	257
E-155. pCN-pH diagram for pNi = 4.0 and $p[\text{Fe}(\text{CN})_6^{4-}] = 4.0$	258
E-156. pNi-pCN diagram for pH = 12.0	258
E-157. pNi-pCN diagram for pH = 11.0	259
E-158. pNi-pCN diagram for pH = 10.0	259
E-159. pNi-pCN diagram for pH = 9.0	260
E-160. pNi-pCN diagram for pH = 8.0	260
E-161. pNi-pCN diagram for pH = 7.0	261
E-162. Eh-pH diagram for pNi = 2.0 and pCN = 2.0	261
E-163. pFe(II)-pH diagram with no ligands	262
E-164. pFe(II)-pH diagram for $p\text{CO}_3 = 3.0$	262
E-165. pFe(II)-pH diagram for $p[\text{Fe}(\text{CN})_6^{4-}] = 4.0$	263
E-166. pFe(III)-pH diagram with no ligands	263
E-167. pFe(III)-pH diagram for $p[\text{Fe}(\text{CN})_6^{4-}] = 4.0$	264
E-168. Eh-pH diagram for pFe = 2.0 and $p[\text{Fe}(\text{CN})_6^{4-}] = 4.0$	264

TABLES

2-1. Nomenclature of carbon(II) species derived from cyanide	7
2-2. Nomenclature of carbon(III) species derived from cyanide	8
2-3. Nomenclature of carbon(IV) species derived from cyanide	12
4-1. Existence of metal complexes and basis of thermodynamic data	23
5-1. Ultraviolet-visible spectroscopic data for free cyanide and derived species in aqueous solution	35
5-2. Ultraviolet-visible spectroscopic data for metal cyanide species in aqueous solution	37
5-3. Ultraviolet-visible spectroscopic data for auxiliary species in aqueous solution	39
6-1. Infrared spectroscopic data for free cyanide and derived species	45
6-2. Infrared spectroscopic data for metal cyanide species in aqueous solution	45
7-1. Oxidation reactions of free cyanide and derived species	51
7-2. Conversion of free cyanide to thiocyanate	51
7-3. Water addition and hydrolysis reactions of free cyanide and derived and related species	66
8-1. Comparison of stability constants of metal complexes with cyanide and other ligands	72
8-2. Substitution reactions of pentacyanocobaltates(III)	75
8-3. Substitution reactions of pentacyanoferrates(II)	76
8-4. Nonoxidative decomposition of metal cyanide species	79
8-5. Oxidative decomposition of metal cyanide species	80
8-6. Standard reduction potentials of metal cyanide species at 25° C	81
8-7. Reactions of free cyanide and metal cyanide species with polysulfide ions or sulfur	82
8-8. Minimum free ligand concentrations required for predominance of soluble metal complexes with the ligand	83
10-1. Solubility products of some heavy-metal hexacyanoferrates at 25° C	94
10-2. Relative stabilities of some metal cyanide complexes	95
10-3. Some reactions of metal oxide compounds with cyanide	96
10-4. Reactions of copper(II) with cyanide species	102
B-1. Thermodynamic formation data for free cyanide and derived and related species at 25° C	121
B-2. Equilibrium data for reactions of free cyanide and derived species	123
B-3. Solubilities of solid compounds derived from cyanide in water at 25° C	126
C-1. Thermodynamic formation data for auxiliary species at 25° C	129
C-2. Equilibrium data for reactions of auxiliary species	131
D-1. Standard Gibbs free energies of formation of aqueous metal ions at 25° C	137
D-2. Thermodynamic data for zinc(II) species at 25° C	138
D-3. Thermodynamic data for cadmium(II) species at 25° C	140
D-4. Thermodynamic data for mercury(I) species at 25° C	142

TABLES—Continued

	<i>Page</i>
D-5. Thermodynamic data for mercury(II) species at 25° C	143
D-6. Thermodynamic data for copper(I) species at 25° C	147
D-7. Thermodynamic data for copper(II) species at 25° C	149
D-8. Thermodynamic data for silver(I) species at 25° C	151
D-9. Thermodynamic data for gold(I) species at 25° C	153
D-10. Thermodynamic data for gold(III) species at 25° C	155
D-11. Thermodynamic data for nickel(II) species at 25° C	157
D-12. Thermodynamic data for cobalt(II) species at 25° C	159
D-13. Thermodynamic data for cobalt(III) species at 25° C	161
D-14. Thermodynamic data for iron(II) species at 25° C	163
D-15. Thermodynamic data for iron(III) species at 25° C	165
D-16. Thermodynamic data for manganese(II) species at 25° C	167
D-17. Thermodynamic data for manganese(III) species at 25° C	168
D-18. Thermodynamic data for chromium(III) species at 25° C	170
D-19. Thermodynamic data for thallium(I) species at 25° C	172
D-20. Thermodynamic data for thallium(III) species at 25° C	173
D-21. Thermodynamic data for lead(II) species at 25° C	174
D-22. Thermodynamic data for magnesium(II) species at 25° C	176
D-23. Thermodynamic data for calcium(II) species at 25° C	177
D-24. Thermodynamic data for gallium(III) and indium(III) species at 25° C	178
D-25. Standard Gibbs free energies of formation of heavy-metal selenides at 25° C	178
E-1. Compilation of equilibrium predominance area diagrams in this appendix	180
F-1. Kinetic data for reaction of cyanide with thiosulfate	266
F-2. Kinetic data for oxidation of thiocyanate by hydrogen peroxide	267
F-3. Kinetic data for addition of water to cyanide	268
F-4. Kinetic data for hydrolysis of formamide	269
F-5. Kinetic data for hydrolysis of cyanogen	270
F-6. Kinetic data for disproportionation of cyanoformamide	271
F-7. Kinetic data for hydrolysis of oxamide	272
F-8. Kinetic data for hydrolysis of oxamic acid	273
F-9. Kinetic data for hydrolysis of cyanogen chloride	274
F-10. Kinetic data for addition of water to cyanamide	275
F-11. Kinetic data for addition of water to cyanate	276
F-12. Kinetic data for bicarbonate-catalyzed addition of water to cyanate	278
F-13. Kinetic data for formation of urea from cyanate and ammonia	279
F-14. Kinetic data for hydrolysis of guanidine ion	280
F-15. Kinetic data for decomposition of thiourea	281
F-16. Kinetic data for hydrolysis of urea	282

UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

Metric

cm	centimeter	mg • L ⁻¹	milligram per liter
cm ⁻¹	reciprocal centimeter	min	minute
cm ⁻¹ • M ⁻¹	reciprocal centimeter per mole per liter	mm	millimeter
g • L ⁻¹	gram per liter	mol	mole
h	hour	mol ⁻¹	reciprocal mole
J	joule	mol • L ⁻¹	mole per liter
J	joule per kelvin	(mol • L ⁻¹) ⁻¹ • Pa ⁻¹	reciprocal mole per liter J • K per pascal
J • mol ⁻¹ • K ⁻¹	joule per mole per kelvin	(mol • L ⁻¹) ⁻¹ • Pa ⁻¹ • s ⁻¹	reciprocal mole per liter per pascal per second
J • s	joule second	(mol • L ⁻¹) ⁻¹ • cm ⁻¹	reciprocal mole per liter per centimeter
K	kelvin	(mol • L ⁻¹) ⁻¹ • s ⁻¹	reciprocal mole per liter per second
kJ	kilojoule	(mol • L ⁻¹) ⁻² • s ⁻¹	reciprocal mole per liter squared per second
kJ • mol ⁻¹	kilojoule per mole		
kJ • V ⁻¹ • equiv ⁻¹	kilojoule per volt per equivalent weight	nm	nanometer
kPa	kilopascal	Pa	pascal
L	liter	pct	percent
m	molality (moles solute per kilogram water)	ppm	part per million
M	molarity (moles solute per liter solution)	s	second
M ⁻¹ • s ⁻¹	reciprocal mole per liter per second	s ⁻¹	reciprocal second
M ⁻² • s ⁻¹	reciprocal mole per liter squared per second	s ⁻¹ • K ⁻¹	reciprocal second per kelvin
m • s ⁻¹	meter per second	V	volt
		μm	micrometer
		°C	degree Celsius

U.S. Customary

atm	atmosphere	tr oz/st	troy ounce per short ton
°F	degree Fahrenheit		

SYMBOLS USED IN THIS REPORT

a	activity	N°	Avogadro's number, $6.02 \times 10^{23} \text{ mol}^{-1}$
A	absorbance	pH	$-\log$ (activity of H^+)
c	concentration	pK	$-\log$ (equilibrium constant)
c	speed of light, $2.998 \times 10^8 \text{ m}\cdot\text{s}^{-1}$	pL	$-\log$ (total activity of free ligand species)
e⁻	electron	pM	$-\log$ (total activity of all dissolved metal species)
E	reduction potential; energy	R	gas constant, $8.3145 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$; reactant (reagent) concentration
E°	standard reduction potential	s	stoichiometric coefficient
Eh	reduction potential relative to the standard H^+/H_2 electrode	S°	standard entropy
F	Faraday constant, $96.485 \text{ kJ}\cdot\text{V}^{-1}\cdot\text{equiv}^{-1}$	t	time
h	Planck's constant, $6.626076 \times 10^{-34} \text{ J}\cdot\text{s}$	T	temperature
I	transmitted light intensity; ionic strength	T	light transmitted
I₀	incident light intensity	v	frequency
k	wave number; rate constant	Z	reactant (substrate)
k'	Boltzmann's constant, $1.38066 \times 10^{-23} \text{ J}\cdot\text{K}^{-1}$	β	cumulative equilibria
K	equilibrium constant	γ	activity coefficient
K_a	acidity constant	ε	molar absorptivity
K_c	concentration equilibrium constant	ΔE*	activation energy
l	length	ΔH*	enthalpy of activation
L	ligand	ΔS*	entropy of activation
L	wavelength	Δ_fG°	standard Gibbs energy of formation
M	metal ion	Δ_fH°	standard enthalpy of formation
n	number	Δ_fS°	standard entropy of formation

CYANIDE CHEMISTRY PRECIOUS METALS PROCESSING AND WASTE TREATMENT

By Charles M. Flynn, Jr., ¹ and Sandra McGill Haslem²

ABSTRACT

This U.S. Bureau of Mines publication is a compilation of fundamental cyanide chemistry data obtained through an extensive review of the scientific literature. It includes information on thermodynamics and chemical equilibria, ultraviolet-visible and infrared spectra, and the chemistry and photochemistry of cyanide, chemical species derived from cyanide, and metal cyanide species. It also includes guidance on the use of the data for solving practical problems in precious metals applications.

This publication is intended mainly for use as a reference by personnel in the precious metals industry and regulatory agencies, and other cyanide users, to provide comprehensive information on cyanide chemistry. The document should assist in the formulation of effective policies for cyanide control in the construction, operation, and closure phases of precious metals mining and metallurgical operations. In addition, the data in this publication will be useful in other contexts, such as dealing with industrial cyanide usage, cyanide-containing wastes, and associated environmental problems.

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CHAPTER 1.—GENERAL INTRODUCTION

INTRODUCTION

Cyanide is used widely in industrial processes, including flotation, extractive metallurgy, electroplating, metal cleaning and finishing, pesticide manufacturing, photography, and steel manufacturing. In the precious metals industry, cyanide has been used for a century to extract gold and silver from ore. The cyanidation process is very efficient, being capable of extracting gold from ores as low in grade as 0.01 tr oz/st with over 90-pct efficiency; the recovery of gold from pregnant solutions is equally efficient (1-2).¹

Cyanidation extraction processes differ depending on the type of ore being processed. Consequently, a variety of cyanide complexes of accessory elements in addition to gold and silver cyanide complexes are present during and after processing. Wastes produced from these operations include piles of spent ore from heap leaching and tailings ponds from ores processed in mills. Large variations in ore properties and treatment methods complicate the investigation of the fate of cyanide from these operations (1-10).

Cyanide from these wastes can cause environmental problems because of its toxicity. A thorough understanding of the transport and fate of cyanide in the environment is necessary because the toxicity of cyanide to different organisms varies with the chemical form of the cyanide. The chemical form of the cyanide depends on pH, exposure to light and air, and the presence and chemical forms of metals, e.g. Zn, Cu, and Fe. The transport of these species depends on solubilities, adsorption on materials such as soils and clays, and interactions with biomass. Much research has been published on the toxicity of cyanide, especially cyanide in natural waters (3, 8-10). Because cyanide complexes of different metals commonly occur in precious metals processing wastes, and because the chemical properties of the metal cyanide complexes differ greatly, the toxicity of cyanide varies tremendously depending on the extent to which it is complexed with metals.

PURPOSE OF THIS PUBLICATION

An adequate understanding of the transport and fate of cyanide in the environment and the toxicity of cyanide as a function of its chemical form requires fundamental data on the chemistry of cyanide, species derived from cyanide, and metal cyanide complexes. The pertinent data compiled in this publication are summarized in the next section.

¹Italic numbers in parentheses refer to items in the list of references at the end of this chapter.

This publication is intended mainly for use as a reference by personnel in the precious metals industry, and regulatory agencies, and other cyanide users, to provide comprehensive information on cyanide chemistry in order to assist in the formulation of effective policies for cyanide control in the construction, operation, and closure phases of mining and metallurgical operations. Beyond the field of mining and extractive metallurgy of precious metals, the data in this publication will be useful in dealing with industrial cyanide usage, cyanide-containing wastes, and associated environmental problems.

CONTENT AND ORGANIZATION OF THIS PUBLICATION

The required fundamental data include thermodynamics and chemical equilibria, ultraviolet-visible and infrared spectra, and the chemistry and photochemistry of cyanide, chemical species derived from cyanide, and metal cyanide chemical species. This publication is a compilation of such data obtained via an extensive review of the literature. Guidance on the use of the data for solving practical problems related to precious metals processing is also included. The following paragraphs summarize the importance of these data and the organization of this publication.

Chapter 2 provides information on the nomenclature of chemical species, which is important in order to avoid confusion among the large number of chemical species mentioned in this publication. For metal complexes, modern nomenclature is emphasized and used because older nomenclature can be confusing.

Chapter 3 surveys the cyanides of the elements to show the extent to which the elements form cyanide species important in mining and extractive metallurgy.

Thermodynamic data define the chemical equilibria of cyanide and its metal complexes and the dependence of those equilibria on pH, redox potential, ionic strength, and the presence of different metal compounds. The pertinent thermodynamic theory and equations, the sources and accuracy of the thermodynamic and equilibrium data, and the presentation of equilibrium data in diagrams are described in chapter 4 and appendix A. The data and diagrams are compiled in appendixes B, C, D, and E. As described in chapter 4, many publications that contain thermodynamic and equilibrium data and diagrams for hydrometallurgy are not fully reliable because obsolete data were used. For this publication, much effort was given to obtaining the most recent and reliable data.

The absorption of light by cyanide, chemical species derived from cyanide, metal cyanide species, and other chemical species is important in connection with the fate of these species in the environment and in artificial

cyanide destruction processes. This is particularly important for certain metal cyanide complexes, particularly those of iron. For these reasons, pertinent data on ultraviolet-visible spectra are compiled in chapter 5. Ultraviolet-visible spectra are also useful for the detection and identification of metal cyanide species.

Infrared spectra are useful for identification of free cyanide and derived species such as cyanate and thiocyanate, and metal cyanide complexes. Pertinent infrared spectral data are compiled in chapter 6.

The extent to which chemical equilibria prevail depends on chemical reaction rates. Chemical reaction rates (chemical kinetics) are as important as thermodynamics in determining the fate of cyanide, species derived therefrom, and metal cyanide species in the environment, and the destruction or recovery of cyanide in industrial processes. Slow reaction rates are often encountered in reactions involving oxygen, slightly soluble solids, or the cyanide complexes of certain metals, notably iron. The rates of chemical reactions depend on solution composition, pH, temperature, and the presence of light when light-absorbing substances are involved.

Cyanide undergoes reactions with different oxidants, which are of interest for cyanide's environmental degradation or artificial destruction. Cyanide and the chemical species formed via its oxidation react with water and accessory chemical species such as ammonia and sulfide. All of the chemical species thus formed are eventually converted to carbon oxide species. The rates of these reactions, which differ greatly, are described in chapter 7, with additional data compiled in appendix F.

The chemistry of metal cyanide species is very important with regard to the environmental behavior of cyanide and industrial processes involving cyanide. Cyanide is a very strong complexing agent, and more often than not it may be present as dissolved metal complexes or slightly soluble metal compounds. Metal cyanide species differ greatly in their reactivities with regard to liberation or oxidation of the complexed cyanide. The chemistry of the cyanide species of individual metals is described in chapter 8.

The cyanide complexes of some metals absorb visible and ultraviolet light. This fact is particularly important for certain metal cyanide complexes, notably those of iron, cobalt, and chromium, which are unreactive toward reagents such as acids and oxidants that destroy other metal cyanide species. The absorption of light by the cyanide complexes of iron, cobalt, and chromium results in photochemical reactions that destroy the complexes. These photochemical reactions are important for the environmental degradation of iron, cobalt, and chromium cyanide complexes, and can be utilized with oxidants for their industrial destruction. Chapter 9 describes the photochemical reactions of metal cyanide complexes applicable to their degradation and destruction.

Metal cyanide complexes usually react with other heavy-metal salts or cations to form slightly soluble compounds. This often occurs when metal-containing cyanide solutions become depleted in cyanide, e.g., during treatment with oxidants to destroy cyanide. Metal cyanide complexes may also be deliberately removed from solution by addition of metal compounds such as iron salts. Chapter 10 describes the reactions between different metal cyanide species and other metal compounds, in particular iron salts.

The use of the data in this publication may not appear straightforward to all users. Chapter 11 provides several illustrations of the use of equilibrium predominance area diagrams or thermodynamic data for the solution of practical problems. Chapter 12 serves a similar purpose with regard to reaction rate problems.

Terminology is introduced, defined, and used in the chapters where needed. To further facilitate the use of this publication, definitions of terms are listed in a glossary, which follows chapter 12.

The illustrations and tables in this publication are numbered by chapter or appendix. For example, figure 7-1 is figure 1 in chapter 7, and table D-10 is table 10 in appendix D. References for the sources of data are given at the ends of the respective chapters or appendixes.

There is need for much additional research on the chemical reactions of cyanide, species derived from cyanide, and metal cyanide species. The gaps in current knowledge are evident from the discussions and data in the respective chapters.

DATA NOT INCLUDED IN THIS PUBLICATION

Data on the toxicity, biochemistry, and environmental behavior (beyond fundamental chemistry) of cyanides, analytical procedures for cyanides, and the engineering details of industrial processes are not included in this publication. Information on the toxicity, biochemistry, and environmental behavior of cyanides is available in several sources (3, 8-10). Sources of mining and metallurgical process and waste treatment information are cited above (1-7). Information on the practical analytical chemistry of cyanide and metal cyanide species has been compiled elsewhere (3, 11-13).

REFERENCES

1. McQuiston, F. W., Jr., and R. S. Shoemaker. Cyanidation Plant Practice Monograph. Soc. Min. Eng. AIME, v. 1, 1975, 187 pp; v. 2, 1981, 263 pp.
2. Schlitt, W. J., and W. C. Larson (eds.). Gold and Silver Leaching, Recovery, and Economics. Soc. Min. Eng. AIME, 1981, 148 pp.
3. Smith, A., and T. Mudder. The Chemistry and Treatment of Cyanidation Wastes. Mining Journal Books, London, 1991, 345 pp.
4. Ritcey, G. M. Tailing Management—Problems and Solutions in the Mining Industry. Elsevier, 1989, pp. 604-649.

5. Palmer, S. A. K., M. A. Breton, T. J. Nunno, D. M. Sullivan, N. F. Surprenant. Metal/Cyanide Containing Wastes—Treatment Technologies. Noyes Data Corp., Pollut. Technol. Rev. 158, 1988, pp. 570-702.
6. Stanton, M. D., T. A. Colbert, and R. B. Trenholme. Environmental Handbook for Cyanide Leaching Projects. U.S. Dep. Interior, Nat. Park Serv., Energy, Min., and Miner. Div., 1986, 57 pp.
7. Knocke, W. R. Electroplating and Cyanide Wastes. J. Water Pollut. Control Fed., v. 56, 1984, pp. 667-677.
8. Towill, L. E., J. S. Drury, B. L. Whitfield, E. B. Lewis, E. L. Galyan, and A. S. Hammons. Reviews of the Environmental Effects of Pollutants. V. Cyanide. U.S. EPA, Health Effects Res. Lab., Off. Res. and Dev., Cincinnati, OH, EPA 600/1-78/027, 1978, 200 pp; NTIS PB 28-9920.
9. Huiatt, J. L., J. E. Kerrigan, F. A. Olson, and G. L. Potter (eds.). Workshop on Cyanide From Mineral Processing. UT Min. and Miner. Resour. Res. Inst., 1982, 142 pp.
10. Van Zyl, D. (ed.). Cyanide and the Environment. CO State Univ., Geotech. Eng. Program, Dep. Civil Eng., 1985, v. 1 and 2, 579 pp.
11. U.S. Environmental Protection Agency. Cyanide. Methods 335.1, 335.2, and 335.3. Ch. in Methods for Chemical Analysis of Water and Wastes. EPA-600/4-79-020, 1979.
12. American Society for Testing and Materials. Standard Test Methods for Cyanide in Water. D-2036 in 1982 Annual Book of ASTM Standards. 1982, pp. 110-135.
13. Greenberg, A. E., R. R. Trussell, and L. S. Cleseri (eds.). Standard Methods for the Examination of Water and Wastewater. Am. Public Health Assoc., Am. Water Works Assoc., and Water Pollut. Control Fed., 16th ed. 1985, pp. 327-352.

CHAPTER 2.—NOMENCLATURE

INTRODUCTION

This chapter discusses nomenclature for chemical species of interest in cyanide chemistry. Nomenclature is important because many chemical species have more than one name, which can cause confusion. Causes of multiple names include (1) historical precedent versus modern systematic nomenclature, (2) industrial practice versus nomenclature derived from fundamental principles, (3) different systems of nomenclature, (4) discovery of new chemical species for which older nomenclature is inadequate, (5) the exponential growth of chemical information since World War II, and (6) nomenclature changes in the indexes of Chemical Abstracts (1-8).¹ Modern chemical nomenclature is based on a systematic hierarchy of rules compiled by the International Union of Pure and Applied Chemistry (IUPAC) (9). The indexes of Chemical Abstracts do not always follow the IUPAC rules; sometimes the more familiar historical or industrial names are used. Chemical species names used historically or in industrial practice are often short, well known, and easily remembered. However, they are rarely systematic. The systematically derived names of IUPAC nomenclature can be unwieldy, but their use may cause less confusion.

This chapter outlines nomenclature for forms of cyanide, species derived from cyanide, and other chemical species that may exist in cyanide process streams. The formulas and names of species derived from cyanide are tabulated, and nomenclature for metal species is discussed.

As a rule, modern nomenclature is adopted in this publication. This use will serve to familiarize readers with it; modern nomenclature is also preferred because of the quantity and variety of chemical data compiled in this publication.

FORMS OF CYANIDE

Free Cyanide

Free cyanide is uncomplexed cyanide ion, CN^- , and molecular hydrogen cyanide, HCN (10). They are related by the acid dissociation of HCN :



The concentration of free cyanide is the sum of the CN^- and HCN concentrations, as illustrated in the equilibrium distribution diagram shown in figure 2-1. Figure 2-1 shows the proportions of free cyanide in the CN^- and HCN forms

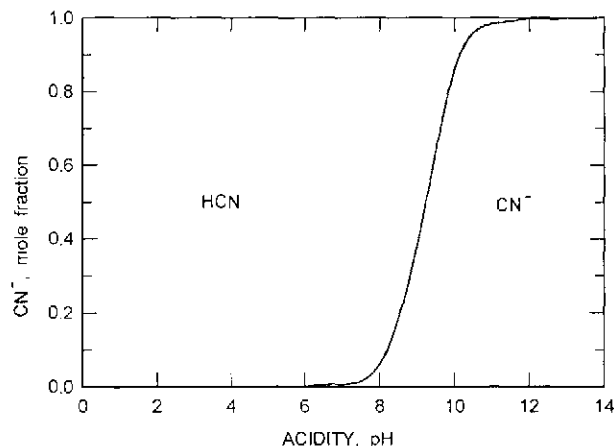
as a function of pH at 25° C and zero ionic strength. At pH above 9.2 CN^- predominates, and at pH below 9.2 HCN predominates. This equilibrium is discussed as an example in chapter 4.

Complexed Cyanide

Cyanide bound to metal ions is referred to as "complexed" cyanide (10). Complexed cyanide may occur as solids $\text{M}(\text{CN})_q(\text{s})$ or dissolved species $[\text{M}(\text{CN})_p]^{q-p}(\text{aq})$, where M^{q+} represents any metal ion of charge or oxidation state $q+$. The strength of the M-CN bonds in complexed cyanides depends on the metal and the CN^- :M mole ratio. The M-CN bond strength is correlated with the equilibrium constant for the formation of the species. The equilibria of some metal cyanides are discussed as examples in chapter 4. A general survey of cyanides of the elements is presented in chapter 3.

Metal cyanide complexes have been classified into two groups in regard to their reactivity with acids (10). The first group of metal cyanide complexes are rapidly and completely decomposed by acids, with all complexed CN^- converted to HCN . These cyanide complexes are termed "weak-acid-dissociable" (WAD). Examples are the cyanide complexes of Zn, Cd, and Ni. The second group of metal cyanide complexes are resistant to decomposition by acids. These cyanide complexes are termed "non-WAD" cyanide complexes. Examples are the cyanide complexes of cobalt and iron. This classification is in reality too simple, because there are some metal cyanide complexes that are only partially decomposed by acids. For these metals,

Figure 2-1



Equilibrium distribution diagram for free cyanide versus pH at 25° C and zero ionic strength.

¹Italic numbers in parentheses refer to items in the list of references at the end of this chapter.

complete decomposition of their cyanide complexes by acids requires the addition of a complexing agent, precipitant, or oxidant. This group may be termed "partially WAD" cyanide complexes. Examples of partially WAD metal cyanide complexes are those of Cu, Ag, Au, and Hg.

Both thermodynamic and kinetic factors determine how readily metal cyanide complexes are decomposed by acids. These factors are discussed in detail in chapter 8. The equilibria of WAD cyanide complexes are usually rapidly established, which determines the chemical behavior of these complexes. These equilibria are presented as diagrams, discussed in chapter 4 and shown in appendix E. The equilibrium data for metal cyanide and other species from which these diagrams are generated are compiled in appendix D.

SPECIES DERIVED FROM CYANIDE

A considerable number of other chemical species are derived from CN^- . These species form via oxidation or reaction with H_2O or other species. Other species that can react with CN^- or derived species are ammonia (NH_3), hydrogen sulfide (SH^-), and certain other sulfur species. Any of these species could form via reactions of CN^- or derived species under appropriate conditions. The large number of conceivable species that are products of all of these reactions have been compiled and systematized as described below. There appears to be no other recent compilation of the nomenclature and chemistry of CN^- and derived species. The reactions that are known or expected to occur and an assessment of which species are important in precious metals mining and closure operations are discussed in chapter 7.

The formulas, names, and Chemical Abstracts Service (CAS) registry numbers of CN^- and derived species are shown in tables 2-1 through 2-3. In many cases more than one name is included because of nomenclature changes in the Chemical Abstracts collective indexes (1-8). As a rule, the names more familiar in industry are used in this publication. Generally, these are the names used in Chemical Abstracts collective indexes 5 through 7 (1-3).

Tables 2-1, 2-2, and 2-3 list the species derived from cyanide for carbon oxidation states 2+, 3+, and 4+, i.e., C(II), C(III), and C(IV), respectively. Species with carbon oxidation state 2+ (C(II)) consist of CN^-/HCN and species formed via reaction with H_2O , NH_3 , or SH^- . Except for CN^- , each of these species consists of one carbon atom bound to one hydrogen atom and two oxygen, nitrogen, or sulfur atoms. Species with carbon oxidation state 3+ (C(III)) consist of cyanogen (NC-CN) and species formed via reaction with H_2O , NH_3 , or SH^- without breaking the C-C bond. Each of these species consists of two carbon atoms, each bound to the other and to one or two oxygen, nitrogen, or sulfur atoms. Species with carbon oxidation state 4+ (C(IV)) consist of cyanogen chloride

(ClCN) and species formed via reaction with H_2O , NH_3 , or SH^- . Each of these species consists of one carbon atom bound to two or three oxygen, nitrogen, or sulfur atoms.

In tables 2-1 through 2-3, the species are arranged by chemical formula. The species are arranged according to increasing number of atoms bound to the carbon atom, then increasing number of oxygen atoms bound to the carbon atom. Abbreviated formulas are also given, which are used in chapter 7. The abbreviated formulas are enclosed in curly brackets, and only the carbon atoms and the atoms bound to the carbon atoms are shown. Species related by gain or loss of H^+ are collectively given one abbreviated formula. For example, oxalic acid and its anions, $\text{H}_2\text{C}_2\text{O}_4$, HC_2O_4^- , and $\text{C}_2\text{O}_4^{2-}$ are collectively given the abbreviated formula $\{\text{OCCOO}\}$. Abbreviated formulas are not used for ClCN , NCO^- (cyanate), and SCN^- (thiocyanate).

The chemical formulas are written to reflect the molecular structures of the species. This is necessary to avoid confusion, because of the existence of isomers. Isomers are species that have the same composition in terms of numbers of atoms and ionic charges, but different molecular structures. Examples of isomers are cyanate and fulminate. Cyanate is often written CNO^- in the metallurgical literature. This creates confusion with fulminate, which is also CNO^- , but with a different structure. Experimentally determined molecular structures show the following: Cyanate is NCO^- or OCN^- , a species with a linear molecular structure, with the carbon atom in the middle. Fulminate is CNO^- or ONC^- , also a species with a linear molecular structure, with the nitrogen atom in the middle (11). Consequently, in this report, cyanate will be written NCO^- , and fulminate CNO^- . Similarly, thiocyanate is SCN^- or NCS^- (not CNS^- ; the carbon atom is in the middle) (11). (The sulfur analog of fulminate, CNS^- , with the nitrogen atom in the middle, is unknown.)

Fulminic acid (HCNO) and fulminate ion (CNO^-) can be thought of as derived from CN^- by oxidation at the nitrogen atom, and formohydroxamic acid (H-CO-NH-OH) by subsequent reaction with H_2O . These species, which contain carbon in the 2+ oxidation state, are listed at the end of table 2-1. Abbreviated formulas are not used for these species. (The silver or gold salts of the fulminate ion CNO^- are not to be confused with "fulminating silver" or "fulminating gold" in the literature. The latter two materials are silver or gold nitride compounds formed in alkaline ammoniacal solutions containing silver or gold (12).)

The arrangement of data for cyanide and derived species in tables 2-1 through 2-3 is incorporated in chapters 5 and 7 and appendixes B and C.

Cyanide and many of the derived species are known to undergo condensation reactions (e.g., cyanamide to cyanoguanidine or melamine). Such condensation products are usually encountered only at high concentrations and are consequently not considered in this publication.

Table 2-1.-Nomenclature of carbon(II) species
derived from cyanide

Formula and abbreviation	CAS ¹ registry number	Name, followed by numbers of <u>Chemical Abstracts</u> collective indexes in parentheses
HCN {HCN}	74-90-8	Hydrocyanic acid (5-12)
CN ⁻ {HCN}	57-12-5	Cyanide (5-12)
H-C(NH)(NH ₂) {HCNN}	463-52-5	Formamidine (5-8) Methanimidamide (9-12)
H-C(NH ₂) ₂ ⁺ {HCNN}	50676-76-1	Methanimidamide, conjugate monoacid (9-12)
H-CS-NH ₂ {HCSN}	115-08-2	Formamide, thio- (5-8) Methanethioamide (9-12)
H-CS-SH {HCSS}	4472-10-0	Formic acid, dithio- (5-7) Methanedithioic acid (8-12)
H-CS ₂ ⁻ {HCSS}	37619-02-6	Methane(dithioic) acid, ion(1-) (9-12)
H-CO-NH ₂ {HCON}	75-12-7	Formamide (5-12)
H-CO-SH {HCOS}	16890-80-5	Formic acid, thio (5-8) Methanethioic acid (9-12)
H-COS ⁻ {HCOS}	37691-01-5	Methanethioic acid, ion(1-) (9-12)
H-CO-OH {HCOO}	64-18-6	Formic acid (5-12)
H-CO ₂ ⁻ {HCOO}	71-47-6	Formates (5-7) Formic acid, ion(1-) (8-12)
HCNO	506-85-4	Fulminic acid (5-12)
CNO ⁻	28269-67-2	Fulminate (5-7) Fulminic acid, ion(1-) (8-9)
H-CO-NH-OH	4312-87-2	Formohydroxamic acid (5-8) Formamide, N-hydroxy- (9-12)
H-CO-NH-O ⁻	78204-40-7	Formamide, N-hydroxy, ion(1-) (10-11)

¹CAS Chemical Abstracts collective index; if no index number is given, the compound does not appear in the collective indexes.

Table 2-2.-Nomenclature of carbon(III) species
derived from cyanide

Formula and abbreviation	CAS ¹ registry number	Name, followed by numbers of <u>Chemical Abstracts</u> collective indexes in parentheses
NC-CN {NCCN}	460-19-5	Cyanogen (5-8) Ethanedinitrile (9-12)
NC-C(NH)-NH ₂ {NCCNN}	37507-70-3	Formamide, 1-cyano (5-6) Carbonocyanidimidic amide (9-12)
NC-CS-NH ₂ {NCCSN}	471-24-9	Formamide, 1-cyanothio- (6-8) Carbonocyanidothioic amide (9-12)
NC-CS-SH {NCCSS}	38093-84-4	Formic acid, cyanodithio- (5-8) Carbonocyanidodithioic acid (9-12)
NC-CS ₂ ⁻ {NCCSS}	44201-42-5	Carbonocyanidodithioic acid, ion(1-) (9)
NC-CO-NH ₂ {NCCON}	4370-12-1	Formamide, 1-cyano- (6-7) Carbonocyanidic amide (9-12)
NC-CO-SH {NCCOS}	57550-98-8	Formic acid, 1-cyanothio- (7-8) Carbonocyanidothioic acid (9-12)
NC-COS ⁻ {NCCOS}	no entries	Carbonocyanidothioic acid, ion(1-)
NC-CO-OH {NCCOO}	19270-07-6	Formic acid, cyano (5-8) Carbonocyanidic acid (9-12)
NC-CO ₂ ⁻ {NCCOO}	no entries	Carbonocyanidic acid, ion(1-)
H ₂ N-C(NH)-C(NH)C-NH ₂ {NNCCNN}	4013-33-6	Oxamidine (5-8) Ethanediimideamide (9-12)
(H ₂ N) ₂ C-C(NH ₂) ₂ ²⁺ {NNCCNN}	132724-41-5	1,2-Ethanediylum, 1,1,2,2-tetraamino- (12)
H ₂ N-C(NH)-CS-NH ₂ {NNCCSN}	no entries	Formamide, amidinothio- Ethanethioamide, aminoimino-
H ₂ N-CS-CS-NH ₂ {NSCCSN}	79-40-3	Oxamide, dithio- (5-8) Ethanedithioamide (9-12)

Table 2-2.-Nomenclature of carbon(III) species
derived from cyanide—Continued

Formula and abbreviation	CAS ¹ registry number	Name, followed by numbers of <u>Chemical Abstracts</u> collective indexes in parentheses
$\text{H}_2\text{N}-\text{C}(\text{NH})-\text{CS}-\text{SH}$ {NNCCSS}	no entries	Formic acid, amidinodithio- Ethane(dithioic) acid, amino- imino-
$\text{H}_2\text{N}-\text{C}(\text{NH})-\text{CS}_2^-$ {NNCCSS}	no entries	Ethane(dithioic) acid, amino- imino, ion(1-)
$\text{H}_2\text{N}-\text{CS}-\text{CS}-\text{SH}$ {NSCCSS}	no entries	Oxamic acid, trithio- Ethane(dithioic) acid, amino- thioxo-
$\text{H}_2\text{N}-\text{CS}-\text{CS}_2^-$ {NSCCSS}	no entries	Ethane(dithioic) acid, amino- thioxo, ion(1-)
$\text{HS}-\text{CS}-\text{CS}-\text{SH}$ {SSCCSS}	82766-65-2	Oxalic acid, tetrathio- Ethanebis(dithioic) acid (9-10, 12)
$\text{S}_2\text{C}-\text{CS}_2^{2-}$ {SSCCSS}	78906-82-8	Ethanebis(dithioic) acid, ion(2-) (10-12)
$\text{H}_2\text{N}-\text{C}(\text{NH})-\text{CO}-\text{NH}_2$ {NNCCON}	no entries	Formamide, amidino- Acetamide, 2-amino-2-imino-
$\text{H}_2\text{N}-\text{CS}-\text{CO}-\text{NH}_2$ {NSCCON}	16475-48-2	Oxamide, thio (6-8) Acetamide, 2-amino-2-thioxo- (9-10, 12)
$\text{H}_2\text{N}-\text{C}(\text{NH})-\text{CO}-\text{SH}$ {NNCCOS}	no entries	Formic acid, amidinothio- Ethanethioic acid, aminoimino-
$\text{H}_2\text{N}-\text{C}(\text{NH})-\text{COS}^-$ {NNCCOS}	no entries	Ethanethioic acid, amino- imino, ion(1-)
$\text{H}_2\text{N}-\text{CS}-\text{CO}-\text{SH}$ {NSCCOS}	no entries	Oxamic acid, 1,2-dithio- Ethanethioic acid, amino- thioxo-
$\text{H}_2\text{N}-\text{CS}-\text{COS}^-$ {NSCCOS}	no entries	Ethanethioic acid, amino- thioxo-, ion(1-)
$\text{H}_2\text{N}-\text{CO}-\text{CS}-\text{SH}$ {SSCCON}	97925-73-0	Oxamic acid, 1,1-dithio- (6-7) Ethane(dithioic) acid, amino- oxo- (10-11)
$\text{H}_2\text{N}-\text{CO}-\text{CS}_2^-$ {SSCCON}	no entries	Ethane(dithioic) acid, amino- oxo-, ion

Table 2-2.-Nomenclature of carbon(III) species
derived from cyanide-Continued

Formula and abbreviation	CAS ¹ registry number	Name, followed by numbers of <u>Chemical Abstracts</u> collective indexes in parentheses
HS-CS-CO-SH {SSCCOS}	no entries	Oxalic acid, trithio- Ethanethioic acid, mercapto- thioxo- (salt only) (9)
S ₂ C-COS ²⁻ {SSCCOS}	no entries	Ethanethioic acid, mercapto- thioxo-, ion
H ₂ N-CO-CO-NH ₂ {NOCCON}	471-46-5	Oxamide (5-8) Ethanediamide (9-12)
H ₂ N-C(NH)-CO-OH {NNCCOO}	27203-24-3	Formic acid, amidino- (7-8) Acetic acid, aminoimino- (9-11)
H ₂ N-C(NH)-CO ₂ ⁻ {NNCCOO}	no entries	Acetic acid, aminoimino- ion(1-)
H ₂ N-CO-CO-SH {NOCCOS}	80487-41-8	Oxamic acid, 2-thio- (5-8) Ethanethioic acid, aminooxo- (9-11)
H ₂ N-CO-COS ⁻ {NOCCOS}	no entries	Ethanethioic acid, aminooxo-, ion(1-)
H ₂ N-CS-CO-OH {NSCCOO}	39894-60-5	Oxamic acid, 1-thio- Acetic acid, aminothioxo- (9-12)
H ₂ N-CS-CO ₂ ⁻ {NSCCOO}	no entries	Acetic acid, aminothioxo-, ion(1-)
HS-CO-CO-SH {SOCCOS}	17148-96-8	Oxalic acid, 1,2-dithio- (5-8) Ethanebis(thioic) acid (9-12)
SOC-COS ²⁻ {SOCCOS}	37183-16-7	Ethanebis(thioic) acid, ion(2-) (9-11)
HS-CS-CO-OH {SSCCOO}	64148-58-9	Oxalic acid, 1,1-dithio- Acetic acid, mercaptothioxo- (9) Formic acid, (dithiocarboxy)- (10-12)
S ₂ C-CO ₂ ²⁻ {SSCCOO}	65194-59-4	Formic acid, (dithiocarboxy)- ion(2-) (10)
H ₂ N-CO-CO-OH {NOCCOO}	471-47-6	Oxamic acid (5-8) Acetic acid, aminooxo- (9-12)

Table 2-2.-Nomenclature of carbon(III) species
derived from cyanide—Continued

Formula and abbreviation	CAS ¹ registry number	Name, followed by numbers of <u>Chemical Abstracts</u> collective indexes in parentheses
$\text{H}_2\text{N}-\text{CO}-\text{CO}_2^-$ {NOCCOO}	598-90-3	Oxamate (5-7) Oxamic acid, ion(1-) (8) Acetic acid, aminooxo-, ion(1-)
$\text{HS}-\text{CO}-\text{CO}-\text{OH}$ {SOCCOO}	2689-56-7	Oxalic acid, thio- (5-8) Acetic acid, mercaptooxo- (9-10)
$\text{SOC}-\text{CO}_2^-$ {SOCCOO}	no entries	Acetic acid, mercaptooxo-, ion(2-)
$\text{HO}-\text{CO}-\text{CO}-\text{OH}$ {OCCOO}	144-62-7	Oxalic acid (5-8) Ethanedioic acid (9-12)
$\text{HO}-\text{CO}-\text{CO}_2^-$ {OCCOO}	920-52-5	Oxalic acid, ion(1-) (8) Ethanedioic acid, ion(2) (9-12)
$\text{O}_2\text{C}-\text{CO}_2^{2-}$ {OCCOO}	338-70-5	Oxalates (5-7) Oxalic acid, ion(2-) (8) Ethanedioic acid, ion(2-) (9-12)

¹CAS Chemical Abstracts collective index; if no index number is given, the compound does not appear in the collective indexes.

Table 2-3.-Nomenclature of carbon(IV) species
derived from cyanide

Formula and abbreviation	CAS ¹ registry number	Name, followed by numbers of <u>Chemical Abstracts</u> collective indexes in parentheses
ClCN	506-77-4	Cyanogen chloride (5-12)
BrCN	506-68-3	Cyanogen bromide (5-12)
NC-NH ₂ {CNN}	420-04-2	Cyanamide (5-12)
NCNH ⁻ {CNN}	67131-47-9	Cyanamide, ion(1-) (10-12)
CN ₂ ²⁻ {CNN}	20328-93-2	Cyanamide, ion(2-) (8-12)
NCS ⁻	302-04-5	Thiocyanate (5-7, 9-12) Thiocyanic acid, ion(1-) and Isothiocyanic acid, ion(1-) (8)
HNCO	420-05-3	Cyanic acid (5-12)
NCO ⁻	661-20-1	Cyanate (5-7, 9-12) Cyanic acid, ion(1-) and Isocyanic acid, ion(1-) (8)
HNC(NH ₂) ₂ {CNNN}	113-00-8	Guanidine (5-12)
C(NH ₂) ₃ ⁺ {CNNN}	25215-10-5	Guanidine, conjugate monoacid (8-12)
SC(NH ₂) ₂ {CSNN}	62-56-6	Urea, thio- (5-8) Thiourea (9-12)
H ₂ N-CS-SH {CSSN}	594-07-0	Carbamic acid, dithio- (5-8) Carbamodithioic acid (9-12)
H ₂ N-CS ₂ ⁻ {CSSN}	4384-82-1	Carbamic acid, dithio-, ion(1-) (8) Carbamodithioic acid, ion(1-) (9-12)
CS(SH) ₂ {CSSS}	594-08-1	Carbonic acid, trithio- (5-8) Carbonotrithioic acid (9-12)
CS ₃ ²⁻ {CSSS}	15644-49-2	Carbonic acid, trithio-, ion(2-) (8) Carbonotrithioate (9-12)
OC(NH ₂) ₂ {CONN}	57-13-6	Urea (5-12)

Table 2-3.-Nomenclature of carbon(IV) species
derived from cyanide-Continued

Formula and abbreviation	CAS ¹ registry number	Name, followed by numbers of <u>Chemical Abstracts</u> collective indexes in parentheses
H ₂ N-CO-SH {COSN}	19045-66-0	Carbamic acid, thio- (5-8) Carbamothioic acid (9-12)
H ₂ N-COS ⁻ {COSN}	63294-87-1	Carbamothioic acid, ion(1-) (10)
CS(OH)(SH) {COSS}	4741-30-4	Carbonic acid, dithio- (5-8) Carbonodithioic acid (9-12)
COS ₂ ²⁻ {COSS}	30981-29-4	Carbonic acid, dithio-, ion(1-) (8) Carbonodithioate (9-12)
H ₂ N-CO-OH {COON}	463-77-4	Carbamic acid (5-12)
H ₂ N-CO ₂ ⁻ {COON}	302-11-4	Carbamic acid, ion(1-) (8-9, 11-12)
CO(OH)(SH) {COOS}	10016-32-7	Carbonic acid, thio- (5-8) Carbonothioic acid (9-12)
CO ₂ S ²⁻ {COOS}	24389-08-0	Carbonic acid, thio-, ion(2-) (8) Carbonothioate (10-11)
CO(OH) ₂ {COOO}	463-79-6	Carbonic acid (5-12)
HO-CO ₂ ⁻ {COOO}	71-52-3	Carbonates, acid (5-7) Carbonate, hydrogen (8-12)
CO ₃ ²⁻ {COOO}	3812-32-6	Carbonates (5-7) Carbonate (8-12)

¹CAS Chemical Abstracts collective index; if no index number is given, the compound does not appear in the collective indexes.

AUXILIARY SPECIES

To describe the equilibria and reactions in situations where CN^- and metal cyanide complexes exist, all other chemical species that might participate must be included. These are referred to in this publication as "auxiliary" species. They include

1. H_2O , H^+ , and OH^- .
2. Uncomplexed metal ions.
3. Any other species that may precipitate or complex with metal ions, e.g. S^{2-} , SO_4^{2-} , CO_3^{2-} , NH_3 , or Cl^- .
4. Other reagents, e.g., added oxidizing agents such as H_2O_2 or ClO^- , and their reduction products.

Especially with WAD cyanide complexes, for which equilibria are usually established rapidly, the species that exist depend on pH and the presence of other species that may precipitate or complex with the metal ions. These equilibria are discussed in chapters 4 and 8, tabulated in appendix D, and diagramed in appendix E.

METAL SPECIES

Insofar as the nomenclature for metal species in much metallurgical literature corresponds to that in the older chemical literature, some readers may not be familiar with modern chemical nomenclature, which is standardized and more systematic (9). This section will address oxidation states, metal complexes and complexing agents, and metal hydroxides.

The modern Roman numeral system for designating oxidation states is used here in preference to historically used suffixes such as "-ous" and "-ic" for cationic and neutral metal species. For anionic metal species, the suffix "ite" is abandoned, and the suffix "-ate" is used with the Roman numeral for the metal oxidation state. This practice is exemplified by metal cyanide complexes, e.g., dicyanoaurate(I) instead of aurocyanide or dicyanoaurite for $[\text{Au}(\text{CN})_2]^-$, and hexacyanoferrate(II) and hexacyanoferrate(III) instead of ferrocyanide and ferricyanide for $[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{Fe}(\text{CN})_6]^{3-}$, respectively. This precise nomenclature is necessary because many metal ions form more than one cyanide complex, which makes the old nomenclature inadequate and confusing. For example, Cu(I) and cyanide form the species $[\text{Cu}(\text{CN})_2]^-$, $[\text{Cu}(\text{CN})_3]^{2-}$, and $[\text{Cu}(\text{CN})_4]^{3-}$, for which the respective names are dicyanocuprate(I), tricyanocuprate(I), and tetracyanocuprate(I).

Metals are often referred to in terms of particular oxidation states in a general context without specifying other details of the chemical composition or environment. In the older chemical literature and in much metallurgical literature, the symbol for the metal ion is commonly used in such situations, e.g., Fe^{2+} for Fe in the 2+ oxidation

state. In the older systems, symbols such as Fe^{2+} are used to specify the uncomplexed ion. In modern nomenclature (9), metals in particular oxidation states without reference to chemical composition or environment are symbolized with the Roman numeral, e.g., Fe(II) for Fe in the 2+ oxidation state. This practice is followed throughout this publication.

The term "ligand" is used for any molecule or ion bound to a metal ion, whether it be H_2O or OH^- or any complexing agent. Abbreviations are often used for organic ligands. In modern nomenclature (9) it is customary to use lowercase letters enclosed in parentheses for such abbreviations. Examples include (H_4edta) and $(\text{edta})^{4-}$ for free ethylenediaminetetraacetic acid and the free ethylenediaminetetraacetate anion, $[\text{Cu}(\text{edta})]^{2-}$ for ethylenediaminetetraacetatocuprate(II), $[\text{Ni}(\text{en})_3]^{2+}$ for tris(ethylenediamine)nickel(II), and $[\text{Fe}(\text{nta})_2]^-$ for bis(nitrilotriacetato)ferrate(III). For further details, the interested reader should consult the literature (9).

The nomenclature regarding precipitated metal "hydroxides" requires comment for three reasons. First, precipitated metal "hydroxides" hardly ever contain stoichiometric ratios of metal oxide to H_2O . Second, many metal oxides do not react with H_2O to form hydroxides. Third, modern techniques such as X-ray diffraction, neutron diffraction, infrared spectroscopy, and nuclear magnetic resonance spectroscopy enable the identification of OH^- groups in solids. Structurally, many precipitated metal "hydroxides" do not contain stoichiometric ratios of OH^- groups to metal atoms, and they should be termed "hydrous metal oxides." When the term "hydrous metal oxide" is appropriate rather than "metal hydroxide," it is used in this publication. This is the case for most heavy metals in oxidation state 3+ or higher.

REFERENCES

1. Chemical Abstracts Service. Chemical Abstracts, v. 41-50, 1947-56, Fifth Decennial Index, Subjects. Am. Chem. Soc., 1960-62, 13,747 pp.
2. Chemical Abstracts Service. Chemical Abstracts, v. 51-55, 1957-61, Sixth Collective Index, Subjects. Am. Chem. Soc., 1964-66, 12,711 pp.
3. Chemical Abstracts Service. Chemical Abstracts, v. 56-65, 1962-66, Seventh Collective Index, Subjects. Am. Chem. Soc., 1969-70, 24,637 pp.
4. Chemical Abstracts Service. Chemical Abstracts, v. 66-75, 1967-71, Eighth Collective Index, Subjects. Am. Chem. Soc., 1972-73, 33,575 pp.
5. Chemical Abstracts Service. Chemical Abstracts, v. 76-85, 1972-76, Ninth Collective Index, Chemical Substances. Am. Chem. Soc., 1977-78, 40,890 pp.
6. Chemical Abstracts Service. Chemical Abstracts, v. 86-95, 1977-81, Tenth Collective Index, Chemical Substances. Am. Chem. Soc., 1982-83, 56,112 pp.
7. Chemical Abstracts Service. Chemical Abstracts, v. 96-105, 1982-86, Eleventh Collective Index, Chemical Substances. Am. Chem. Soc., 1987, 71,720 pp.
8. Chemical Abstracts Service. Chemical Abstracts, v. 106-115, 1987-91, Twelfth Collective Index, Chemical Substances. Am. Chem. Soc., 1992, 93,323 pp.

9. Lide, D. R. (ed.). CRC Handbook of Chemistry and Physics. CRC Press, 72nd ed., 1991, pp. 2-22 through 2-44 (inorganic), 2-45 through 2-74 (organic).

10. Huiatt, J. L., J. E. Kerrigan, F. A. Olson, and G. L. Potter (eds.). Workshop on Cyanide From Mineral Processing. UT Min. and Miner. Resour. Res. Inst., 1982, 142 pp.

11. Greenwood, N. N., and A. Earnshaw. Chemistry of the Elements. Pergamon, 1984, p. 337.

12. Mellor, J. W. A Comprehensive Treatise on Inorganic and Theoretical Chemistry. Longmans Green, 1941, v. 3, pp. 381, 582.

CHAPTER 3.—SURVEY OF CYANIDES OF THE ELEMENTS

INTRODUCTION

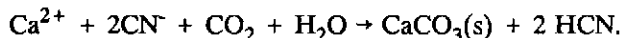
Precious metal ores often contain a variety of accessory elements. In mining and processing, many of the accessory elements can be leached, and transported through the process, where they report to liquid and solid wastes. The question arises as to what extent the accessory elements interact with CN^- . This chapter answers that question by presenting an overview of the cyanide chemistry of the elements. A summary of this overview is provided in figure 3-1. The following paragraphs survey the cyanide chemistry of the elements in each column of the periodic table.

SURVEY OF CYANIDES OF THE ELEMENTS

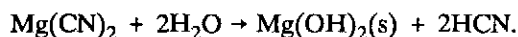
Alkali and Alkaline Earth Metals

The cyanides of the alkali metals Li, Na, K, Rb, and Cs (1)¹ are very soluble in water, with complete dissociation to alkali metal cations and free cyanide ion.

The cyanides of the heavier alkaline earths Ca, Sr, and Ba (2) are also water soluble and are completely dissociated to alkaline-earth metal cations and free cyanide ion. However, they are readily converted to HCN via reaction with CO_2 , because of the insolubility of their carbonates; e.g.,



The cyanides of the lighter alkaline earths beryllium and magnesium (2) are even more readily hydrolyzed, also because of the low solubility of their hydroxides; e.g.,



Lanthanide and Actinide Metals

The cyanides of the lanthanides are poorly known. Cyanides of some lanthanide elements have been prepared, and they are decomposed by H_2O with liberation of HCN (3-4). No information was located for actinide metal cyanides. Like the lanthanide metal cyanides, they are expected to hydrolyze readily because of the insolubility of the metal hydroxides.

Transition Metals

Most of the transition metals form cyanide complexes of differing stabilities (3). As a rough general rule,

stabilities increase with atomic number along each of the three rows of transition metals in the periodic table. The cyanides of Ti, Zr, Hf, Nb, (Cb), and Ta are hardly known, but are expected to hydrolyze readily because of the insolubility of the hydrous metal oxides. Cyanide complexes of niobium in lower oxidation states are known, but they are readily oxidized and hydrolyzed (5).

Among the transition metals, iron is the most common cyanide-forming accessory element in connection with mining and extractive metallurgy. The metals Ni, Co, Mn, Cr and V are less common, but they all form cyanide complexes of differing stabilities. The chemistry of the cyanide complexes of these metals is described in detail in chapters 8, 9, and 10.

Cyanide complexes of Mo, W, and Re are well known, but none of them contain the metal in the highest oxidation state. Stable cyanide species are not known for Mo(V), W(V), or Re(VII). Cyanide complexes of Mo, W, and Re are not likely to be encountered in extractive metallurgy.

The cyanide complexes of the platinum-group metals are among the most stable of all known metal complexes; they are stable even in strongly acid solutions. They may conceivably form if platinum-group metals occur in gold-silver ores treated by cyanidation, but no such occurrences appear to have been reported. Very little is known about the equilibria and reactions of platinum-group metal cyanide species. Therefore they are not discussed in this publication.

Posttransition Metals

The posttransition metals Cu, Ag, Au, Zn, Cd, and Hg are all commercially important, and they all form binary cyanides and cyanide complexes (3). In the mining of precious metals, copper and zinc are the most likely accessory elements besides iron. The metals cadmium or mercury may also be encountered at some locations. The cyanide chemistry of all of these metals is described in detail in chapters 8 and 10.

Boron Group

The cyanides of B, Al, Ga, and In are all known or expected to be completely decomposed by water to oxide compounds and free cyanide (6-7). Indium may form cyanide complexes, judging by the use of cyanide baths for indium electroplating (8), but no fundamental data on indium cyanide complexes in solution exist. Thallium(I) forms TlCN , which like the alkali metal cyanides is water soluble and dissociates completely to Tl^+ and free CN^- (9). Thallium(III) has recently been confirmed to form strong soluble cyanide complexes (10). Thallium(III) is expected

¹Italic numbers in parentheses refer to items in the list of references at the end of this chapter.

Figure 3-1

[illegible]

57La	58Ce	59Pr	60Nd	61Pm	62Sm	63Eu	64Gd	65Tb	66Dy	67Ho	68Er	69Tm	70Yb	71Lu
D	D	D	D	D	D	D	D	D	D	D	d	d	d	d
89Ac	90Th	91Pa	92U	93Np	94Pu	95Am	96Cm	97Bk	98Cf	99Es	100Fm	101Md	102No	103Lr
X	D	D	D	D	D	D	D	D	D	X	X	X	X	X

to be reduced to Tl(I) by CN^- , as shown by the thermodynamic data in tables B-1 and D-1. However, the rate of this reaction was reported to be slow (months) in acid solution; in alkaline solution with free CN^- present, the rate of the redox reaction may be faster (10). Thallium is rarely if ever reported as an accessory element in precious metals hydrometallurgy, so Tl(III) cyanide complexes may not be a significant problem. Thermodynamic data for thallium species are compiled in tables D-19 and D-20.

Carbon Group

Carbon forms a variety of binary neutral and anionic cyanide compounds known as cyanocarbons (11); none of them are likely to be encountered in extractive metallurgy.

The cyanides of Si, Ge, and Sn are all known or expected to be completely decomposed by water to oxide compounds and free cyanide (7, 12). Lead(II) is reported to form a slightly soluble mixed hydroxide cyanide when Pb(II) salt solutions are treated with an alkali metal cyanide (13), or when $\text{PbO} \cdot x\text{H}_2\text{O}$ is treated with HCN (14, p. 141). Cyanide complexes of Pb(II) in solution are probably weak; there is no reliable published information on them.

Nitrogen Group

The most important cyanide compound of nitrogen is the well-known cyanamide, H_2NCN . The chemistry of H_2NCN is described in chapter 7 in connection with oxidation products of cyanide. Dicyanamide, $\text{HN}(\text{CN})_2$ (15), is not important metallurgically. Tricyanamide, $\text{N}(\text{CN})_3$, is unknown.

The cyanides of P, As, Sb, and Bi are all known or expected to be completely decomposed by water to oxide compounds and free cyanide (12; 14, p. 427).

Oxygen Group

The sole cyanide compound of oxygen of interest is the well-known cyanate ion, NCO^- , which is the major oxidation product of cyanide. The formation of NCO^- in oxidation reactions of cyanide and its hydrolysis and further oxidation are described in chapter 7.

The most important sulfur cyanide species is the well-known thiocyanate ion, SCN^- . Other sulfur cyanide species exist, but they are all decomposed by water to give SCN^- , CN^- or HCN , and NCO^- (14, pp. 916-917). The formation of SCN^- from cyanide and sulfur species and the oxidation of SCN^- are described in chapter 7.

Selenium forms selenocyanate ion, SeCN^- , by dissolution of elemental selenium in cyanide solutions. It is readily decomposed by acids, with liberation of free cyanide (14,

p. 967). Tellurium does not form stable cyanide species, e.g., TeCN^- , in aqueous solutions (18).

Halogen Group

The halogens all form the well-known cyanogen halides, e.g., cyanogen chloride, ClCN . These compounds are all hydrolyzed by water to halide and NCO^- ions. The formation of ClCN from cyanide and chlorinating agents and its hydrolysis are described in chapter 7.

Rare Gas Group

The rare gases He, Ne, Ar, Kr, and Xe do not form cyanides.

REFERENCES

1. Jenks, W. R. Cyanides (Alkali Metal). Ch. in Kirk-Othmer Encyclopedia of Chemical Technology. Wiley, 3rd ed., v. 7, 1979, pp. 320-331.
2. Booth, R. B. Alkaline Earth Metal Cyanides. Ch. in Kirk-Othmer Encyclopedia of Chemical Technology. Wiley, 2nd ed., v. 6, 1965, pp. 601-604.
3. Sharpe, A. G. The Chemistry of Cyano Complexes of the Transition Metals. Academic, 1976, 302 pp.
4. McColm, L. J., and S. Thompson. The Preparation of Anhydrous Lanthanide Cyanides. J. Inorg. Nucl. Chem., v. 34, 1972, pp. 3801-3807.
5. Kiernan, P. M., and W. P. Griffith. Studies on Transition-Metal Cyano Complexes. Part 1. Octacyanonitobates(III), Niobates(IV), Molybdates(V), and Tungstates(V). J. Chem. Soc., Dalton Trans., 1975, pp. 2489-2494.
6. Bailar, J. C., Jr., H. J. Emeleus, R. S. Nyholm, and A. F. Trotman-Dickenson (eds.). Comprehensive Inorganic Chemistry. Pergamon, v. 1, 1973, pp. 1032, 1090, 1143.
7. Lappert, M. F., and H. Pyszora. Pseudohalides of Group IIIB and IVB Elements. Ch. in Advances in Inorganic Chemistry and Radiochemistry, ed. by H. J. Emeleus and A. G. Sharpe. Academic, 1966, v. 9, pp. 142-152.
8. Lowenheim, F. A. Electroplating. Ch. in Kirk-Othmer Encyclopedia of Chemical Technology. Wiley, 3rd ed., v. 8, 1979, p. 848.
9. Penneman, R. A., and E. Staritzky. Infrared and Crystallographic Investigation of the $\text{TiCN-KCN-H}_2\text{O}$ System; The Lack of Ti(I)-Cyanide Complexes. J. Inorg. Nucl. Chem., v. 6, 1958, pp. 112-118.
10. Blixt, B., B. Gyoeri, and J. Glaser. Determination of Stability Constants for Thallium(III) Cyanide Complexes in Aqueous Solution by Means of ^{13}C and ^{205}Tl NMR. J. Am. Chem. Soc., v. 111, 1989, pp. 7784-7791.
11. Webster, O. W. Cyanocarbons. Ch. in Kirk-Othmer Encyclopedia of Chemical Technology. Wiley, 3rd ed., v. 7, 1979, pp. 359-369.
12. Bither, T. A., W. H. Knoth, R. V. Lindsey, Jr., and W. H. Sharkey. Trialkyl- and Triaryl(iso)cyanosilanes. J. Am. Chem. Soc., v. 80, 1958, pp. 4151-4153.
13. Meites, L. Hydrolytic Titration of Lead(II) with Potassium Cyanide. J. Am. Chem. Soc., v. 70, 1948, pp. 1659-1660.
14. Bailar, J. C., Jr., H. J. Emeleus, R. S. Nyholm, and A. F. Trotman-Dickenson (eds.). Comprehensive Inorganic Chemistry. Pergamon, v. 2.
15. Rappoport, Z. (ed.). The Chemistry of the Cyano Group. Wiley-Interscience, 1970, pp. 546-547.

CHAPTER 4.—CHEMICAL EQUILIBRIA

INTRODUCTION

The extent to which a chemical reaction proceeds is determined by thermodynamics and kinetics. Thermodynamics determines how far a chemical reaction can proceed, by means of the standard Gibbs energy change for the reaction. Kinetics determines the rate at which the reaction proceeds. The role of kinetics is described in chapter 7 in the context of reactions of free $\text{CN}^\cdot$ and derived species. This chapter outlines the pertinent thermodynamic theory and equations, discusses thermodynamic data requirements and sources, and describes graphical methodology for presenting equilibrium information. It concludes with examples showing how information on equilibria can be obtained by inspection of log K data.

FUNDAMENTAL THERMODYNAMIC EQUATIONS

This section presents an outline of pertinent thermodynamic equations. For further details, the interested reader is referred to any of several standard texts on thermodynamics. The equations presented in this section are provided to assist the reader in doing calculations with the data in appendixes B, C, and D.

Individual Species

All thermodynamic data are relative to a standard state. The data of interest here are the standard enthalpy of formation $\Delta_f H^\circ$, standard Gibbs energy of formation $\Delta_f G^\circ$, and standard entropy S° . For pure solid or liquid substances, the standard state is the form that is stable at the temperature of interest and a pressure of 10^5 Pa (1 bar or 750.06 mm Hg or (1/1.01325) atm). The standard temperature for tables of $\Delta_f H^\circ$, $\Delta_f G^\circ$, and S° of chemical species is 25.00°C (298.15 K or 77.00°F). If the species is gaseous, the standard state is the ideal gas at a pressure of 10^5 Pa. The definition of the standard state for aqueous dissolved species is discussed below in connection with activity coefficients.

In the older data tables, the standard pressure is 1 atm. The change in standard pressure entails small changes in S° and $\Delta_f G^\circ$ values where gaseous species are involved. For most purposes, these changes are inconsequential. For example, S° for a gas species is changed by R (gas constant) $\ln(1/1.01325) = -0.1094\text{ J}\cdot\text{K}^{-1}$ at 25°C . The corresponding change in $\Delta_f G^\circ$ values is RT (gas constant times absolute temperature) $\ln(1/1.01325) = -0.0326\text{ kJ}$ at 25°C , per mole of gas species in the formation reaction.

The standard Gibbs energies of formation $\Delta_f G^\circ$, standard enthalpies of formation $\Delta_f H^\circ$, and standard entropies

of formation $\Delta_f S^\circ$ of a chemical species are related as follows:

$$\Delta_f G^\circ = \Delta_f H^\circ - T \Delta_f S^\circ. \quad (4-1)$$

where T = absolute temperature,

and $\Delta_f S^\circ$ = standard entropy of formation, which is given by

$$\Delta_f S^\circ = S^\circ_{\text{species}} - \sum_i s_i S^\circ_i, \quad (4-2)$$

where S°_{species} = standard entropy of species in equation 4-1,

S°_i = standard entropies of i elements contained in the species,

and s_i = stoichiometric coefficients for formation of the species from the i elements.

Chemical Reactions

For a chemical reaction,

$$\sum_i s_{r,i} (\text{reactant species})_{r,i} \rightarrow \sum_i s_{p,i} (\text{product species})_{p,i}, \quad (4-3)$$

$$\Delta_r G^\circ = \sum_i s_{p,i} (\Delta_f G^\circ)_{p,i} - \sum_i s_{r,i} (\Delta_f G^\circ)_{r,i}, \quad (4-4)$$

$$\Delta_r H^\circ = \sum_i s_{p,i} (\Delta_f H^\circ)_{p,i} - \sum_i s_{r,i} (\Delta_f H^\circ)_{r,i}, \quad (4-5)$$

$$\Delta_r S^\circ = \sum_i s_{p,i} (S^\circ)_{p,i} - \sum_i s_{r,i} (S^\circ)_{r,i}. \quad (4-6)$$

In equations 4-3 through 4-6, the $s_{p,i}$ and $s_{r,i}$ are the stoichiometric coefficients for the products and reactants, respectively, in the reaction; the Gibbs energy, enthalpy, and entropy terms have corresponding meanings.

The thermodynamic equilibrium constant K is defined by

$$\Delta_r G^\circ = -RT \ln K \quad (4-7)$$

$$= -2.3026 RT \log K \quad (4-8)$$

$$= -5.708 \log K \text{ at } 25^\circ\text{C}, \quad (4-9)$$

where T = absolute temperature,

and R = the gas constant, $8.3145 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$.

The thermodynamic equilibrium constant K is related to the activities of the reactants and products by the mass-action equation

$$K = \frac{\prod_i (a^s)_{p,i}}{\prod_i (a^s)_{r,i}} \quad (4-10)$$

In logarithmic form,

$$\log K = \sum_i s_{p,i} \log a_{p,i} - \sum_i s_{r,i} \log a_{r,i} \quad (4-11)$$

where $a_{p,i}$ and $a_{r,i}$ = activities of the i th product and reactant species, respectively.

For gaseous species, fugacity is used instead of activity. Under conditions encountered in hydrometallurgy, gases can be considered ideal, so that fugacity is equal to partial pressure. An example is the dissociation of HCN:

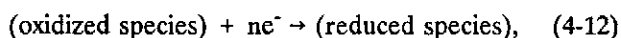
	$\Delta_r G^\circ, \text{ kJ}$	$\log K$	K
$\text{HCN} \rightarrow \text{H}^+ + \text{CN}^-$	+52.6	-9.21	6.2×10^{-10}
$\text{CN}^- + \text{H}^+ \rightarrow \text{HCN}$	-52.6	+9.21	1.6×10^9

For two or more reactions in sequence, the standard Gibbs energy changes $\Delta_r G^\circ$ and the $\log K$ values are added, and the K values are multiplied to give the values for the combined reactions. For example:

	$\Delta_r G^\circ, \text{ kJ}$	$\log K$	K
$\text{CN}^- + \text{H}^+ \rightarrow \text{HCN}$	-52.6	+9.21	1.6×10^9
$\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^-$	+79.9	-14.00	1.0×10^{-14}
$\text{CN}^- + \text{H}_2\text{O} \rightarrow \text{HCN} + \text{OH}^-$	+27.3	-4.79	1.6×10^{-5}

Redox Reactions

Redox half-reactions are by convention written as reductions:



where e^- = electron

and n = number of electrons.

The standard reduction potential E° of half-reaction 4-12 is given by

$$E^\circ = -\Delta_{\text{hr}} G^\circ / nF, \quad (4-13)$$

where $\Delta_{\text{hr}} G^\circ$ = standard Gibbs energy change for the half-reaction,

n = number of electrons transferred,

and F = Faraday constant, $96.485 \text{ kJ} \cdot \text{V}^{-1} \cdot \text{equiv}^{-1}$.

The potential E of a half-reaction in any solution is related to the standard potential E° by the Nernst equation:

$$E = E^\circ - (RT/nF) \ln Q \quad (4-14)$$

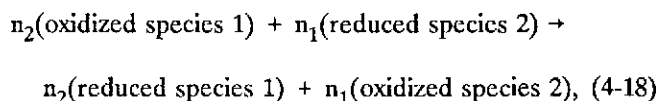
$$= E^\circ - (2.3026RT/nF) \log Q \quad (4-15)$$

$$= E^\circ - 0.05916 \log Q \text{ at } 25^\circ \text{ C}, \quad (4-16)$$

$$\text{where } \log Q = \log a_{\text{Ox}} - \log a_{\text{Rd}}, \quad (4-17)$$

where a_{Ox} and a_{Rd} = activities of the oxidized and reduced species, respectively.

For the redox reaction



the thermodynamic quantities are

$$E_r^\circ = E_1^\circ - E_2^\circ, \quad (4-19)$$

$$\Delta_r G^\circ = -n_1 n_2 F E_r^\circ, \quad (4-20)$$

and, from equations 4-8 and 4-9,

$$\log K = n_1 n_2 F E_r^\circ / 2.3026 RT \quad (4-21)$$

$$= 5039.7 n_1 n_2 E_r^\circ / T \quad (4-22)$$

$$= n_1 n_2 E_r^\circ / 0.05916 \text{ at } 25^\circ \text{ C}. \quad (4-23)$$

Activity, Activity Coefficients, and Equilibrium Constants

The definition of the thermodynamic equilibrium constant K was given above in equations 4-10 and 4-11 in terms of activities rather than concentrations. In this section, activity and activity coefficient are defined, and the relationship of experimentally determined equilibrium constants to the thermodynamic equilibrium constant is described.

The activity of a pure solid or liquid species is equal to 1 by definition. For a dissolved species, the activity a is related to the concentration c by the dimensionless activity coefficient γ :

$$a = \gamma c. \quad (4-24)$$

For aqueous solutions, γ approaches 1 as c approaches zero, so that at very low concentrations, $a = c$. For aqueous species the standard state is defined as unit activity, which is equivalent to a hypothetical ideal concentration of 1 mol solute per kilogram H_2O with $\gamma = 1$.

As noted, the thermodynamic equilibrium constant K for a reaction is defined in terms of activities rather than concentrations. However, equilibrium constants are usually determined experimentally in terms of concentrations. Equilibrium constants thus determined are called concentration equilibrium constants K_c . According to equation 4-24, activity coefficients vary with concentration, so concentration equilibrium constants must be determined under conditions where activity coefficients are constant. This is achievable by conducting the determinations in solutions that contain an added inert electrolyte. The concentrations of the species that participate in the equilibrium being studied are usually maintained at low values relative to the concentration of added inert electrolyte. Under these conditions, all activity coefficients depend only on the concentration of inert electrolyte. The variation of the activity coefficients with inert electrolyte concentration is proportional to the sum of the concentrations and squared charges of the ions, a quantity termed the "ionic strength." The ionic strength is defined and discussed in appendix A. When equilibrium constants are reported, the ionic strength must therefore be specified, along with the temperature. To obtain the thermodynamic equilibrium constant K , the concentration equilibrium constant K_c is determined at several different values of ionic strength. A plot of $\log K_c$ versus ionic strength approaches $\log K$ as the ionic strength approaches zero, and $\log K$ is accordingly obtained by extrapolation. In practice, K_c may be approximated as K at ionic strengths below 0.01M.

The notation in use for equilibrium constants requires comment. In the literature on equilibrium data, the symbol K is usually used for equilibrium constants both at zero and finite ionic strengths. In multistep equilibria such as metal complex formation, the symbol K is usually used for single-step equilibria (e.g., $\text{ML}_2 + \text{L} \rightleftharpoons \text{ML}_3$, with metal ion M and ligand L) and β for cumulative equilibria (e.g., $\text{M} + 3\text{L} \rightleftharpoons \text{ML}_3$). Martell and Smith (1-4)¹ in their authoritative compilations use only the symbol K , and that

practice will be followed in this publication. Appropriate subscripts will be used where necessary to distinguish K values for different equilibria, as in the examples discussed in the last section of this chapter.

DATA AND SOURCES

This section outlines the data requirements and data sources pertinent to aqueous chemical equilibria of interest in cyanide systems. The data tables in this publication are described.

Data Requirements

Thermodynamic data are required for delineating the chemical equilibria in any system. In the context of this publication, data are required for the following categories of chemical species:

- Free cyanide and derived species.
- Solid and dissolved metal cyanide species.
- Auxiliary species.
- Metal oxides, hydroxides, and aqueous ions.
- Species that may react with cyanide and derived species.
- Species that may precipitate or complex with metal ions.
- Solid metal compounds and soluble metal complexes with auxiliary species.

For equilibria at 25° C, the required data consist of the standard Gibbs energies of formation $\Delta_f G^\circ$ of each chemical species. The standard enthalpies of formation $\Delta_f H^\circ$ and entropies S° of the chemical species are required for equilibria at other temperatures.

Chemical equilibria depend on other variables that are readily measured:

- Temperature.
- Pressure.
- pH.
- Oxidation-reduction (redox) potential.
- Ionic strength.

The pH is measurable by means of a glass electrode and is not the same as acidity or alkalinity determined by titration.

The redox potential may be measured relative to any reference electrode, then converted to the value relative to the standard H^+/H_2 electrode. Redox potentials in thermodynamic or equilibrium data compilations are always relative to the standard H^+/H_2 electrode.

The concept of ionic strength is reviewed in appendix A. A conductivity measurement may be used to estimate

¹Italic numbers in parentheses refer to items in the list of references at the end of this chapter.

the ionic strength if most of the total electrolyte concentration is due to a single salt, e.g., NaCl. In such cases, the salt concentration may be determined from conductivity versus concentration data. Otherwise, chemical analysis of the solution is required.

Summary of Data Tables

The thermodynamic data are compiled in appendixes B, C, and D. An outline of the tabulated data and the major source compilations follows:

Table B-1: $\Delta_f H^\circ$ and $\Delta_f G^\circ$ for free cyanide and derived species at 25° C. The major source is the NBS tables (5).

Table B-2: Log K for aqueous reactions of free cyanide and derived species. Data are tabulated for temperatures 0°, 10°, 25°, 40°, 60°, and 90° C and ionic strengths 0M, 0.1M, 1.0M, and 3.0M. The temperature range includes temperatures for published reaction rate data as well as temperatures likely to be encountered in practice. The major data sources are the compilations of Martell and Smith (1-4) and Christensen and others (6).

Table B-3: Solubilities of compounds derived from or related to cyanide. These data were used to obtain some of the values in table B-1, as shown by the references cited.

Table C-1: $\Delta_f H^\circ$ and $\Delta_f G^\circ$ for auxiliary species at 25° C. The format is the same as in table B-1. The major data sources are the NBS tables (5) and a CODATA report (7).

Table C-2: Log K for aqueous reactions of auxiliary species. The format is the same as in table B-2. The major data sources are the compilations of Martell and Smith (1-4) and Christensen and others (6). The review of Wilhelm and others (8) provided sources of gas solubility data.

Table D-1: $\Delta_f G^\circ$ for aqueous metal ions at 25° C. The NBS tables (5) and the CODATA report (7) provided some data; more recent primary sources (listed in appendix D) also provided many values.

Tables D-2 through D-24: Log K for formation of solid metal compounds and soluble metal complexes in aqueous solution at 25° C and ionic strength 0, 0.1, 1.0, and 3.0M. Data for equilibria at other temperatures are insufficient for doing meaningful calculations, so they are not given here. Tables D-2 through D-23 also include $\Delta_f G^\circ$ values for solid metal compounds and metal species in aqueous solution at 25° C. Most of the equilibrium data are from Martell and Smith (1-4). Additional equilibrium data for metal ion hydrolysis and precipitation of hydrous metal oxides were obtained from Baes and Mesmer (9). Gibbs energies of formation of metal oxides and sulfides were taken mainly from USBM bulletins (10-11); the compilation of Mills (12) was also consulted for metal sulfides.

Data for metal cyanide species were also obtained from the monograph by Sharpe (13) and the review by Beck (14).

For all of the tables in appendixes B, C, and D, primary sources were consulted for more extensive or more recent data. These primary sources are referenced in the respective appendixes and cited in the columns "Additional references."

Additional Details Concerning Data for Metal Species

Older references for thermodynamic data on metal species, such as Latimer (15), Garrels and Christ (16), Sillen and Martell (17-18), or Pourbaix (19) are obsolete. The recent compilation of Bard and others (20) is a successor to Latimer (15). In its attempt to be comprehensive, it references some of the older compilations (15, 17-19, 21) for data not located in more recent sources.

The literature contains discrepancies for log K values. Some recent publications on cyanide chemistry in precious-metal hydrometallurgy give tables of log K data for metal cyanide species, some of which are obsolete and unreliable. For example, Huiatt and others (22) and Smith and Mudder (23) compiled values from Sharpe (13); Smith and Mudder (23) also tabulated some data from Caruso (24). Some data quoted by Caruso (24) and Broderius (25) disagree with the compilations of Martell and Smith (1-4). The authors have chosen the most up-to-date and accurate log K data for this report.

Data have been compiled for the aqueous ions and solid compounds and soluble complexes of Zn(II), Cd(II), Hg(I), Hg(II), Cu(I), Cu(II), Ag(I), Au(I), Au(III), Ni(II), Co(II), Co(III), Fe(II), Fe(III), Mn(II), Mn(III), Cr(III), Ti(I), Ti(III), and Pb(II). Species involving Cr(II), V(II), V(III), V(IV), and V(V) are excluded because sufficient thermodynamic data are not available to construct equilibrium predominance area diagrams. No thermodynamic data are available for any vanadium cyanide complexes. Further, V(II), V(III), and Cr(II) are so readily oxidized that they are unlikely to be encountered in hydrometallurgical or environmental situations.

Besides the solid cyanides and soluble cyanide species, data are included for the solid oxides, hydroxides, sulfides, and carbonates, and for the soluble complexes with OH⁻, Cl⁻, SH⁻, S₂O₃²⁻ (thiosulfate), SO₄²⁻ (sulfate), NCS⁻ (thiocyanate), and NH₃ (ammonia). Data are also included for the aqueous ions, hydroxides, and carbonate and sulfate species of magnesium and calcium.

In the thermodynamics tables, coordinated H₂O is omitted from all species, including complexes often formulated with coordinated H₂O such as amine and cyanide complexes of Co, Cr, or Fe. For example, [Fe(CN)₅(H₂O)]³⁻ is tabulated as [Fe(CN)₅]³⁻.

The log K values for reactions of metal species are rounded to the nearest 0.1 unit, because the accuracy of most experimental determinations is of that order of magnitude. An uncertainty of 0.10 in log K° at 25° C corresponds to an uncertainty of 0.57 kJ in $\Delta_r G^\circ$, in accordance with equation 4-8. The $\Delta_r G^\circ$ values for metal oxides and sulfides taken from the literature are rounded to the nearest 1 kJ·mol⁻¹, which corresponds to the accuracy of most of the data.

Often data are not given for zero ionic strength. Estimated values at zero ionic strength were made by comparison with analogous systems for which data at zero and finite ionic strengths are available (1-4). Details of these estimates are given with the data in tables D-2 through D-23.

For metal oxides and sulfides, the $\Delta_r G^\circ$ values were combined with $\Delta_r G^\circ$ data for the metal ions (table D-1) and H₂O, OH⁻, or H₂S (table C-1) to calculate log K

values for solubility equilibria at zero ionic strength. For all other species, the log K values at zero ionic strength were combined with $\Delta_r G^\circ$ values for metal ions (table D-1), cyanide and derived species (table B-1), and auxiliary species (table C-1), to calculate $\Delta_r G^\circ$ values via equation 4-8. Values of $\Delta_r G^\circ$ in tables D-2 through D-23 thus obtained from log K values are calculated to 0.1·kJ·mol⁻¹ precision to minimize roundoff errors during subsequent calculations.

Generally, any given metal ion does not form complexes or insoluble compounds with all of the auxiliary species mentioned above. A summary of the existence of metal complexes and insoluble compounds is given in table 4-1. Table 4-1 also indicates the accuracy of the published log K data for metal species and the generation of estimates where data are not available. Full details are given in tables D-2 through D-23.

Table 4-1.—Existence of metal complexes¹ and basis of thermodynamic data²

Metal ion	M ⁿ⁺ (aq)	CN ⁻		O ²⁻ , OH ⁻ s	OH ⁻ c	Cl ⁻		S ²⁻ s	SH ⁻ c	S ₂ O ₃ ²⁻ c	SO ₄ ²⁻		NH ₃ c	CO ₃ ²⁻ s	NCS ⁻	
		c	s			c	s				c	s			c	s
Zn(II)	A	A	R	A	R	R		R	I	I	I		A	U	R	
Cd(II)	A	A	U	A	U	R		R	I	I	I		A	U	R	
Hg(I)	A	N	N	N	R	N	A	N	N	N	I	A	N	U	N	A
Hg(II)	A	A	A	A	R	I	R	R	I	I	I		I	U	R	R
Cu(I)	A	U	U	A	X	I	R	R	X	I	X		I	N	I	U
Cu(II)	A	O		A	R	R		R	O	O	R		A	U	R	
Ag(I)	A	A	A	A	A	R	A	A	U	I	R		A	R	R	
Au(I)	U	E	E	X	E	E	U	U	U	E	X		E	N	E	X
Au(III)	U	E		R	E	E		O	O	O	W		E	N	EX	
Ni(II)	A	A	R	A	U	I		R	N	N	R		A	U	I	
Co(II)	A	U	X	A	U	I		R	N	N	R		R	U	I	
Co(III)	R	E		UX	X	XO		O	O	O	X		E	N	O	
Fe(II)	A	R	X	A	U	X		R	N	N	X		X	U	U	
Fe(III)	A	R		A	R	R		O	O	O	R		N	N	R	
Mn(II)	R	E	X	A	UX	I		R	O	O	R		I	U	I	
Mn(III)	R	E		A	IX	XO		O	O	O	X		N	N	O	
Cr(III)	U	E		RU	I	IX		U	N	N	X		E	N	IX	
Tl(I)	A	N		N	N	R	A	R	I	I	R		N	N	I	R
Tl(III)	R	I		R	R	R		O	O	O	IX		N	N	O	
Pb(II)	A	N		A	R	R	R	R	N	I	R	R	N	U	I	R

¹aq, aqueous; c, in solution; s, solid phase.

²More than one symbol may be entered if several species exist:

A Reliable published data, ± 1 kJ·mol⁻¹ or better.

E Estimates based on incomplete data.

I Data at finite ionic strengths; data at zero ionic strength estimated.

N No data; complexes probably weak or species not likely to exist under anticipated conditions.

O Redox reaction.

R Reliable published data, $\pm 1-3$ kJ·mol⁻¹.

U Published data of uncertain accuracy, ± 3 or more kJ·mol⁻¹.

X No published data; estimates based on qualitative information or trends in data for related systems.

EQUILIBRIUM PREDOMINANCE AREA DIAGRAMS

Equilibrium data are presented in appendix E in the form of equilibrium predominance area diagrams (EPAD, singular or plural). An EPAD shows the predominant chemical species in a system as a function of certain independent variables. The independent variables are chosen based on the nature of the system and the information to be displayed.

This section discusses the variables involved in EPAD for aqueous equilibria; the treatment of solution, solid, and gaseous species; the construction of EPAD; and the reliability of EPAD.

Variables in EPAD for Aqueous Systems

For aqueous systems, an EPAD shows the predominant chemical species in a system as a function of temperature, pressure, and composition variables. Temperature and total pressure are constant in all EPAD in this publication at values of 25° C (298.15 K or 77° F) and 10⁵ Pa (1 bar or (1/1.01325) atm), respectively. The four composition variables are pH, pM, pL, and Eh:

- pH = -log (activity of H⁺) = -log a(H⁺).
- pM = -log (total activity of all dissolved metal species). For example, if M is zinc, pM = pZn = -log [a(Zn²⁺) + a(Zn(OH)⁺) + a(Zn(OH)₂) + ... + terms for each of all other dissolved Zn species]. This total includes complexes, e.g., the Zn²⁺/CN⁻ species if HCN/CN⁻ is present as a ligand. If more than one metal is present, separate pM's are defined for each metal. For example, if zinc and copper are both present, pM' = pZn and pM'' = pCu are used.
- pL = -log (total activity of free ligand species). For example, if L is cyanide, pL = pCN = -log [a(CN⁻) + a(HCN)]; if L is carbonate, pL = pCO₃ = -log [a(CO₃²⁻) + a(HCO₃⁻) + a(CO₂(aq))]. If more than one ligand is present, separate pL's are defined for each ligand. For example, if cyanide and carbonate are both present, pL' = pCN and pL'' = pCO₃ are used.
- Eh = reduction potential relative to the standard H⁺/H₂ electrode, E°[2H⁺ + 2e⁻ = H₂(g)] = 0.

To generate EPAD, two of these four composition variables are chosen as independent variables, and the other two are held constant. The six possible kinds of EPAD, therefore, include the following:

- Eh-pH diagrams (pM, pL constant).
- pM-pH diagrams (Eh, pL constant).
- pM-pL diagrams (Eh, pH constant).
- pL-pH diagrams (Eh, pM constant).
- Eh-pM diagrams (pH, pL constant).
- Eh-pL diagrams (pM, pH constant).

Not all four composition variables may be involved in an EPAD. For example, a pL-pH diagram may be drawn to show the equilibria of a ligand without any metal ions. Constant oxidation state is often used as an alternative to constant Eh. The choice among these six kinds of EPAD depends on the problem of interest, as shown by examples in chapter 11.

Solution Species

EPAD are constructed from thermodynamic data, which consist of Δ_fG° data for all of the species in the system. Hence, they are based on activities of species, which become numerically equal to concentrations at ionic strengths below 0.1M. Because they are based on activities, EPAD are independent of ionic strength. At ionic strengths above 0.1M, equation 4-24 may be used with known or estimated activity coefficients to obtain concentrations.

Solid Phases

If slightly soluble solid phases, e.g., metal compounds, exist, EPAD can be constructed to show the approximate solubility contours. The solubility contours are approximate; they give solubilities lower than the true values to the extent that the predominant solution species in equilibrium with the solid phase constitutes less than 100 pct of the total solution species in equilibrium with that solid phase.

Gaseous Species

If a gaseous species, e.g., a volatile free-ligand species, is involved, approximate isobars for its partial pressure in the system can be displayed on EPAD. The isobars are approximate to the extent that the predominant solution species in equilibrium with the gaseous species constitutes less than 100 pct of the total solution species in equilibrium with that gaseous species.

Construction of EPAD

EPAD are constructed via computer programs, typically by the following procedure:

1. Inputting the standard Gibbs energies of formation Δ_fG° of all species;
2. Writing all possible reactions between species;
3. Calculating the standard Gibbs energy changes Δ_rG° and equilibrium constants K of each of the reactions according to equations 4-4 and 4-8;
4. Expressing the equilibria for the reactions as equations in logarithmic form in accordance with equation 4-11;

5. Plotting these equations against the chosen independent composition variables;

6. Examining the plots to determine the predominant species, and retaining only those equations and plots that define the areas of predominant species. Each predominant species occupies an area bounded by straight lines, which separate it from areas occupied by other predominant species. The straight lines that bound the areas of predominant species correspond to the equilibria that relate them.

For this publication, EPAD were generated by the program "SYSTEM," which is part of the CSIRO-SGTE thermodynamics program package (26). The input to the SYSTEM program consists of the standard Gibbs energies $\Delta_f G^\circ$ of formation of all species (tables B-1, C-1, and D-1 through D-23), along with the other parameters required to specify the desired diagram.

Reliability of EPAD

To obtain reliable diagrams, reliable thermodynamic data must be input. Unfortunately, some of the compilations often cited by authors of published diagrams are obsolete. In this report, much effort was made to obtain the most reliable thermodynamic data. A large number of EPAD were calculated from the thermodynamic data in tables B-1, C-1, and D-1 through D-23 and are presented in appendix E.

Osseo-Asare and others (27) published EPAD for metal-cyanide systems in 1984. The data base from which their diagrams are generated is not completely up to date; the references cited there include some of the obsolete references mentioned previously (15-17, 19). Consequently, the accuracy of their diagrams is limited. In the case of cobalt, the diagram is incorrect because of erroneous information on the cyanide complexes.

Wang and Forssberg (28) published several EPAD in 1990, involving metal cyanide species. They cited Smith and Martell (7), Bard and others (20), and some of the older compilations (16-18) for their input data. Overall, their input data are more recent and more reliable than the data used by Osseo-Asare and others (27).

In systems where there are known species for which no thermodynamic data are available, those species are usually not shown in published EPAD (27-28). This can result in misleading diagrams. If sufficient data are not available, estimates of the missing data should be employed and specified. Tolerable estimates can be made from semiquantitative or even qualitative chemical information about the system. Otherwise, the EPAD should be clearly labeled or captioned with regard to missing data. In this publication, missing data were estimated; the details

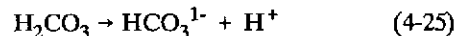
of the estimates are given in the data tables in appendixes B, C, and D.

INFORMATION OBTAINABLE BY INSPECTION OF LOG K DATA

A list of equilibria and log K values for a system may seem bewildering. However, it is possible, as shown below, to extract useful information from log K data tables and visualize what EPAD for a system look like. All of the data in the examples below are taken from the tables in appendixes C and D. The following examples include a polyprotic acid, metal ion hydrolysis, and some systems of metal complexes.

Example 1: Polyprotic Acid

For an example of a polyprotic acid, consider the pH-EPAD for carbonic acid (H_2CO_3). The equilibria are as follows:



$$K_{a1} = [\text{HCO}_3^{1-}][\text{H}^+]/[\text{H}_2\text{CO}_3] = 1/K_{f2} \quad (4-27)$$

$$K_{a2} = [\text{CO}_3^{2-}][\text{H}^+]/[\text{HCO}_3^{1-}] = 1/K_{f1} \quad (4-28)$$

For acid dissociation equilibria, the notation $\text{p}K_a = -\log K_a$ is commonly used. The $\log K_f$ notation is introduced to show the similarity of polyprotic acid dissociation equilibria with metal-ligand equilibria described subsequently. Multiplication of equation 4-27 by equation 4-28 gives

$$\begin{aligned} K_{a12} &= [\text{CO}_3^{2-}][\text{H}^+]^2/[\text{H}_2\text{CO}_3] = 1/K_{f12} \\ &= K_{a1}K_{a2} = 1/K_{f2}K_{f1}. \end{aligned} \quad (4-29)$$

The values are $\log K_{a1} = -\text{p}K_{a1} = -\log K_{a2} = -6.3$ and $\log K_{a2} = \text{p}K_{a2} = -\log K_{f1} = -10.3$, from table C-2. From equation 4-29, $K_{a12} = 1/K_{f12} = 10^{-16.6}$, or $\log K_{a12} = -\log K_{f12} = -16.6$. The quantities K_{f1} , K_{f2} , and K_{f12} constitute formation constants of HCO_3^{1-} and H_2CO_3 from CO_3^{2-} and H^+ . K_{f1} and K_{f2} are stepwise formation constants, and K_{f12} is the cumulative formation constant. This formation constant terminology exactly parallels the terminology for metal complexes as shown below. From the data, equations 4-27 and 4-28, and the definition of predominance areas, the values

$$\begin{aligned} \text{pH}_{12} &= 6.3 = -\log [\text{H}^+]_{12} \\ &= -\log K_{a1} = \log K_{f2} \end{aligned} \quad (4-30)$$

$$\begin{aligned}\text{and } \text{pH}_{01} &= 10.3 = -\log [\text{H}^+]_{01} \\ &= -\log K_{a2} = \log K_{f1} \quad (4-31)\end{aligned}$$

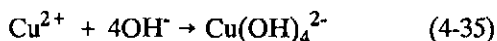
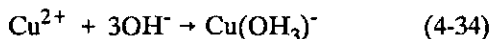
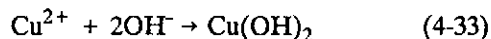
divide the predominance areas H_2CO_3 versus HCO_3^- and HCO_3^- versus CO_3^{2-} , respectively. Thus in a pL-pH EPAD of a weak acid, the boundaries of the predominance areas occur at pH values equal to the $\text{pK}_a = -\log K_a$ values. The H_2CO_3 example is illustrated in figure E-2.

Example 2: Hydrolyzable Metal Ion

The hydrolysis of metal ions results from the fact that metal ions behave like polyprotic acids. Alternatively, the hydrolysis of metal ions can be viewed as complex formation of the metal ions with the ligand OH^- . Metal ion hydrolysis equilibria are tabulated by Martell and Smith (I-4) and in appendix D in terms of the cumulative formation constants from the metal ion and OH^- . These equilibria can be alternatively expressed as ionization of a weak acid, as shown in the subsequent paragraph.

Solution Species

As an example, consider the hydrolysis of Cu^{2+} and the corresponding pM-pH EPAD. The equilibria are



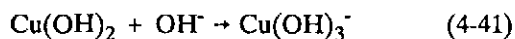
$$K_{f1} = [\text{Cu}(\text{OH})^+]/[\text{Cu}^{2+}][\text{OH}^-] \quad (4-36)$$

$$K_{f12} = [\text{Cu}(\text{OH})_2]/[\text{Cu}^{2+}][\text{OH}^-]^2 \quad (4-37)$$

$$K_{f123} = [\text{Cu}(\text{OH})_3^-]/[\text{Cu}^{2+}][\text{OH}^-]^3 \quad (4-38)$$

$$K_{f1234} = [\text{Cu}(\text{OH})_4^{2-}]/[\text{Cu}^{2+}][\text{OH}^-]^4 \quad (4-39)$$

Note the similarity of equations 4-36 through 4-39 to equations 4-27 and 4-28. The tabulated values are $\log K_{f1} = 6.5$, $\log K_{f12} = 11.8$, $\log K_{f123} = 15.0$, and $\log K_{f1234} = 16.4$, from table D-7. To visualize the equilibria, the remaining stepwise equilibria are derived:



$$K_{f2} = [\text{Cu}(\text{OH})_2]/[\text{Cu}(\text{OH})^+][\text{OH}^-] \quad (4-43)$$

$$K_{f3} = [\text{Cu}(\text{OH})_3^-]/[\text{Cu}(\text{OH})_2][\text{OH}^-] \quad (4-44)$$

$$K_{f4} = [\text{Cu}(\text{OH})_4^{2-}]/[\text{Cu}(\text{OH})_3^-][\text{OH}^-] \quad (4-45)$$

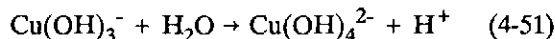
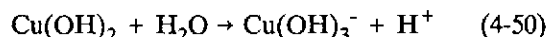
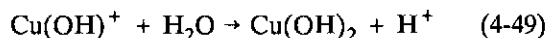
The second stepwise constant, $\log K_{f2}$, is defined by equations 4-40 and 4-43, and is $11.8 - 6.5 = 5.3$. Similarly, $\log K_{f3}$ from equations 4-41 and 4-44 is 3.2, and $\log K_{f4}$ from equations 4-42 and 4-45 is 1.4.

To obtain pH values for visualizing the EPAD, the equilibrium for the dissociation of H_2O ,



$$K_w = [\text{H}^+][\text{OH}^-], \quad (4-47)$$

with $\log K_w = -\text{p}K_w = -14.0$, is required. By combining equations 4-46 and 4-47 with the stepwise equilibria 4-32, 4-36, and 4-40 through 4-45, the equilibria are expressed as acid dissociations:



$$K_{a1} = [\text{Cu}(\text{OH})^+][\text{H}^+]/[\text{Cu}^{2+}] \quad (4-52)$$

$$K_{a2} = [\text{Cu}(\text{OH})_2][\text{H}^+]/[\text{Cu}(\text{OH})^+] \quad (4-53)$$

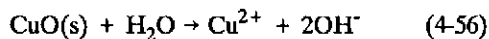
$$K_{a3} = [\text{Cu}(\text{OH})_3^-][\text{H}^+]/[\text{Cu}(\text{OH})_2] \quad (4-54)$$

$$K_{a4} = [\text{Cu}(\text{OH})_4^{2-}][\text{H}^+]/[\text{Cu}(\text{OH})_3^-] \quad (4-55)$$

Therefore $\log K_{a1} = 6.5 - 14.0 = -7.5$, and similarly, $\log K_{a2} = -8.7$, $\log K_{a3} = -10.8$, and $\log K_{a4} = -12.6$. The pH values 7.5, 8.7, 10.8, and 12.6 divide the respective predominance areas of Cu^{2+} , $\text{Cu}(\text{OH})^+$, $\text{Cu}(\text{OH})_2$, $\text{Cu}(\text{OH})_3^-$, and $\text{Cu}(\text{OH})_4^{2-}$. Thus, in a pM-pH EPAD of the hydrolysis of a metal ion, the boundaries of the predominance areas occur at pH values equal to the $\text{pK}_a = -\log K_a$ values for the metal ion considered as a polyprotic acid.

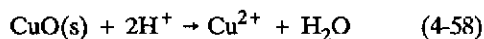
Slightly Soluble Compounds

Slightly soluble metal oxide compounds universally appear in the hydrolysis of metal ions. In this example, they are amorphous or crystalline $\text{Cu}(\text{OH})_2$ or CuO . To illustrate with CuO ,



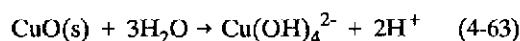
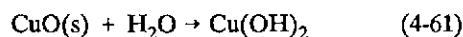
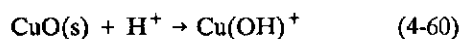
$$K_{s0} = [\text{Cu}^{2+}][\text{OH}^-]^2. \quad (4-57)$$

The value of $\log K_{s0}$ is -20.4. Expressing this equilibrium in terms of H^+ , equations 4-56 and 4-57 with the aid of equations 4-46 and 4-47 are replaced by



$$K_{s0}^* = [\text{Cu}^{2+}]/[\text{H}^+]^2. \quad (4-59)$$

The value of $\log K_{s0}^*$ is $-20.4 + 28.0 = 7.6$. Next, the equilibria of CuO(s) with the hydrolyzed species are written with the aid of equations 4-48 through 4-55:



$$K_{s1}^* = [\text{Cu(OH)}^+]/[\text{H}^+] \quad (4-64)$$

$$K_{s2}^* = [\text{Cu(OH)}_2] \quad (4-65)$$

$$K_{s3}^* = [\text{Cu(OH)}_3^-]/[\text{H}^+] \quad (4-66)$$

$$K_{s4}^* = [\text{Cu(OH)}_4^{2-}]/[\text{H}^+]^2 \quad (4-67)$$

The respective values of $\log K_{s1}^*$ through K_{s4}^* are 0.1, -8.6, -19.4, and -32.0. By combining this information with the hydrolysis species predominance areas obtained in the preceding paragraph, and equations 4-64 through 4-67, the solubility curve for CuO(s) is obtained. The curve is divided into segments that correspond to the pH region of predominance of each solution species. The CuO(s) solubility curve runs from $\text{pM} = 0$ at $\text{pH} = 3.8$, to $\text{pM} = 7.4$ at $\text{pH} = 7.5$, to $\text{pM} = 8.6$ at $\text{pH} = 8.7$, to $\text{pM} = 8.6$ at $\text{pH} = 10.8$, to $\text{pM} = 6.8$ at $\text{pH} = 12.6$, to $\text{pM} = 4.0$ at $\text{pH} = 14.0$. The EPAD for Cu_2^+ hydrolysis with CuO(s) is illustrated in figure E-95.

As indicated above, the solid phase may be some oxide other than CuO . Consider the case where the solid phase is amorphous Cu(OH)_2 . The values of $\log K_{s0}$ and $\log K_{s0}^*$ for the equilibria corresponding to equations 4-56 through 4-59 are respectively -18.8 and 9.2. These values are 1.6 units more positive than the values for CuO(s) , so amorphous Cu(OH)_2 is more soluble. Per mole of H^+ , the values are 0.8 units higher. The result is that on the EPAD, the solubility curve for amorphous Cu(OH)_2 is shifted -0.8 pM units relative to the curve for CuO(s) .

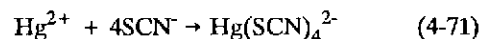
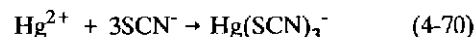
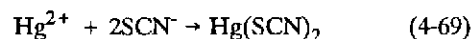
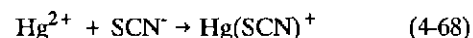
Although this example appears long and time consuming, it is straightforward, and one can perform the computations easily in tabular form. To summarize, the computation may be diagramed, where n = number of OH^- groups bound to Cu^{2+} . The arrows indicate the path through which the computations are executed:

n	$\log K_{fl..n}$	$\log K_n$	$\log K_{an}$	$\log K_{sn}^*$	pM, pH
0	—	—	—	7.6 →	0.0, 3.8
1	6.5 →	6.5 →	-7.5 →	0.1 →	7.4, 7.5
2	11.8 →	5.3 →	-8.7 →	-8.6 →	8.6, 8.7
3	15.0 →	3.2 →	-10.8 →	-19.4 →	8.6, 10.8
4	16.4 →	1.4 →	-12.6 →	-32.0 →	6.8, 12.6
					4.0, 14.0

The values pM, pH in the last column give the coordinates of the solubility profile of CuO on the EPAD.

Example 3: Metal Complex Formation

The dissociation equilibria of polyprotic acids and the formation equilibria of metal complexes are mathematically analogous, as demonstrated below. For the first example of metal complexes, consider the Hg^{2+} - SCN^- system. The cumulative formation equilibria are



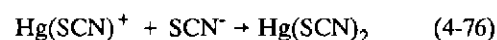
$$K_{f1} = [\text{Hg(SCN)}^+]/[\text{Hg}^{2+}][\text{SCN}^-] \quad (4-72)$$

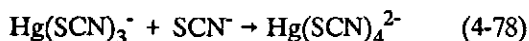
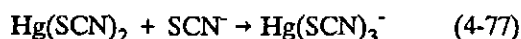
$$K_{f12} = [\text{Hg(SCN)}_2]/[\text{Hg}^{2+}][\text{SCN}^-]^2 \quad (4-73)$$

$$K_{f123} = [\text{Hg(SCN)}_3^-]/[\text{Hg}^{2+}][\text{SCN}^-]^3 \quad (4-74)$$

$$K_{f1234} = [\text{Hg(SCN)}_4^{2-}]/[\text{Hg}^{2+}][\text{SCN}^-]^4. \quad (4-75)$$

The respective values of $\log K_{f1}$ through $\log K_{f1234}$ are 9.2, 17.3, 20.0, and 21.8, from table D-5. The remaining stepwise equilibria are





$$K_{f2} = [\text{Hg}(\text{SCN})_2]/[\text{Hg}(\text{SCN})^+][\text{SCN}^-] \quad (4-79)$$

$$K_{f3} = [\text{Hg}(\text{SCN})_3^-]/[\text{Hg}(\text{SCN})_2][\text{SCN}^-] \quad (4-80)$$

$$K_{f4} = [\text{Hg}(\text{SCN})_4^{2-}]/[\text{Hg}(\text{SCN})_3^-][\text{SCN}^-] \quad (4-81)$$

The respective values of $\log K_{f2}$, $\log K_{f3}$, and $\log K_{f4}$, defined by equations 4-76 through 4-81, are $17.3 - 9.2 = 8.1$, $20.0 - 17.3 = 2.7$, and $21.8 - 20.0 = 1.8$. It follows in the same way as with a polyprotic acid that the $\text{pSCN} = -\log [\text{SCN}^-] = \text{pL} = -\log [\text{L}]$ values $\text{pL}_{01} = 9.2$, $\text{pL}_{12} = 8.1$, $\text{pL}_{23} = 2.7$, and $\text{pL}_{34} = 1.8$ divide the respective predominance areas of Hg^{2+} , $\text{Hg}(\text{SCN})^+$, $\text{Hg}(\text{SCN})_2$, $\text{Hg}(\text{SCN})_3^-$, and $\text{Hg}(\text{SCN})_4^{2-}$.

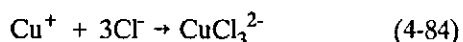
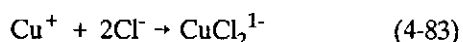
The analogy of metal complex formation and pM-pL EPAD versus hydrolyzable metal ions and polyprotic acids and pM-pH and pL-pH EPAD shows in the correspondence of EPAD variables and the equations above:

L^a (e.g., CO_3^{2-})	M^{n+} (e.g., Cu^{2+})	M^{n+} (e.g., Hg^{2+})
H^+	H^+	L (e.g., SCN^-)
pL-pH	pM-pH	pM-pL

In the example of $\text{Hg}^{2+} - \text{SCN}^-$, the successive stepwise $\log K_f$ values are monotonically ordered, $9.2 > 8.1 > 2.7 > 1.8$. The significance of this is that every species in the system appears on the EPAD. There are many systems of metal complexes where this is not the case, and such a case is provided in the following example.

Example 4: Metal Complex Formation With Disproportionation

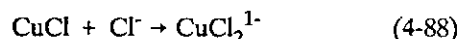
Consider the $\text{Cu}^+ - \text{Cl}^-$ system, for which the equilibria are



$$K_{f1} = [\text{CuCl}]/[\text{Cu}^+][\text{Cl}^-] \quad (4-85)$$

$$K_{f12} = [\text{CuCl}_2^{1-}]/[\text{Cu}^+][\text{Cl}^-]^2 \quad (4-86)$$

$$K_{f123} = [\text{CuCl}_3^{2-}]/[\text{Cu}^+][\text{Cl}^-]^3 \quad (4-87)$$



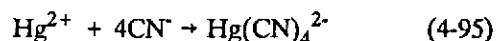
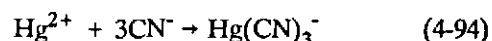
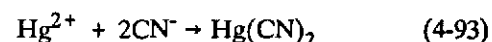
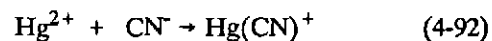
$$K_{f2} = [\text{CuCl}_2^{1-}]/[\text{CuCl}][\text{Cl}^-] \quad (4-90)$$

$$K_{f3} = [\text{CuCl}_3^{2-}]/[\text{CuCl}_2^{1-}][\text{Cl}^-] \quad (4-91)$$

The tabulated data are $\log K_{f1} = 2.7$, $\log K_{f12} = 5.5$, and $\log K_{f123} = 5.7$, respectively, from table D-6. The values of $\log K_{f2}$ and $\log K_{f3}$ are 2.8 and 0.2, respectively. These successive stepwise $\log K_f$ values are in the order $2.7 < 2.8 > 0.2$, so the order is not monotonic. The significance of nonmonotonic ordering of successive stepwise $\log K_f$ values is that the species responsible for the nonmonotonic ordering is relatively unstable and disproportionates to species with fewer and more bound ligands. The result is that the relatively unstable species, CuCl in this example, is never predominant and never appears on an EPAD. To complete solution of the problem, the relatively unstable species is deleted. In this example, that means equations 4-83 and 4-86 are used instead of equations 4-82, 4-85, 4-88, and 4-90. The result is that $\text{pCl} = -\log [\text{Cl}^-] = \text{pL} = -\log \text{L}$ values $\text{pL}_{02} = 5.5/2 = 2.75$ and $\text{pL}_{23} = 0.2$ divide the respective predominance areas of Cu^+ , CuCl_2^{1-} , and CuCl_3^{2-} .

Example 5: Metal Complex Formation With a Hydrolyzable Metal Ion and a Ligand Derived From a Weak Acid

When the ligand is derived from a weak acid, or the metal ion hydrolyzes, the picture is complicated by pH dependence of the equilibria. Consider the $\text{Hg}^{2+} - \text{CN}^-$ system. This system contains both a weak-acid ligand and a hydrolyzable metal ion. The complex-formation equilibria for Hg^{2+} and CN^- are



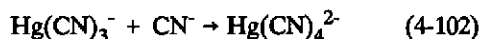
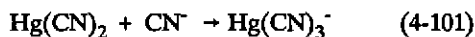
$$K_{f1} = [\text{Hg}(\text{CN})^+]/[\text{Hg}^{2+}][\text{CN}^-] \quad (4-96)$$

$$K_{f12} = [\text{Hg}(\text{CN})_2]/[\text{Hg}^{2+}][\text{CN}^-]^2 \quad (4-97)$$

$$K_{f123} = [\text{Hg}(\text{CN})_3^-]/[\text{Hg}^{2+}][\text{CN}^-]^3 \quad (4-98)$$

$$K_{f1234} = [\text{Hg}(\text{CN})_4^{2-}]/[\text{Hg}^{2+}][\text{CN}^-]^4 \quad (4-99)$$

The respective values of $\log K_{f1}$ through $\log K_{f4}$ are 17.0, 32.8, 36.3, and 39.0, from table D-5. The remaining stepwise equilibria are:



$$K_{f2} = [\text{Hg}(\text{CN})_2]/[\text{Hg}(\text{CN})^+][\text{CN}^-] \quad (4-103)$$

$$K_{f3} = [\text{Hg}(\text{CN})_3^-]/[\text{Hg}(\text{CN})_2][\text{CN}^-] \quad (4-104)$$

$$K_{f4} = [\text{Hg}(\text{CN})_4^{2-}]/[\text{Hg}(\text{CN})_3^-][\text{CN}^-] \quad (4-105)$$

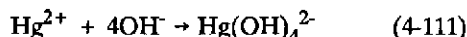
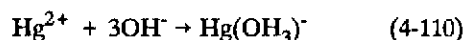
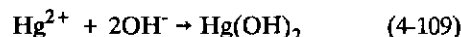
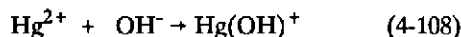
The values of $\log K_{f2}$, $\log K_{f3}$, and $\log K_{f4}$ are 15.8, 3.5, and 2.7, respectively. For the weak acid HCN,



$$K_a = [\text{CN}^-][\text{H}^+]/[\text{HCN}], \quad (4-107)$$

and $K_a = 9.2$ (table B-2). Consequently, HCN predominates at $\text{pH} < 9.2$ and CN^- at $\text{pH} > 9.2$.

For the hydrolysis of Hg^{2+} , the equilibria are



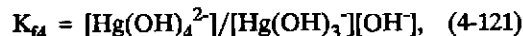
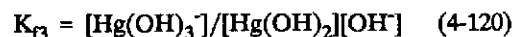
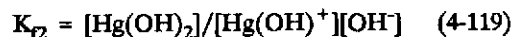
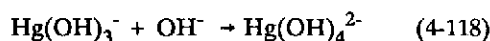
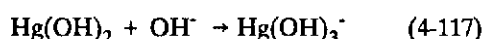
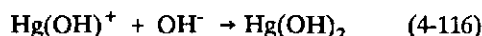
$$K_{f1} = [\text{Hg}(\text{OH})^+]/[\text{Hg}^{2+}][\text{OH}^-] \quad (4-112)$$

$$K_{f12} = [\text{Hg}(\text{OH})_2]/[\text{Hg}^{2+}][\text{OH}^-]^2 \quad (4-113)$$

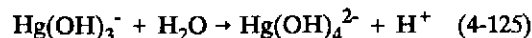
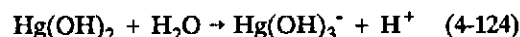
$$K_{f123} = [\text{Hg}(\text{OH})_3^-]/[\text{Hg}^{2+}][\text{OH}^-]^3 \quad (4-114)$$

$$K_{f1234} = [\text{Hg}(\text{OH})_4^{2-}]/[\text{Hg}^{2+}][\text{OH}^-]^4 \quad (4-115)$$

The tabulated values of $\log K_{f1}$ through $\log K_{f1234}$ are 10.6, 21.8, 20.9, and 18.9, respectively, from table D-5. The remaining stepwise equilibria are



for which $\log K_{f2}$, $\log K_{f3}$, and $\log K_{f4}$ are 11.2, -0.9, and -2.0, respectively. The equilibria as acid dissociations are:



$$K_{a1} = [\text{Hg}(\text{OH})^+][\text{H}^+]/[\text{Hg}^{2+}] \quad (4-126)$$

$$K_{a2} = [\text{Hg}(\text{OH})_2][\text{H}^+]/[\text{Hg}(\text{OH})^+] \quad (4-127)$$

$$K_{a3} = [\text{Hg}(\text{OH})_3^-][\text{H}^+]/[\text{Hg}(\text{OH})_2] \quad (4-128)$$

$$K_{a4} = [\text{Hg}(\text{OH})_4^{2-}][\text{H}^+]/[\text{Hg}(\text{OH})_3^-], \quad (4-129)$$

for which $\log K_{a1} = -3.4$, $\log K_{a2} = -2.8$, $\log K_{a3} = -14.9$, and $\log K_{a4} = -16.0$. This series of $\log K_a$ is not monotonic, with the result that $\text{Hg}(\text{OH})^+$ never appears on any EPAD. Therefore equations 4-122, 4-123, 4-126, and 4-127 are combined to give



$$K_{a12} = [\text{Hg}(\text{OH})_2][\text{H}^+]^2/[\text{Hg}^{2+}], \quad (4-131)$$

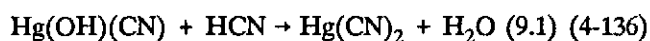
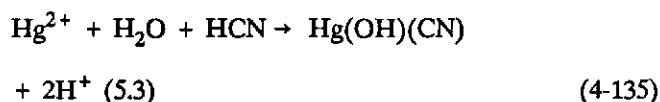
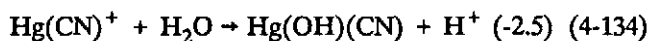
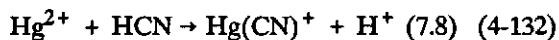
with $\log K_{a12} = -6.2$. The pH values $6.2/2 = 3.1$, 14.9, and 16.0 divide the respective predominance areas of Hg^{2+} , $\text{Hg}(\text{OH})_2$, $\text{Hg}(\text{OH})_3^-$, and $\text{Hg}(\text{OH})_4^{2-}$. In this case, $\text{Hg}(\text{OH})_3^-$ and $\text{Hg}(\text{OH})_4^{2-}$ predominate at $\text{pH} > 14$, and would not usually be shown on EPAD.

In summary, Hg^{2+} predominates at $\text{pH} < 3.1$, and $\text{Hg}(\text{OH})_2$ at $\text{pH} > 3.1$; HCN predominates at $\text{pH} < 9.2$, and CN^- at $\text{pH} > 9.2$. Hence, all of the EPAD are divided into three regions: (1) $\text{pH} < 3.1$, where Hg^{2+} and HCN predominate, (2) $3.1 < \text{pH} < 9.2$, where $\text{Hg}(\text{OH})_2$ and HCN predominate, and (3) $\text{pH} > 9.2$, where $\text{Hg}(\text{OH})_2$ and CN^- predominate.

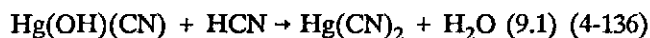
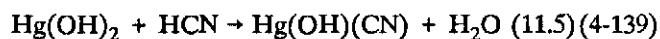
To proceed further, the complex-formation equilibria in equations 4-92, 4-96, 4-100 through 4-105, 4-130, and 4-131 are rewritten in terms of the predominant uncomplexed metal and free ligand species in each region. This is a straightforward but time-consuming procedure. The system also contains the species $\text{Hg}(\text{OH})(\text{CN})$ and

Hg(OH)(CN)_2^- (table D-5). The equilibria are, with their log K values in parentheses,

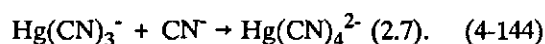
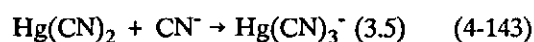
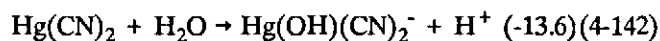
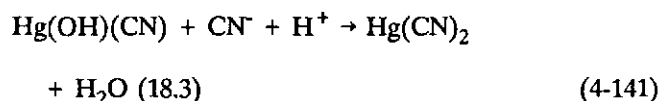
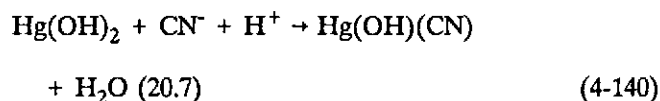
At pH < 3.1:



At 3.1 < pH < 9.2:



At pH > 9.2:



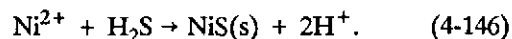
Note that many of equations 4-132 through 4-144 involve H^+ , so that the corresponding predominance area boundaries are pH dependent. Generation of EPAD from these equilibria manually is a time-consuming procedure that involves trial-and-error calculations. Accordingly, EPAD of complex systems such as this are preferably calculated via computer programs. The EPAD for the Hg^{2+} -CN⁻ system are illustrated in figures E-54 through E-73, some of which include other ligands.

Example 6: Generation of Additional EPAD

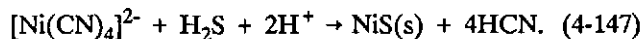
Often an EPAD is desired for a solution composition different from the compositions for which EPAD are provided. As an example, consider the reaction of $[\text{Ni(C-N)}_4]^{2-}$ with $\text{SH-H}_2\text{S}$. Figure E-149 is an EPAD for this system at $\text{pCN} = -\log a(\text{free cyanide}) = 2.0$ and $\text{pS} = -\log a(\text{free sulfide}) = 6.0$. Suppose one is interested in the $[\text{Ni(CN)}_4]^{2-}$ -NiS(s) boundary at other solution compositions. The equation for that boundary is given by the difference of the formation reactions for the predominant Ni species along it. In the pH range of interest, $\text{pH} < 7$, the predominant ligand species are HCN and H_2S . Therefore, the formation reactions are



and



The reaction for the $[\text{Ni(CN)}_4]^{2-}$ -NiS(s) boundary is the difference of reactions 4-145 and 4-146, namely,



From the Gibbs energy data in tables B-1, C-1, and D-11, or the log K data in tables B-2 and D-11, log K for reaction 4-147 is +9.7. The equation for the $[\text{Ni(CN)}_4]^{2-}$ -NiS(s) boundary is

$$-4\text{pCN} + \text{pS} + 2\text{pH} - \log a(\text{Ni}) = 9.7, \quad (4-148)$$

recalling equation 4-11 and the definitions of the composition variables for EPAD described in a previous section of this chapter. The slope of equation 4-148 is +2 pH units per unit of log $a(\text{Ni})$. With $\text{pCN} = 2.0$ and $\text{pS} = 6.0$, $\text{pH} = 5.85$ at $\log a(\text{Ni}) = 0.0$, which checks with figure E-149. With $\text{pCN} = 2.0$ and $\text{pS} = 4.0$, $\text{pH} = 6.85$ at $\log a(\text{Ni}) = 0.0$, and the $[\text{Ni(CN)}_4]^{2-}$ -NiS(s) boundary is shifted 1.0 pH units to the right. Equation 4-148 also shows that at a given pH, $a(\text{Ni})$ is lowered 1 unit for every 1 unit of increase of pS. In other words, if the H_2S concentration is raised by a factor of 10, the nickel solubility drops by a factor of 10, at constant pH.

If in equation 4-148 a different value of pCN were considered, a similar calculation would ensue. However, in this case, as shown by comparing figures E-141 through E-145 with figure E-149, $\text{Ni(CN)}_2(\text{s})$ must be considered. This calls for an equation for the $\text{Ni(CN)}_2(\text{s})$ -NiS(s) boundary, which may be constructed as in the foregoing discussion. Consequently, the reaction of interest may be the conversion of $\text{Ni(CN)}_2(\text{s})$ to NiS(s) instead of reaction 4-147.

REFERENCES

1. Martell, A. E., and R. M. Smith. Critical Stability Constants. V. 3, Other Organic Ligands. Plenum, 1977, 495 pp.
2. Smith, R. M., and A. E. Martell. Critical Stability Constants. V. 4, Inorganic Complexes. Plenum, 1976, 257 pp.
3. Martell, A. E., and R. M. Smith. Critical Stability Constants. V. 5, First Supplement. Plenum, 1982, 604 pp.
4. Smith, R. M., and A. E. Martell. Critical Stability Constants. V. 6, Second Supplement. Plenum, 1989, 662 pp.
5. Wagman, D. D., W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney, and R. L. Nuttall. The NBS Tables of Chemical Thermodynamic Properties. J. Phys. Chem. Ref. Data, v. 11, Supplement 2, 1982, 392 pp.
6. Christensen, J. J., L. D. Hansen, and R. M. Izatt. Handbook of Proton Ionization Heats and Related Thermodynamic Quantities. Wiley-Interscience, 1976, 269 pp.
7. International Council of Scientific Unions. CODATA Recommended Key Values for Thermodynamics, 1977. Report of the CODATA Task Group on Key Values for Thermodynamics, 1977. J. Chem. Thermodyn., v. 10, 1978, pp. 903-906.
8. Wilhelm, E., R. Battino, and R. J. Wilcock. Low-Pressure Solubility of Gases in Liquid Water. Chem. Rev., v. 77, 1977, pp. 219-262.
9. Baes, C. F., Jr., and R. E. Mesmer. The Hydrolysis of Cations. Wiley, 1976, 489 pp.
10. Pankratz, L. B. Thermodynamic Properties of Elements and Oxides. BuMines B 672, 1982, 509 pp.
11. Pankratz, L. B., A. D. Mah, and S. W. Watson. Thermodynamic Properties of Sulfides. BuMines B 689, 1987, 427 pp.
12. Mills, K. C. Thermodynamic Data for Inorganic Sulphides, Selenides, and Tellurides. Butterworths, London, 1974, 845 pp.
13. Sharpe, A. G. The Chemistry of Cyano Complexes of the Transition Metals. Academic, 1976, 302 pp.
14. Beck, M. T. Critical Survey of Stability Constants of Cyano Complexes. Pure Appl. Chem., v. 59, 1987, pp. 1703-1720.
15. Latimer, W. L. The Oxidation States of the Elements and Their Potentials in Aqueous Solution. Prentice-Hall, 2nd ed., 1952, 392 pp.
16. Garrels, R. M., and C. L. Christ. Solutions, Minerals, and Equilibria. Harper and Row, 1965, 450 pp.
17. Sillen, L. G., and A. E. Martell. Stability Constants of Metal-Ion Complexes. Chem. Soc. (London), Spec. Publ. No. 17, 1964, 754 pp.
18. Sillen, L. G., and A. E. Martell. Stability Constants of Metal-Ion Complexes. Supplement No. 1. Chem. Soc. (London), Spec. Publ. No. 25, 1971, 865 pp.
19. Pourbaix, M. Atlas of Electrochemical Equilibria in Aqueous Solutions. Pergamon, 1966, 644 pp.
20. Bard, A. J., R. Parsons, and J. Jordan, (eds.). Standard Potentials in Aqueous Solution. Marcel Dekker, 1985, 834 pp.
21. Rossini, F. D., D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe. Selected Values of Chemical Thermodynamic Properties. NBS Circ. 500, 1952.
22. Huiatt, J. L., J. E. Kerrigan, F. A. Olson, and G. L. Potter (eds.). Workshop on Cyanide From Mineral Processing. UT Min. and Miner. Resour. Res. Inst., 1982, p. 4-12.
23. Smith, A., and T. Mudder. The Chemistry and Treatment of Cyanidation Wastes. Mining Journal Books, London, 1991, pp. 12, 53.
24. Caruso, S. C. The Chemistry of Cyanide Compounds and Their Behavior in the Aquatic Environment. Carnegie Mellon Inst. Res., 1975.
25. Broderius, S. J. Determination of Molecular Hydrocyanic Acid in Water and Studies of the Chemistry and Toxicity to Fish of Metal-cyanide Complexes. Ph.D. Thesis, OR State Univ., Corvallis, OR, 1973, 313 pp.; Diss. Abstr. Int. B., 1973, v. 34, No. 3, p. 1018.
26. Turnbull, A. G., and M. W. Wadsley. SYSTEM (part of CSIRO-SGTE THERMODATA System, version V). CSIRO, Inst. Energy and Earth Resour. Div. Miner. Chem., Port Melbourne, Victoria, Australia, computer program, 1985.
27. Osseo-Asare, K., T. Xue, and V. S. T. Ciminelli. Solution Chemistry of Cyanide Leaching Systems. Ch. in Precious Metals: Mining, Extraction and Processing, ed. by V. Kudryk, D. A. Corrigan, and W. W. Liang. Metall. Soc. AIME, 1984, pp. 173-197.
28. Wang, X., and K. S. E. Forssberg. The Chemistry of Cyanide-Metal Complexes in Relation to Hydrometallurgical Processes of Precious Metals. Miner. Process. Extra. Metall. Rev., v. 6, 1990, pp. 81-125.

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CHAPTER 5.—ULTRAVIOLET AND VISIBLE SPECTRA

INTRODUCTION

Sunlight plays an important role in the degradation of cyanide and metal cyanide species because photochemical reactions are involved. The extent to which a chemical species undergoes photochemical reactions depends on how much light is absorbed by the species at given wavelengths and how the species reacts upon absorption of light. Many metal cyanide species absorb light in the wavelength range 300 to 450 nm (near ultraviolet to blue), and solar radiation in this wavelength range reaches the Earth's surface (*I*).¹ Many metal cyanide species absorb ultraviolet light of wavelengths shorter than 300 nm, but solar radiation in this wavelength range is absorbed by the ozone layer and does not reach the Earth's surface (*I*).

ABSORPTION OF LIGHT BY CHEMICAL SPECIES

The absorption of light by a chemical species is determined by measuring its absorption spectrum with a spectrophotometer. The relationship of measured quantities is

$$A = \epsilon cl, \quad (5-1)$$

where A = absorbance, dimensionless,

ϵ = molar absorptivity, $(\text{mol L}^{-1})^{-1} \cdot \text{cm}^{-1}$,

c = molar concentration, M ($\text{mol} \cdot \text{L}^{-1}$),

and l = absorption path length, cm.

The quantity ϵ depends on the species, solvent, and light wavelength. The dependence of ϵ on temperature is usually slight. If ϵ is independent of c , equation 5-1 expresses the well-known Lambert-Beer law. This is normally the case when ϵ pertains to a single species.

The absorbance A is related to the fraction of light transmitted by

$$\text{pct } T = 100(I/I_0) = 100e^{-A}, \quad (5-2)$$

where $\text{pct } T$ = percent of light transmitted,

I = transmitted light intensity,

and I_0 = incident light intensity.

Some representative values of A and $\text{pct } T$ are

A	3.0	2.0	1.0	0.1	0.01	0.001
$\text{pct } T$	5.0	13.5	36.8	90.5	99.0	99.9

In a mixture of n light-absorbing species,

$$A = l(\epsilon_1 c_1 + \epsilon_2 c_2 + \dots + \epsilon_n c_n). \quad (5-3)$$

The fraction of light absorbed by the i th species is proportional to $\epsilon_i c_i$.

Light of shorter wavelengths is as a rule more strongly absorbed, and is absorbed by many more chemical species, than is light of longer wavelengths. Many chemical species are pale yellow or colorless because they absorb little or no visible light, yet they strongly absorb ultraviolet light. The practical lower wavelength limit for obtaining ultraviolet absorption data is 180 to 200 nm because oxygen, water, and the fused-quartz sample containers absorb light at shorter wavelengths.

For many chemical species that absorb light, the absorption spectrum is characterized by maximum absorptions at certain wavelengths. On either side of the absorption maximum, absorbance decreases over a range of wavelengths. The shapes of these absorption curves, termed "bands," approximate Gaussian (bell-shaped) curves. Often multiple absorption bands occur, and the respective bands are superimposed. The result of superimposition of absorption bands is often the obliteration of absorption maxima, and the absorption spectrum consists of steeply increasing absorption with decreasing wavelength.

DATA PRESENTATION

This chapter contains a compilation of ultraviolet and visible spectroscopic data for cyanide and derived species, metal cyanide complexes, and auxiliary species. It is important to know the molar absorptivities at 300 to 450 nm for auxiliary species and species derived from cyanide in order to assess their interference with photochemical cyanide destruction.

In the literature, spectra are reported as functions of wavelength L , wave number k , or more rarely frequency ν . These quantities are related to each other and the speed of light c :

$$k = 1/L, \quad (5-4)$$

$$c = L\nu = \nu/k. \quad (5-5)$$

¹Italic numbers in parentheses refer to items in the list of references at the end of this chapter.

In this publication, all visible-ultraviolet spectral data are tabulated with respect to wavelength L .

Literature sources for spectroscopic data often quote only absorption maxima and do not show the complete spectra. This practice is more frequent in the more recent literature. However, the complete spectra are needed to evaluate the contribution of species to light absorption in a range of wavelengths. Accordingly, most of the references cited on the tables in this chapter report complete spectra. In this chapter, the molar absorptivities are tabulated at the absorption maxima and at selected wavelengths. The selected wavelengths are 400, 350, and 300 nm, which cover the range of wavelengths of solar ultraviolet light reaching the Earth's surface. Often the molar absorptivity varies greatly with wavelength at wavelengths other than at maximum molar absorptivity. The variation of molar absorptivity can exceed 20 pct per nanometer. Consequently, most of the molar absorptivities quoted at the selected wavelengths are approximate and often given to only one significant figure.

FREE CYANIDE AND DERIVED SPECIES

Ultraviolet and visible spectroscopic data for free cyanide and derived species in aqueous solution are compiled in table 5-1. The species are arranged in the same order as in the tables in chapter 2. Nearly all derived species are colorless, with absorptions at wavelengths <400 nm; some species, including HCN and CN^- , are transparent to 200-220 nm. All of the data are from primary sources (2-30), which give complete spectra for the majority of the most important derived species. For many other auxiliary species, the sources quote only absorption maxima and do not show complete spectra. However, the derived species that are the strongest near-ultraviolet absorbers, 300 to 400 nm, are easily oxidized sulfur compounds that are not expected to occur at significant concentrations; see chapter 7.

METAL CYANIDE SPECIES

Ultraviolet and visible spectroscopic data for metal cyanide species are compiled in table 5-2. The spectra of the metal complexes differ greatly, depending on the metal, its oxidation state, and the composition of the complex. Most of the data are available in Sharpe's monograph (31). Primary sources were consulted for more recent data and complete spectra (32-57).

The cyanide complexes of Zn, Cd, and Hg are colorless and are transparent to below 300 nm, so none of them absorb sunlight. The cyanide complexes of Cu(I), Ag, and Au(I) are all colorless, but have strong ultraviolet absorption maxima. Only the copper complexes absorb significantly at 300 to 350 nm.

The cyanide complexes of Ni(II) and Co(III) are generally yellow and absorb in the blue through the ultraviolet. Nothing is known about dinuclear Co(III) cyanide complexes.

Spectra have been published for several mononuclear and dinuclear iron cyanide complexes. Iron is the most abundant accessory element in precious metals mining, and its cyanide complexes are the strongest ultraviolet absorbers among metal cyanide species. This fact is important for the photochemical degradation of iron cyanide species, which is discussed in chapter 9. Generally there are few or no data for wavelengths below 300 to 350 nm. The mononuclear complexes are all different shades of yellow; the dinuclear complexes have different colors. The data for the dinuclear complexes are approximate, and the molar absorptivities are uncertain by as much as a factor of 2. The data from references 51, 52, and 54 are entered in table 5.2 because in those references spectra for related species were reported, and their relative molar absorptivities are probably reliable.

The spectral data for manganese cyanide complexes are inadequate and do not agree (31); this is attributed to their instability in the absence of excess CN^- . There are no more recent reliable data. The tabulated Cr(III) cyanide complexes are yellow. The vanadium cyanide complexes are known to exist in complex equilibria in aqueous solution (58), and reliable spectra of pure species have not been reported.

Further details of the chemistry of metal cyanide complexes are discussed in chapter 8. The spectra of the Fe, Co, and Cr cyanide complexes are important for their photochemical destruction; see chapter 9.

AUXILIARY SPECIES

Table 5-3 compiles spectroscopic data for auxiliary species (3, 59-86). Most of the oxoanions and their acids do not show absorption maxima at wavelengths above 200 nm. In most cases, complete spectra were located.

Many of the tabulated auxiliary species are oxidants that might be used to destroy cyanides, as well as the species to which these oxidants are thus reduced. These include O_3 , $\text{H}_2\text{O}_2/\text{HO}_2$, and species containing chlorine or bromine. The halate ions ClO_3^- and BrO_3^- form during decomposition of the hypohalites or ClO_2 and ClO_2^- . No spectra of the peroxomonosulfate species HSO_5^- and SO_5^{2-} , the presumed intermediates in SO_2 -air oxidation processes, were located. The spectra of SO_2 and sulfites are also included. Most of the oxidant species just mentioned absorb in the 300- to 350-nm range.

Other auxiliary species, such as S, Se, P, and As species, are derived from the leaching of accessory minerals. The polysulfides, S_n^{2-} , form when sulfur dissolves in sulfide solutions; they are stable only in a very narrow range of

Table 5-1.-Ultraviolet-visible spectroscopic data for free cyanide and derived species in aqueous solution

Species	Wave-length, maximum, nm	Molar absorptivity, ^{1,2} (mol L ⁻¹) ⁻¹ cm ⁻¹				References
		Maximum	300 nm	350 nm	400 nm	
C(II):						
HCN	³ <200	N	<0.1	<0.1	<0.1	2
CN ⁻	170	N	<.1	<.1	<.1	3, 4
H-CS-NH ₂	⁴ 263	1.25E4	N	N	N	5
H-CS ₂ ⁻	386	8.4 E4	N	N	N	6
	331	9.6 E6				
	225	2.9 E6				
H-CO-NH ₂	189	8. E6	N	N	N	2, 7
H-COS ⁻	246	8.6 E6	N	N	N	6
	208	5.5 E6				
H-CO ₂ H	208	4.6 E1	<.1	<.1	<.1	8, 9
H-CO ₂ ⁻	205	1.00E2	<.1	<.1	<.1	9
C(III):						
NC-CN	222	1.1 E1	<.1	<.1	<.1	10
	211	3.7 E1				
	201	6.0 E1				
NC-CS-NH ₂	⁵ 438	3.2 E1	N	N	N	11
	294	7.4 E3				
NC-CO-NH ₂	206	3.47E3	<1?	<.1?	<.1?	10
NC-CO-NH ⁻	220	5.12E3	<10?	<.1?	<.1?	10
H ₂ N-CS-CS-NH ₂	⁶ 483	2.2 E1	1.0E4	3. E3	8. E1	12
	312	1.12E4				
C ₂ S ₄ ²⁻	⁴ 342	N	N	N	N	13
	278					
H ₂ N-CS-CO-NH ₂	⁶ 411	2.9 E1	7. E3	1.2E2	3. E1	12
	301	6.6 E3				
	229	4.6 E3				
H ₂ N-CO-CO-NH ₂	202	8.3 E3	<1?	<.1?	<.1?	10
H ₂ C ₂ O ₄	<200	N	<.1	<.1	<.1	14
HC ₂ O ₄ ⁻	<200	N	<.1	<.1	<.1	14
C ₂ O ₄ ²⁻	<200	N	<.1	<.1	<.1	14

Table 5-1.-Ultraviolet-visible spectroscopic data for free cyanide and derived species in aqueous solution-Continued

Species	Wave-length, maximum, nm	Molar absorptivity, ^{1,2} (mol L ⁻¹) ⁻¹ cm ⁻¹				References
		Maximum	300 nm	350 nm	400 nm	
C(IV):						
ClCN	³ 179	N	N	N	N	15, 16
BrCN	³ 202	N	N	N	N	15, 16
NCNH ₂	<200	N	<1?	<.1?	<.1?	17, 18
NCNH ⁻	<200	N	<1?	<.1?	<.1?	
NCS ⁻	216 187	3.4 E3 N	<.1	<.1	<.1	4, 19, 20, 21
NCSe ⁻	235 211 183	3.7 E3 N N	<1?	<.1	<.1	4, 19
NCO ⁻	194	1.0 E3	<.1	<.1	<.1	4, 22, 23
HNC(NH ₂) ₂	<200	N	<.1	<.1	<.1	17
C(NH ₂) ₃ ⁺	<200	N	<.1	<.1	<.1	17
CS(NH ₂) ₂	235 194	1.3 E4 1.1 E4	N	N	N	24
H ₂ NCS ₂ ⁻			N	N	N	25, 26
CS ₃ ²⁻	400 336 223	3. E1 1. E4 1. E4	N	N	N	27, 28
CO(NH ₂) ₂	189	1.5 E3	<.1	<.1	<.1	7, 17
H ₂ NCOS ⁻	225	5.2 E4	N	N	N	29
COS ₂ ²⁻	272	N	N	N	N	28
CO ₃ ²⁻	<200	N	<.1	<.1	<.1	27, 28
CNO ⁻	⁴ 280	5. E1	4. E1	5.	<1?	30

N No data.

¹En = 10ⁿ, e.g. 1.25E4 = 1.25×10⁴.²Question marks denote uncertain values due mainly to long extrapolations.³Gas.⁴In methanol.⁵In dichloromethane-heptane.⁶In ethanol.

Table 5-2.-Ultraviolet-visible spectroscopic data for
metal cyanide species in aqueous solution

Species	Wave-length, maximum, nm	Molar absorptivity, ¹ (mol L ⁻¹) ⁻¹ cm ⁻¹				Additional references
		Maximum	300 nm	350 nm	400 nm	
Zn(CN) ₄ ²⁻	<200	N	<0.1	<0.1	<0.1	32
Cd(CN) ₄ ²⁻	<200	N	<.1	<.1	<.1	32
Hg(CN) ₂	<200	N	<.1	<.1	<.1	33
Hg(CN) ₃ ⁻	<200	N	N	N	N	
Hg(CN) ₄ ²⁻	<200	N	<.1	<.1	<.1	32
Cu(CN) ₂ ⁻	234	1.1 E4	1. E2	<1	<.1	33, 34, 35
	222	1.1 E4				
	209	2.0 E4				
Cu(CN) ₃ ²⁻	238	1.1 E4	1. E2	<1	<.1	34, 35
	202	2.0 E4				
Cu(CN) ₄ ³⁻	235	1.1 E4	1. E2	<1	<.1	34, 35
	206	2.0 E4				
Ag(CN) ₂ ⁻	196	2.1 E4	<1	<.1	<.1	33, 36
Ag(CN) ₃ ²⁻	N	N	N	N	N	
Ag(CN) ₄ ³⁻	N	N	N	N	N	
Au(CN) ₂ ⁻	240	3.3 E3	<1	<.1	<.1	33, 36
	230	3.6 E3				
	211	1.0 E4				
	205	1.2 E4				
Au(CN) ₄ ⁻	<200	N	<1	<.1	<.1	37
Ni(CN) ₄ ²⁻	310	7.0 E2	6. E2	1.8E2	5.	32, 36, 38
	286	4.4 E3				
	268	1.2 E4				
Co(CN) ₆ ³⁻	313	1.9 E2	1.6E2	3. E1	.5	39, 40, 41
	260	1.4 E2				
Co(H ₂ O)(CN) ₅ ²⁻	380	2.8 E2	1.0E2	1.5E2	2.0E2	40, 41, 42
	280	1.0 E2				
Co(OH)(CN) ₅ ³⁻	375	2.4 E2	2.0E2	1.7E2	1.6E2	42
	288	2.4 E2				
Fe(CN) ₆ ⁴⁻	322	3.1 E2	4. E2	1.6E2	5.	43, 44, 45
	218	2.3 E4				

Table 5-2.-Ultraviolet-visible spectroscopic data for
metal cyanide species in aqueous solution-Continued

Species	Wave-length, maximum, nm	Molar absorptivity, ¹ (mol L ⁻¹) ⁻¹ cm ⁻¹				Additional references
		Maximum	300 nm	350 nm	400 nm	
Fe(CN) ₆ ³⁻	420 302	1.0 E3 1.6 E3	1.6E3	3.3E2	9. E2	43, 45
Fe(H ₂ O)(CN) ₅ ³⁻	440	6.5 E2	5. E2	1.8E2	3.5E2	46, 47, 48, 49
Fe(H ₂ O)(CN) ₅ ²⁻	395 340	7.4 E2 7.5 E2	9. E2	7. E2	7. E2	45, 49, 50
Fe(OH)(CN) ₅ ³⁻	390	1.6 E3	7. E2	9. E2	1.6E3	45, 50
Fe ₂ (CN) ₁₁ ⁷⁻	380 315	8. E2 1.6 E3	1.7E3	1.0E3	7. E2	51
Fe ₂ (CN) ₁₁ ⁶⁻	1300	3. E3	3. E3	1.6E3	1.1E3	51
Fe ₂ (CN) ₁₁ ⁵⁻	560 400 295	8. E2 2. E3 4.5 E3	4. E3	2. E3	2. E3	51
Fe ₂ (CN) ₁₀ ⁶⁻	390	1.0 E3	1.0E3	8. E2	9. E2	48, 52, 53
Fe ₂ (CN) ₁₀ ⁵⁻	1280 390 350	6. E3 1.7 E3 1.7 E3	3. E3	1.7E3	1.6E3	52
Fe ₂ (CN) ₁₀ ⁴⁻	560 400 360	2.7 E3 2.5 E3 2.5 E3	4. E3	2.4E3	2.5E3	45, 50, 52, 54, 55
Fe ₂ (H ₂ O)(CN) ₁₀ ⁶⁻	N	N				
Fe ₂ (H ₂ O)(CN) ₁₀ ⁵⁻	>1000 400	>1. E3 2. E3	N	N	2. E3	55
Fe ₂ (H ₂ O)(CN) ₁₀ ⁴⁻	525 400	1.1 E3 2. E3	N	N	2. E3	55
Fe ₂ (OH)(CN) ₁₀ ⁵⁻	610	6. E2	N	N	3. E3	55
Cr(CN) ₆ ³⁻	377 307	8.6 E1 6.0 E1	5. E1	4. E1	6. E1	56
Cr(H ₂ O)(CN) ₅ ²⁻	405 320	1.1 E2 5. E1	4. E1	5. E1	1.1E2	57
Cr(OH)(CN) ₅ ³⁻	415 355	1.2 E2 8. E1	3. E1	8. E1	1.1E2	57

N No data.

¹En = 10ⁿ, e.g., 1.1 E4 = 1.1×10⁴.

Table 5-3.-Ultraviolet-visible spectroscopic data for auxiliary species in aqueous solution

Species	Wave-length, maximum, nm	Molar absorptivity, ^{1,2} (mol L ⁻¹) ⁻¹ cm ⁻¹				References
		Maximum	300 nm	350 nm	400 nm	
O ₃	260	3.3 E3	N	N	N	59
OH ⁻	<200	N	<0.1	<0.1	<0.1	60
H ₂ O ₂	<200	N	1.0	<.1	<.1	61
HO ₂ ⁻	<200	N	2.7E1	1.	<.1	61
Cl ₂	324	7.7 E1	5. E1	4. E1	3.	62, 63
Cl ⁻	<200	N	<.1	<.1	<.1	64
HClO	233	9.7 E1	2.4E1	2.2E1	.2	62, 65, 66
ClO ⁻	292	3.5 E2	3.2E2	2. E1	.5	65, 66
ClO ₂ ⁻	260	1.49E2	7. E1	2.	.1	67
ClO ₂	360	1.20E3	1.2E3	3. E2	6. E2	67
ClO ₃ ⁻	<200	N	<.1	<.1	<.1	3, 68
Br ₂	390	1.5 E2	8.	7. E1	1.5E2	63, 69
Br ⁻	<200	N	<.1?	<.1	<.1	70
HBrO	262	9. E1	5. E1	3. E1	1. E1	66, 69, 71
BrO ⁻	329	3.5 E2	1.6E2	2.5E2	5.	66, 69, 71, 72
BrO ₃ ⁻	<200	N	<.1?	<.1	<.1	3, 68, 72
H ₂ S	<200	N	<.1?	<.1	<.1	73
SH ⁻	230	7.1 E3	5.	<.1?	<.1	74, 75
S ₂ ²⁻	358	8.5 E2	3. E2	8. E2	1.8E2	76
S ₃ ²⁻	417	9.5 E1	1.2E3	9. E1	8. E1	76
	303	1.14E3				
S ₄ ²⁻	368	3.2 E2	1.2E3	3. E2	1.8E2	76
	303	1.14E3				
S ₅ ²⁻	375	6.4 E2	2.0E3	7. E2	5. E2	76
	299	2.0 E3				
S ₂ O ₃ ²⁻	215	3.7 E3	.4	<.1	<.1	3, 77, 78
SO ₂	276	5.0 E2	1.8E2	<.1?	<.1	78, 79
HSO ₃ ⁻	<200	N	<.1	<.1	<.1	78, 80
S ₂ O ₅ ²⁻	255	2.6 E3	1.1E2	<.1?	<.1	78, 80
SO ₃ ²⁻	<200	N	<.1	<.1	<.1	3, 80
SO ₄ ²⁻	<200	N	<.1	<.1	<.1	3
H ₂ SeO ₃	³ <200	N	<.1	<.1	<.1	81
HSeO ₃ ⁻	<200	N	<.1	<.1	<.1	81
SeO ₃ ²⁻	<200	N	<.1	<.1	<.1	81
SeO ₄ ²⁻	<200	N	<.1	<.1	<.1	81
NH ₃	<200	N	<.1	<.1	<.1	73
NH ₄ ⁺	<200	N	<.1	<.1	<.1	82
NH ₂ Cl	⁴ 243	4.6 E2	6.	<.1	<.1	66, 83, 84
NH ₂ Br	⁵ 278	3.8 E2	2.3E2	3.	<.1?	66, 69, 71
NO ₂ ⁻	355	2.2 E1	9.	2.1 E	1.	3, 84, 85
	210	5.4 E3				
NO ₃ ⁻	301	7.1	7.0	<.1	<.1	3, 84, 86
	200	1.0 E4				

Table 5-3.-Ultraviolet-visible spectroscopic data for auxiliary species in aqueous solution-Continued

Species	Wave-length, maximum, nm	Molar absorptivity, ^{1,2} (mol L ⁻¹) ⁻¹ cm ⁻¹				References
		Maximum	300 nm	350 nm	400 nm	
H ₃ PO ₄	<200	N	<.1	<.1	<.1	3
H ₂ PO ₄ ⁻	⁶ <200	N	<.1	<.1	<.1	
HPO ₄ ²⁻	<200	N	<.1	<.1	<.1	60
PO ₄ ³⁻	<200	N	<.1	<.1	<.1	60
H ₃ AsO ₃	⁷ <200	N	<.1	<.1	<.1	
H ₂ AsO ₃ ⁻	⁷ <200	N	<.1	<.1	<.1	
HAsO ₃ ²⁻	⁷ <200	N	<.1	<.1	<.1	
H ₃ AsO ₄	⁸ <200	N	<.1	<.1	<.1	
H ₂ AsO ₄ ⁻	⁸ <200	N	<.1	<.1	<.1	
HAsO ₄ ²⁻	⁸ <200	N	<.1	<.1	<.1	
AsO ₄ ³⁻	⁸ <200	N	<.1	<.1	<.1	

N No data.

¹En = 10³, e.g., 3.3 E3 = 3.339×10³.²Question marks denote uncertainty due to long extrapolation.³All data estimated from trend of data for SeO₃²⁻ and HSeO₃⁻.⁴The cited references also give data for NHCl₂ and NCl₃.⁵The cited references also give data for NHBBr₂ and NBr₃.⁶All data estimated from data for H₃PO₄, HPO₄²⁻, and PO₄³⁻ in references 3 and 60.⁷All data estimated from data for HPO₃²⁻ in reference 3 and data for S(IV) and Se(IV) species in references 78-81.⁸All data estimated from data for SeO₄²⁻ versus SO₄²⁻ and data for corresponding P(V) species, in references 3, 60, and 81.

pH and Eh in the absence of cyanides. Selenide and polyselenide species are not included; they are very easily oxidized by air. Phosphorus species are rare in the context of precious metals mining; the data for them were used to predict data for arsenic species, for which no data were located. Except for the polysulfides, the tabulated S, Se, P, and As species absorb only at wavelengths below 300 nm.

Inorganic nitrogen species that may form during cyanide oxidation are also included. These consist primarily of NH₃/NH₄⁺, N₂, NO₂⁻, and NO₃⁻. The haloamines NH₂Cl and NH₂Br form when NH₃ reacts with hypohalites. The species NH₃/NH₄⁺ are transparent at wavelengths above 200 nm. The other nitrogen species absorb weakly at 300 to 400 nm.

REFERENCES²

1. Lide, D. R. (ed.). CRC Handbook of Chemistry and Physics. CRC Press, 72nd ed., 1991, p. 14-8.

2. Nagata, T., T. Kondo, Y. Ozaki, and K. Kuchitsu. Absorption Spectra of Hydrogen Cyanide and Deuterium Cyanide in the 130-80 nm Range. Chem. Phys., v. 57, 1981, pp. 45-53.

3. Buck, R. P., S. Singhadeja, and L. B. Rogers. Ultraviolet Absorption Spectra of Some Inorganic Ions in Aqueous Solution. Anal. Chem., v. 26, 1954, pp. 1240-1242.

4. Fox, M. F., and E. Hayon. The Far-Ultraviolet Solution Spectroscopy of Cyanide, Cyanate, Selenocyanate, and Tellurocyanate. J. Chem. Soc., Faraday Trans., v. 86, 1990, pp. 257-263.

5. Tull, R., and L. M. Weinstock. A New Synthesis of Thioformamide. Angew. Chem. Int. Ed. Engl., v. 8, 1969, pp. 278-279.

6. Engler, R., G. Gattow, and M. Draeger. Untersuchungen Ueber Thioameisensäuren. 2. Darstellung und Eigenschaften von Dithioformaten (Investigations on Thioformic Acid. 2. Preparation and Properties of Dithioformates). Z. Anorg. Allg. Chem., v. 388, 1972, pp. 229-237.

7. Gru, B. A., V. A. Kozlova, and V. S. Kuzub. (Ultraviolet Absorption Spectra of Some Amides). Zh. Org. Khim., v. 7, 1971, pp. 1308-1309; Chem. Abstr., v. 75, 1971, No. 97888e.

8. Caswell, L. R., M. F. Howard, and T. M. Onisto. Solvent and Substituent Effects Upon the A → Pi⁺ Transition of Aliphatic Carboxylic Acids and Esters. J. Org. Chem., v. 41, 1976, pp. 3312-3316.

9. Szyper, M., and P. Zuman. Electronic Absorption of Carboxylic Acids and Their Anions. Anal. Chim. Acta., v. 85, 1976, pp. 357-373.

10. Wang, Y. L., H. D. Lee, M. W. Beach, and D. W. Margerum. Kinetics of Base Hydrolysis of Cyanogen and l-Cyanoformamide. Inorg. Chem., v. 26, 1987, pp. 2444-2449.

²A title in parentheses is a translation from the language in which the work was published.

11. Fabian, J., H. Viola, and R. Mayer. Quantitative Beschreibung der UV-S-Absorptionen Einfacher Thiocarbonylverbindungen (Quantitative Description of UV-Visible Absorptions of Simple Thiocarbonyl Compounds). *Tetrahedron*, v. 23, 1967, pp. 4323-4329.
12. Persson, B., and J. Sandstroem. The Electronic Spectra of Thioamides and Thiohydrazides. Part VI. Conjugation and Steric Effects in Thioamide Derivatives. *Acta Chem. Scand.*, v. 18, pt. 2, 1964, pp. 1059-1077.
13. Reynolds, J. R., F. E. Karasz, C. P. Lillya, and J. C. W. Chien. Electrically Conducting Transition Metal Complexes of Tetrathiooxalate. *J. Chem. Soc. Chem. Commun.*, 1985, pp. 268-269.
14. Cruywagen, J. J., and J. B. B. Heyns. Determination of the Dissociation Constants of Oxalic Acid and the Ultraviolet Spectra of the Oxalate Species in 3M Perchlorate Medium. *Talanta*, v. 30, 1983, pp. 197-200.
15. King, G. W., and A. W. Richardson. The Ultraviolet Absorption of Cyanogen Halides. Part 1. Identification and Correlation. *J. Mol. Spectrosc.*, v. 21, 1966, pp. 339-352.
16. Felps, W. S., K. Rupnik, and S. P. McGlynn. Electronic Spectroscopy of the Cyanogen Halides. *J. Phys. Chem.*, v. 95, 1991, pp. 639-656.
17. Takimoto, M. (Ultraviolet Spectra and Structure of Cyanamide Derivatives). *Nippon Kagaku Zasshi*, v. 85, 1964, pp. 159-168; *Chem. Abstr.* v. 61, 1964, No. 2937g.
18. Beck, M. T., and I. Banyai. (Acid-Base Properties and Dimerization of Cyanamide.) *Magy. Kem. Foly.*, v. 88, 1982, pp. 126-130; *Chem. Abstr.* v. 96, 1982, No. 224114k.
19. Gusarsky, E., and A. Treinin. The Relation Between Electrochemical and Spectroscopic Properties of the Halide and Pseudohalide Ions in Solution. *J. Phys. Chem.*, v. 69, 1965, pp. 3176-3177.
20. McDonald, J. R., V. M. Scherr, and S. P. McGlynn. Lower-Energy Electronic States of HNCS, NCS⁻, and Thiocyanate Salts. *J. Chem. Phys.*, v. 51, 1969, pp. 1723-1731.
21. Fox, M. F., C. B. Smith, and E. Hayon. Far-Ultraviolet Solution Spectroscopy of Thiocyanate. *J. Chem. Soc., Faraday Trans. I*, v. 77, 1981, pp. 1497-1502.
22. Leopold, J., D. Shamra, and A. Treinin. The 200-nm Band of NCO⁻. *J. Phys. Chem.*, v. 74, 1970, pp. 4585-4587.
23. Rabalais, J. W., J. R. McDonald, and S. P. McGlynn. Electronic States of HNCO, Cyanate Salts, and Organic Isocyanates. II. Absorption Studies. *J. Chem. Phys.*, v. 51, 1969, pp. 5103-5111.
24. Kjaer, A., R. Zahradnik, K. Dusek, and J. Klaban. Physical-Chemical Properties of N-Substituted Thioureas. *Acta Chem. Scand.*, v. 16, 1962, pp. 2041-2049.
25. Gattow, G., and V. Hahnkamm. Untersuchungen Ueber Dithiocarbamidsaure SC(SH)(NH₂). 1. Darstellung und Eigenschaften der Freien Saure (Investigations on Dithiocarbamic Acid SC(SH)(NH₂). 1. Preparation and Properties of the Free Acid). *Z. Anorg. Allg. Chem.*, v. 364, 1969, pp. 161-176.
26. Oktavel, D., J. Stefance, B. Siles, and V. Konecny. Electronic Spectra of Salts of Dithiocarbamic Acids. *Collect. Czech. Chem. Commun.*, v. 44, 1979, pp. 2487-2493.
27. Mueller, A., H. Seidel, and W. Rittner. Elektronenabsorptionsspektren und HMO-Rechnung von Trichalkogenocarbonationen (Electronic Absorption Spectra and HMO Calculations for Trichalcocarbonate Ions). *Spectrochim. Acta*, v. 23A, 1967, pp. 1619-1626.
28. Draeger, M., and G. Gattow. Chalcogenocarbonic Acids and their Anions. *Angew. Chem. Int. Ed. Engl.*, v. 7, 1968, pp. 868-879.
29. Klaeser, K., and G. Gattow. Untersuchungen Ueber Monothiocarbamidsauren. 1. Darstellung und Eigenschaften von Monothiocarbamaten (Investigations on Monothiocarbamic Acid. 1. Synthesis and Properties of Monothiocarbamates). *Z. Anorg. Allg. Chem.*, v. 480, 1981, pp. 122-128.
30. Iqbal, Z., and A. D. Yoffe. Electronic Structure and Stability of the Inorganic Fulminates. *Proc. R. Soc. London A*, v. 302, 1967, pp. 35-49.
31. Sharpe, A. G. The Chemistry of Cyano Complexes of the Transition Metals. Academic, 1976, 302 pp.
32. Brigando, G. Recherches sur Quelques Complexes Metalliques. IV. Etude de Quelques Cyanures Complexes (Research on Metal Complexes. IV. Study of Some Cyanide Complexes). *Bull. Soc. Chim. Fr.*, 1957, pp. 503-516.
33. Mason, W. R. Electronic Structure and Spectra of Linear Dicyano Complexes. *J. Am. Chem. Soc.*, v. 95, 1973, pp. 3573-3581.
34. Simpson, E. A., and G. M. Waind. Ultraviolet Absorption Spectra and Stability Constants of Cuprous Cyanide Complexes. *J. Chem. Soc.*, 1958, pp. 1746-1749.
35. Horvath, A., and K. L. Stevenson. Spectral and Photochemical Characterization of the Chlorodicyanocuprate(I) Complex in Aqueous Solution. *Inorg. Chim. Acta*, v. 186, 1991, pp. 61-66.
36. Perumareddi, J. R., A. D. Liehr, and A. W. Adamson. Ligand Field Theory of Transition Metal Cyanide Complexes. Part I. The Zero, One, and Two Electron or Hole Configurations. *J. Am. Chem. Soc.*, v. 85, 1963, pp. 249-259.
37. Mason, W. R., III, and H. B. Gray. Electronic Structures and Spectra of Square-Planar Gold(III) Complexes. *Inorg. Chem.*, v. 7, 1968, pp. 55-58.
38. Kida, S., J. Fujita, K. Nakamoto, and R. Tsuchida. Ultraviolet Absorption Spectra and the Electronic Structure of Metallic Complexes. II. Cyanide Complexes. *Bull. Chem. Soc. Jpn.*, v. 31, 1958, pp. 79-87.
39. Fujita, J., and Y. Shimura. The Absorption Spectra of Cobalt(III) Complexes. III. The Spin-Forbidden Bands. *Bull. Chem. Soc. Jpn.*, v. 36, 1963, pp. 1281-1285.
40. Adamson, A. W., A. Chiang, and E. Zinato. Photochemistry of Aqueous Cobalt(III) Cyano Complexes. *J. Am. Chem. Soc.*, v. 91, 1969, pp. 5467-5475.
41. Scandola, M. A., and F. Scandola. Photosensitized Reactions of Cobalt(III) Complexes. Photoaquation Mechanism of the Hexacyanocobaltate(III) Ion. *J. Am. Chem. Soc.*, v. 94, 1972, pp. 1805-1810.
42. Wrighton, M., and D. Bredezen. Photochemistry of Aquo- and Hydroxopentacyanocobaltate(III). *Inorg. Chem.*, v. 12, 1973, pp. 1707-1709.
43. Cohen, S. R., and R. A. Plane. The Association of Ferrocyanide Ion With Various Cations. *J. Phys. Chem.*, v. 61, 1957, pp. 1096-1100.
44. Shirom, M., and G. Stein. Excited State Chemistry of the Ferrocyanide Ion in Aqueous Solution. I. Formation of the Hydrated Electron. *J. Chem. Phys.*, v. 55, 1971, pp. 3372-3378.
45. Fuller, M. W., K. F. Le-Brocq, E. Leslie, and I. R. Wilson. The Photolysis of Aqueous Solutions of Potassium Hexacyanoferrate(III). *Aust. J. Chem.*, v. 39, 1986, pp. 1411-1419.
46. Toma, H. E., E. Giesbrecht, J. M. Malin, and E. Fluck. Correlations of Moessbauer and Visible-UV Spectra With the Aqueous Substitution Reactivity of Several Substituted Pentacyanoferrate(II) Complexes. *Inorg. Chim. Acta*, v. 14, 1975, pp. 11-15.
47. Toma, H. E. Iron(II) Catalysis on the Oxidation of the Aquopentacyanoferrate(II) Complex by Molecular Oxygen. *Inorg. Chim. Acta*, v. 15, 1975, pp. 205-211.
48. Davies, G., and A. R. Garafalo. Some Observations on Equilibria Involving Monomeric and Dimeric Pentacyanoiron(II) Complexes in Aqueous Solution. *Inorg. Chim. Acta*, v. 19, 1976, pp. L3-L4.
49. James, A. D., R. S. Murray, and W. C. E. Higginson. Iron(II) Catalysis in Substitution Reactions of Amminepentacyano- and Aquopentacyanoferrate(III) Ions. *J. Chem. Soc., Dalton Trans.*, 1974, pp. 1273-1278.
50. Espenson, J. H., and S. G. Wolenuk, Jr. Kinetics and Mechanisms of Some Substitution Reactions of Pentacyano-ferrate(III) Complexes. *Inorg. Chem.*, v. 11, 1972, pp. 2034-2041.

51. Glauser, R., U. Hauser, F. Herren, A. Ludi, P. Roder, E. Schmidt, H. Siegenthaler, and F. Wenk. Mixed-Valence Spectrum and Cyclic Voltammetry of Binuclear Iron Cyano Complexes. *J. Am. Chem. Soc.*, v. 95, 1973, pp. 8457-8458.
52. Emschwiller, G., and C. K. Jorgensen. Electron Transfer Bands of Binuclear Iron(II, III) Complexes Containing Two Cyanide Bridges. *Chem. Phys. Lett.*, v. 5, 1970, pp. 561-563.
53. Wolfe, S. K., C. Andrade, and J. H. Swinehart. Kinetic Studies of the Pentacyanonitrosylferrate(2-) Azide and Hydroxylamine Reactions. *Inorg. Chem.*, v. 13, 1974, pp. 2567-2572.
54. James, A. D., and R. S. Murray. Substitution Reactions of Di- μ -cyano-bis[tetracyanoferrate(II)] in Aqueous Solution. *J. Chem. Soc., Dalton Trans.*, 1976, pp. 1182-1186.
55. James, A. D., W. C. E. Higginson, and R. S. Murray. The Hydrolysis of Di- μ -cyano-bis[tetracyanoferrate(III)], and Its Formation From Aquopentacyanoferrate(III). *J. Chem. Res.*, 1977, pp. M1084-M1094.
56. Krishnamurthy, R., W. B. Schaap, and J. R. Perumareddi. Interpretation of the Spectra of Cyanoaquo Complexes of Chromium(III) by the Theory of Noncubic Ligand Fields. *Inorg. Chem.*, v. 6, 1967, pp. 1338-1352.
57. Sakabe, Y., and Y. Matsumoto. The Synthesis of Potassium Pentacyanohydroxochromate(III). *Bull. Chem. Soc. Jpn.*, v. 54, 1981, pp. 1253-1254.
58. Levenson, R. A., R. J. G. Dominguez, M. A. Willis, and F. R. Young, III. Characterization of Heptacyanovanadate(III). *Inorg. Chem.*, v. 13, 1974, pp. 2761-2764.
59. Hart, E. J., K. Sehested, and J. Holman. Molar Absorptivities of Ultraviolet and Visible Bands of Ozone in Aqueous Solutions. *Anal. Chem.*, v. 55, 1983, pp. 46-49.
60. Halmann, M., and I. Platzner. The Photochemistry of Phosphorus Compounds. Part II. Far Ultraviolet Absorption Spectra of Some Phosphorus Oxyanions in Aqueous Solution. *J. Chem. Soc.*, 1965, pp. 1440-1449.
61. Morgan, M. S., P. F. van Trieste, S. M. Garlick, M. J. Mahon, and A. L. Smith. Ultraviolet Molar Absorptivities of Aqueous Hydrogen Peroxide and Hydroperoxyl Anion. *Anal. Chim. Acta*, v. 215, 1988, pp. 325-329.
62. Zimmerman, E., and F. C. Strong. Equilibria and Spectra of Aqueous Chlorine Solutions. *J. Am. Chem. Soc.*, v. 79, 1957, pp. 2063-2066.
63. Gutmann, H., M. Lewin, and B. Perlmutter-Hayman. The Ultraviolet Absorption Spectra of Chlorine, Bromine, and Bromine Chloride in Aqueous Solution. *J. Phys. Chem.*, v. 72, 1968, pp. 3671-3673.
64. Fox, M. F., and E. Hayon. Far Ultraviolet Solution Spectroscopy of Chloride Ion. *J. Chem. Soc., Faraday Trans. I*, v. 74, 1978, pp. 1776-1785.
65. Molina, L. T., and M. J. Molina. Ultraviolet Spectrum of HOCl. *J. Phys. Chem.*, v. 82, 1978, pp. 2410-2414.
66. Soulard, M., F. Bloc, and A. Hatterer. Diagrams of Existence of Chloramines and Bromamines in Aqueous Solution. *J. Chem. Soc., Dalton Trans.*, 1981, pp. 2300-2310.
67. Fabian, I., and G. Gordon. Complex Formation Reactions of the Chlorite Ion. *Inorg. Chem.*, v. 30, 1991, pp. 3785-3787.
68. Treinin, A., and M. Yaacobi. The Electronic Spectra of the Halate Ions in Solution. *J. Phys. Chem.*, v. 68, 1964, pp. 2487-2492.
69. Galal-Gorchev, H., and J. C. Morris. Formation and Stability of Bromamide, Bromimide, and Nitrogen Tribromide in Aqueous Solution. *Inorg. Chem.*, v. 4, 1965, pp. 899-905.
70. Fox, M. F., and E. Hayon. Far-Ultraviolet Solution Spectroscopy of the Bromide Ion. *J. Chem. Soc., Faraday Trans. I*, v. 73, 1977, pp. 872-882.
71. Wajon, J. E., and J. C. Morris. Rates of Formation of N-Bromamines in Aqueous Solution. *Inorg. Chem.*, v. 21, 1982, pp. 4258-4263.
72. Amichai, O., and A. Treinin. On the Oxybromine Radicals. *J. Phys. Chem.*, v. 74, 1970, pp. 3670-3674.
73. Stevenson, D. P., G. M. Coppinger, and J. W. Forbes. Solvent Effects on n to π^* Transitions of the Bases Water, Ammonia, Hydrogen Sulfide, and Phosphine. *J. Am. Chem. Soc.*, v. 83, 1961, pp. 4350-4352.
74. Giggenbach, W. Optical Spectra of Highly Alkaline Sulfide Solutions and the Second Dissociation Constant of Hydrogen Sulfide. *Inorg. Chem.*, v. 10, 1971, pp. 1333-1338.
75. Fox, M. F., and E. Hayon. Far-Ultraviolet Solution Spectroscopy of Hydrosulphide Ion. *J. Chem. Soc., Faraday Trans. I*, v. 75, 1979, pp. 1380-1389.
76. Giggenbach, W. Optical Spectra and Equilibrium Distribution of Polysulfide Ions in Aqueous Solution. *Inorg. Chem.*, v. 11, 1972, pp. 1201-1207.
77. Sperling, R., and A. Treinin. Charge Transfer to Solvent Spectra of Polyvalent Anions. II. The Electronic Spectrum of $S_2O_3^{2-}$. *J. Phys. Chem.*, v. 68, 1964, pp. 897-903.
78. Eriksen, T. E., and J. Lind. Spectrophotometric Determination of Sulphur Dioxide and Thiosulphate in Aqueous Solutions of Hydrogen Sulphite. *Acta Chem. Scand.*, v. 26, 1972, pp. 3325-3332.
79. Huss, A., Jr., and C. A. Eckert. Equilibria and Ion Activities in Aqueous Sulfur Dioxide Solutions. *J. Phys. Chem.*, v. 81, 1977, pp. 2268-2270.
80. Hayon, E., A. Treinin, and J. Wilf. Electronic Spectra, Photochemistry, and Autoxidation Mechanism of the Sulfite-Bisulfite-Pyrosulfite Systems. The $SO_2^{\cdot -}$, $SO_3^{\cdot -}$, $SO_4^{\cdot -}$, and $SO_5^{\cdot -}$ Radicals. *J. Am. Chem. Soc.*, v. 94, 1972, pp. 47-57.
81. Treinin, A., and J. Wilf. Electronic Spectra of the Oxyanions of Selenium in Solution. *J. Phys. Chem.*, v. 74, 1970, pp. 4131-4137.
82. Yamashita, H. Vacuum Ultraviolet Absorption Spectra of Ammonium Halides. *J. Phys. Soc. Jpn.*, v. 29, 1970, p. 1391.
83. Yiin, B. S., and D. W. Margerum. Non-Metal Redox Kinetics: Reactions of Trichloramine With Ammonia and With Dichloramine. *Inorg. Chem.*, v. 29, 1990, pp. 2135-2141.
84. Valentine, R. L., K. I. Brandt, and C. T. Jafvert. A Spectrophotometric Study of the Formation of an Unidentified Monochloramine Decomposition Product. *Water Res.*, v. 20, 1986, pp. 1067-1074.
85. Strickler, S. J., and M. Kasha. Solvent Effects on the Electronic Absorption Spectrum of Nitrite Ion. *J. Am. Chem. Soc.*, v. 85, 1963, pp. 2899-2901.
86. Gaffney, J. S., N. A. Marley, and M. M. Cunningham. Measurement of the Absorption Constants for Nitrate in Water Between 270 and 335 nm. *Envir. Sci. Technol.*, v. 26, 1992, pp. 207-209.

CHAPTER 6.—INFRARED SPECTRA

INTRODUCTION

Infrared spectra result from the absorption of light at wavelengths corresponding to molecular vibrations. Absorption maxima are commonly quoted in units of reciprocal wavelength centimeters. The absorption maxima are usually sharp and narrow and are commonly referred to as "absorption frequencies" in the literature.

Cyanide in the form of free or complexed cyanide, or the CN group in derived species such as ClCN , NCO^- , or SCN^- , or in organic nitriles such as CH_3CN absorbs strongly in the region around $2,000\text{ cm}^{-1}$. Water absorbs over large wavelength regions of the infrared spectrum, but it is transparent in the region around $2,000\text{ cm}^{-1}$, where absorption due to the vibration of the CN group occurs. Infrared spectra are therefore useful for detecting and identifying solid, gaseous, or aqueous species that contain the CN group.

This chapter contains a compilation of infrared spectroscopic data for the CN vibration in cyanide and derived species and in metal cyanide species.

FREE CYANIDE AND DERIVED SPECIES

Free cyanide and derived species show infrared maxima near $2,000\text{ cm}^{-1}$. Data for these species are compiled in table 6-1. A major reference for infrared spectra of inorganic species is Nakamoto's compilation (1),¹ from which most of the data in table 6-1 were obtained. Data are also given for gaseous molecules and for ions in solid potassium salts for comparison with the aqueous solution data. These data presumably approximate spectra that are unknown for species in aqueous solution. Additional data were obtained from primary sources (2-7).

METAL CYANIDE SPECIES

Data for metal cyanide complexes are compiled in table 6-2. All of the data were taken from Nakamoto (1) and Sharpe (8). The molar absorption coefficients differ greatly and depend mainly on molecular structure. There are very few data for dinuclear cyanide complexes, e.g. of iron, or for cyanide complexes that contain other ligands

such as H_2O or OH^- . Data for solid compounds can also be found in Nakamoto (1) and Sharpe (8). In solid compounds more than one CN infrared absorption frequency often occurs because of asymmetry effects.

METAL THIOCYANATE SPECIES

Metal thiocyanate complexes show infrared absorption due to the CN bond at $2,050$ to $2,150\text{ cm}^{-1}$ in the solid state (1), so absorption in this region may be expected for the complexes in aqueous solution. However, equilibrium data (appendix D) indicate that thiocyanate complexes of the metals of interest in this publication will not be important. A free thiocyanate concentration of $0.01M$ to $0.1M$ is required to form thiocyanate complexes of zinc or cadmium. The thiocyanates of Cu, Ag, and Hg are relatively insoluble, and at a free thiocyanate concentration of $0.01M$, the concentrations of metal thiocyanate species in equilibrium with the solid metal thiocyanates would be of the order of $10^{-4}M$, $10^{-6}M$, and $10^{-2}M$, respectively. However, CN^- complexes Cu, Ag, and Hg much more strongly than SCN^- , so the concentrations of thiocyanate complexes under process conditions would be insignificant.

REFERENCES

1. Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*. Wiley, 4th ed., 1986, pp. 107, 116, 129, 239-240, 272-290.
2. Penneman, R. A., and L. H. Jones. Infrared Absorption Studies of Aqueous Complex Ions. II. Cyanide Complexes of Cu(I) in Aqueous Solution. *J. Chem. Phys.*, v. 24, 1956, pp. 293-296.
3. Jones, L. H. Force Field of Cyanogen From Vibrational Spectra of Isotopic Species. *J. Mol. Spectrosc.*, v. 49, 1974, pp. 82-90.
4. Fronaeus, S., and R. Larsson. Studies on Metal Complexes in Aqueous Solution by Infrared Spectrophotometry. II. An Investigation of Some First-Row Transition Metal Thiocyanate Complexes. *Acta. Chem. Scand.*, v. 16, 1962, pp. 1433-1446.
5. Morgan, H. W. Vibrational Spectrum of the NCSe^- Ion. *J. Inorg. Nucl. Chem.*, v. 16, 1961, pp. 367-368.
6. Beck, W., P. Swoboda, K. Feldl, and R. S. Tobias. Eigenschaften und IR-Spektrum der Knallsäure HCNO . (Properties and Infrared Spectrum of Fulminic Acid HCNO .) *Chem. Ber.*, v. 104, 1971, pp. 533-543.
7. Beck, W. Das IR-Spektrum des Fulminat-Ions. (The IR Spectrum of Fulminate Ion.) *Chem. Ber.*, v. 95, 1962, pp. 341-344.
8. Sharpe, A. G. *The Chemistry of Cyano Complexes of the Transition Metals*. Academic, 1976, 302 pp.

¹Italic numbers in parentheses refer to items in the list of references at the end of this chapter.

Table 6-1.-Infrared spectroscopic data for free cyanide and derived species

Species	CN absorption				Additional references
	Gas (g) or K salt (s)		Aqueous solution		
	Type	Frequency, cm^{-1}	Frequency, cm^{-1}	Molar absorp- tivity, cm^2M^{-1}	
HCN	g	2,097	2,095	64	2
CN ⁻	s	2,080	2,080	29	2
NC-CN	g	2,065	N	N	3
ClCN	g	2,219	N	N	
BrCN	g	2,200	N	N	
HNCO	g	2,274	N	N	
NCO ⁻	s	2,155	N	N	
NCS ⁻	s	2,053	2,066	537	4
NCSe ⁻	s	2,070	2,075	N	5
HCNO	g	2,198	N	N	6
CNO ⁻	s	2,052	2,121 2,052	N N	7

N No data.

Table 6-2.-Infrared spectroscopic data for
metal cyanide species in aqueous solution

Species	Frequency, cm^{-1}	Molar absorptivity $\text{cm}^{-1} \text{ M}^{-1}, \times 10^{-3}$
$\text{Zn}(\text{CN})_4^{2-}$	2,149	0.11
$\text{Cd}(\text{CN})_4^{2-}$	2,140	.08
$\text{Hg}(\text{CN})_2^-$	2,194	.003
$\text{Hg}(\text{CN})_3^{2-}$	2,161	.026
$\text{Hg}(\text{CN})_4^{2-}$	2,143	.11
$\text{Cu}(\text{CN})_2^-$	2,125	.16
$\text{Cu}(\text{CN})_3^{2-}$	2,094	1.09
$\text{Cu}(\text{CN})_4^{3-}$	2,076	1.66
$\text{Ag}(\text{CN})_2^-$	2,135	.26
$\text{Ag}(\text{CN})_3^{2-}$	2,105	.38
$\text{Ag}(\text{CN})_4^{3-}$	2,092	.56
$\text{Au}(\text{CN})_2^-$	2,146	N
$\text{Au}(\text{CN})_4^-$	2,189	N
$\text{Ni}(\text{CN})_4^{2-}$	2,124	1.1
$\text{Co}(\text{CN})_6^{3-}$	2,129	N
$\text{Fe}(\text{CN})_6^{4-}$	2,044	N
$\text{Fe}(\text{CN})_6^{3-}$	2,118	N
$\text{Cr}(\text{CN})_6^{3-}$	2,128	N

N No data.

CHAPTER 7.—REACTIONS OF FREE CYANIDE AND DERIVED SPECIES

INTRODUCTION

General Remarks

The treatment of liquids and solids containing waste cyanide and the fate of CN^- in the environment have been the subject of numerous studies and publications. The question of what chemical reactions cyanide undergoes, naturally or artificially, is therefore critical. No recent comprehensive review of the inorganic chemistry of free CN^- or species derived therefrom appears to exist. This chapter provides such a review by compiling data on the reactions of free CN^- and derived species.

Free CN^- is subject to reactions that convert it to products that in turn undergo further reactions. The reaction products are the derived species tabulated in chapter 2. The reactions that occur include oxidation, hydration, reactions with auxiliary species, and hydrolysis. The auxiliary species that may react with cyanide include ammonia (NH_3), sulfides, or species derived from the incomplete oxidation of sulfides. Ammonia is a product of the hydrolysis of CN^- and NCO^- (cyanate). Sulfides are derived from minerals, and they are subject to oxidation to other sulfur species, which react with free CN^- .

The ultimate fate of cyanide carbon in the presence of air is predicted to be CO_2 or carbonates, according to thermodynamic data. The ultimate fate of cyanide nitrogen depends on the availability of reactive oxidants, and may be NH_3 , N_2 , NO_2 , or NO_3^- . However, many of the steps in the process leading to the final products are slow, and knowledge of the rates of the intermediate reactions is important.

This chapter contains a brief review of the fundamentals of reaction rates or kinetics, a classification of types of chemical reactions, and a description of the organization of the data that constitute the bulk of this chapter. Most of the data pertain to oxidation, addition, hydrolysis, and exchange reactions of free CN^- and derived species. The chemistry of selenium in cyanide solutions is discussed in a subsequent section. Finally, industrial observations on cyanide degradation are discussed.

Reaction Rate Fundamentals

Thermodynamic Versus Kinetic Control of Chemical Reactions

In chapter 4, it was stated that the extent to which a chemical reaction can proceed is determined by thermodynamics and kinetics. The role of thermodynamics was discussed in chapter 4. If the standard Gibbs energy change

for a chemical reaction is negative, the reaction can proceed. The rate at which the reaction proceeds is determined by kinetics, through the rate constant and the activation parameters, as described below. Practically all of the reactions described in this chapter have negative standard Gibbs energy changes, so the extent to which they proceed is kinetically controlled.

Reaction Order and Rate Constant

Reactions proceed in elementary steps that consist of simple reactions involving usually only one or two molecules. This sequence of simple reactions collectively expresses the reaction mechanism. The slowest of these steps, the rate-limiting step, determines the reaction rate. Most reactions consist of more than one elementary step, so that the stoichiometry of the reaction corresponds to the sum of all of the elementary steps, not to any individual step. In most reactions, the rate-limiting step is first or second order. In a first-order reaction, the rate depends directly on the concentration of one reactant species, denoted Z:

$$\text{rate} = -d[\text{Z}]/dt = k[\text{Z}], \quad (7-1)$$

where k = the rate constant,

and $[\text{Z}]$ = concentration of reactant species Z.

In a second-order reaction, the rate depends on the concentrations of two reactant species, denoted Z and R, or on the square of the concentration of one reactant:

$$\text{rate} = -d[\text{Z}]/dt = k[\text{Z}][\text{R}] \quad (7-2)$$

$$\text{or} \quad \text{rate} = -d[\text{Z}]/dt = k[\text{Z}]^2. \quad (7-3)$$

In the case represented by equation 7-2, the reaction is first order each in $[\text{Z}]$ and $[\text{R}]$, and second order overall. Equations 7-1 through 7-3 are termed "rate equations." In this publication, most reaction rates conform to equations 7-1 or 7-2. The term "substrate" is applied to the reactant of primary interest, namely cyanide or a derived species, which is denoted Z. Reactants that are reagents are denoted R. Water is often a reactant, but its concentration does not appear in rate equations for reactions in aqueous solution because it is present in very large and constant excess, namely, 50M to 55M. Rate equations are treated further in chapter 12, which is a users' guide for solving reaction rate problems.

Dependence of Reaction Rates on pH

Reaction rates in aqueous solution usually depend on pH. Reactants are often weak acids or bases that therefore exist as different species depending on the pH. These species have different reactivities. Reactions often proceed faster in acid or alkaline solutions, without consumption of acid or base, and are accordingly termed, respectively, acid or base "catalyzed." Two general references on the subject are Jones (1) and Hammett (2).¹ The dependence of reaction rates on pH is addressed further with examples in chapter 12.

Dependence of Reaction Rates on Temperature

The rate of a chemical reaction depends on temperature through the activation energy ΔE^* . The variation of the rate constant k with absolute temperature T depends on ΔE^* and is given by

$$k = A \exp (-\Delta E^*/RT). \quad (7-4)$$

Equation 7-4 is the well-known Arrhenius relationship (3). The quantity A is termed the "preexponential factor," and R is the gas constant. A larger ΔE^* results in a steeper variation of k with T .

In the older literature, authors treat their data by equation 7-4. Advances in reaction rate theory have led to an improved equation for expressing the variation of the reaction rate constant with temperature. The recommended equation for fitting experimental data is (3)

$$k = T(k'/h) [\exp (\Delta S^*/R)] [\exp (-\Delta H^*/RT)], \quad (7-5)$$

where k = rate constant,

T = absolute temperature,

k' = Boltzmann constant, $1.38066 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}$,

h = Planck's constant, $6.626076 \times 10^{-34} \text{ J} \cdot \text{s}$,

k'/h = $2.08367 \times 10^{10} \text{ s} \cdot \text{K}^{-1}$ (4),

ΔS^* = entropy of activation,

ΔH^* = enthalpy of activation,

and R = gas constant, $8.3145 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$.

Equating the derivatives dk/dT of equations 7-4 and 7-5 gives the relation between ΔE^* and ΔH^* :

$$\Delta E^* = \Delta H^* + RT. \quad (7-6)$$

The derived ΔE^* and ΔH^* are averages obtained from data over a range of temperature, so an average value of T should be used in equation 7-6. At 25°C (77°F , 298.15 K), RT is $2.5 \text{ kJ} \cdot \text{mol}^{-1}$. For fitting experimental data, equation 7-5 is put in logarithmic form:

$$\ln (k/T) = \ln (k'/h) + (\Delta S^*/R) - (\Delta H^*/R)(1/T). \quad (7-7)$$

The independent variable is $1/T$, the dependent variable is $\ln (k/T)$, $\ln (k'/h)$ and R are the constants defined above, and ΔH^* and ΔS^* are determined during data fitting.

The dependence of reaction rates on temperature is addressed further in chapter 12, where an equation that is more suitable for practical computations is presented and applied to an example.

Classification of Types of Reactions

A variety of chemical reactions are discussed in this publication, and some terminology to distinguish or classify them is appropriate. The first distinction is whether changes in oxidation state occur in a reaction. Reactions in which oxidation-state changes occur are termed "redox" reactions. Beyond that distinction, further classification is useful, as outlined below with examples:

- Addition or combination reaction, $X + Y \rightarrow Z$. An example is $\text{HCN} + \text{H}_2\text{O} \rightarrow \text{H-CO-NH}_2$. This is an example of a hydration reaction, i.e., addition of H_2O . In this example, H_2O is split into 2H^+ and O^{2-} , which appear in the same product molecule.

- Elimination or decomposition reaction, $Z \rightarrow X + Y$. This is the reverse of an addition reaction. An example is $\text{HNCS}_2 \rightarrow \text{SCN}^- + \text{SH}^-$.

- Condensation reaction, $nA \rightarrow B$. This term is applied to reactions in which the substrate molecules combine with each other. Sometimes elimination of small molecules such as H_2O occurs. Examples are $3\text{ClCN} \rightarrow (\text{ClCN})_3$ and $2\text{CO}(\text{NH}_2)_2 \rightarrow \text{H}_2\text{N-CO-NH-CO-NH}_2 + \text{NH}_3$.

- Exchange or metathesis reaction, $\text{AX} + \text{BY} \rightarrow \text{AY} + \text{BX}$. An example is $\text{NH}_3 + \text{HOCl} \rightarrow \text{NH}_2\text{Cl} + \text{H}_2\text{O}$. In this reaction, e.g., A and B are respectively NH_2 and OH , and X and Y are respectively H and Cl . Another example is $\text{H-CO-NH}_2 + \text{H}_2\text{O} \rightarrow \text{H-CO-OH} + \text{NH}_3$. This is an example of a hydrolysis reaction. In a hydrolysis reaction, H_2O is split into H^+ and OH^- , or 2H^+ and O^{2-} , with the H^+ and OH^- or O^{2-} appearing in different molecules.

- Atom or group transfer reaction, $A + \text{BX} \rightarrow \text{AX} + \text{B}$. An example is $\text{CN}^- + \text{O}_3 \rightarrow \text{NCO}^- + \text{O}_2$, in which A is

¹Italic numbers in parentheses refer to items in the list of references at the end of this chapter.

CN⁻, B is O₂, and X is O. This class also includes hydrogen-ion transfer reactions, e.g., CN⁻ + H₂O → HCN + OH⁻, in which A is CN⁻, B is OH⁻, and X is H⁺.

- Substitution reaction, AX + Y → AY + X. An example is ClCN + SH⁻ → SCN⁻ + Cl⁻ + H⁺, in which A is CN⁺, X is Cl⁻, and Y is S²⁻.

- Redistribution reaction. A redistribution reaction is an exchange reaction in which atoms or groups bound to a single atom are exchanged. An example is 2HCOS⁻ → HCS₂⁻ + HCO₂⁻.

- Disproportionation or dismutation reaction. This is a redox reaction in which a species with an element initially in one oxidation state is converted to species with that element in two different oxidation states. An example is NC-CN + 2OH⁻ → CN⁻ + NCO⁻ + H₂O. In this reaction, a species with carbon in the 3+ oxidation state disproportionates into species with carbon in the 2+ and 4+ oxidation states.

- Conproportionation reaction. This is the opposite of a disproportionation reaction. An example is 2H₂S + SO₂ → 3S + 2H₂O. In this reaction, the reactants contain sulfur in the 2- and 4+ oxidation states, and the product contains sulfur all in the zero oxidation state.

This classification is employed in the rest of this chapter, as described in the next section.

Data Organization and Presentation

Data Organization

The following sections describe the reactions of free CN⁻ and derived species. Oxidation of CN⁻ by different oxidants is described first. These reactions produce NCO⁻, ClCN (cyanogen chloride), NC-CN (cyanogen), and SCN⁻ (thiocyanate). Then the reactions of SCN⁻ and NCO⁻ with oxidants are described.

In subsequent sections, the addition, exchange, and substitution reactions of free CN⁻ and derived species are described. The names, structural chemical formulas, and the abbreviated formulas used in this chapter for the derived species are compiled in chapter 2. The derived species are classified first by carbon oxidation state, respectively 2+, 3+, and 4+, that is, C(II), C(III), and C(IV). For each of the three carbon oxidation states, the reactions are classified as follows: (1) addition or substitution reactions with H₂O, NH₃, and H₂S/SH⁻ (hydrogen sulfide); (2) exchange reactions, in which nitrogen- and sulfur-containing species react with NH₃ or H₂S/SH⁻ or undergo redistribution reactions; and (3) hydrolysis reactions of the species formed in the addition and exchange reactions.

For C(II), the initial species is CN⁻/HCN, {HCN}. Cyanide undergoes addition reactions with H₂O, NH₃, and H₂S/SH⁻. Exchange reactions may also occur among the products of the addition reactions. The products of these

reactions undergo hydrolysis, and the ultimate product is formate (HCO₂⁻, {HCOO⁻}).

For C(III), the initial species is NC-CN, {NCCN}. Cyanogen undergoes addition reactions with H₂O, NH₃, and H₂S/SH⁻. Exchange reactions may also occur among the products of the addition reactions. The products of these reactions undergo hydrolysis or disproportionation. The ultimate product of hydrolysis is oxalate (C₂O₄²⁻, {OOCOO⁻}). Disproportionation results in formation of CN⁻ and a C(IV) species.

For C(IV), the initial species is ClCN or NCO⁻. Cyanogen chloride undergoes substitution reactions with H₂O, NH₃, or H₂S/SH⁻ to form NCO⁻, NCNH₂ (cyanamide), and SCN⁻, respectively. Further addition and exchange reactions may occur, followed by hydrolysis reactions. The ultimate product is carbonate (CO₃²⁻, {COOO⁻}).

Data are incomplete or unavailable for many of the species of interest in this publication. Where possible, inferences are made from better known reactions of organic analogs. In chemical formulas of organic species so mentioned, R represents an alkyl group.

The number of reactions in the classification outlined above is large. In the following section, all of the addition and substitution reactions are systematized, and the reactions likely to be most important in practice are indicated.

Data Presentation

Rate data are compiled in tables in appendix F for reactions with sufficient data to generate pH and temperature profiles. In appendix F, the rate equations are in the form

$$- [Z]^{-1} [R]^{-1} d[Z]/dt = \sum_i k_i [f(\text{pH})]_i \quad (7-8)$$

$$= k(\text{pH}) \quad (7-9)$$

where k_i = rate constant,

and $[f(\text{pH})]_i$ = pH-dependent factor.

Equation 7-8 is derived from equations 7-1, 7-2, or 7-3 by division by $[Z]$, $[Z][R]$, or $[Z]^2$, respectively, and introducing the pH dependence of k . The summation term is defined in equation 7-9 as $k(\text{pH})$, which may be plotted versus pH to give a rate-pH profile. For reactions that are only first order in Z, the $[R]$ term is omitted from equation 7-8. In that case, the pH-dependent half-life of Z is

$$t_{0.50} = 0.693 / k(\text{pH}). \quad (7-10)$$

For the reactions with water, described below, the substrate half-lives $t_{0.50}$ are given for pH 11.0, which is a typical pH value in cyanide process solutions. Reactions for which sufficient data exist are illustrated with rate-pH profiles, and the pertinent tables in appendix F are cited.

OXIDATION REACTIONS

Free CN^- and SCN^- are oxidizable by many oxidants, such as hydrogen peroxide (H_2O_2), ozone (O_3), hypochlorite (ClO^-), or peroxomonosulfate (HSO_5^-). Peroxomonosulfate is the presumed intermediate in the SO_2 -air process. Sulfur species such as elemental sulfur, polysulfides, and thiosulfate ($\text{S}_2\text{O}_3^{2-}$) oxidize CN^- to SCN^- . Strong oxidants such as O_3 or ClO^- also oxidize species such as NCO^- , in which the bound nitrogen is oxidized, e.g., to N_2 . The following paragraphs describe the reactions of free CN^- , SCN^- , and NCO^- with different oxidants. The oxidation reactions are schematized in figure 7-1. Figure 7-2 provides a comparison of the reduction potentials of different oxidants. The reduction potentials were calculated from the Gibbs energy data in appendix C. The oxidation reactions and their standard Gibbs energy changes are compiled in tables 7-1 and 7-2.

The oxidation of metal cyanide species by different oxidants is discussed in chapter 8.

Oxidation of Cyanide to Cyanate

Oxidation of CN^- to NCO^- occurs in basic solution with many oxidants, in particular those oxidants of interest for cyanide destruction. Those oxidants include H_2O_2 , O_3 , $\text{HSO}_5^-/\text{SO}_5^{2-}$, and ClO^-/HClO . In oxidation by ClO^-/HClO , ClCN is formed, which hydrolyzes to NCO^- . There is evidence that oxidation of CN^- to NCO^- by O_2 occurs, especially in the presence of certain catalysts.

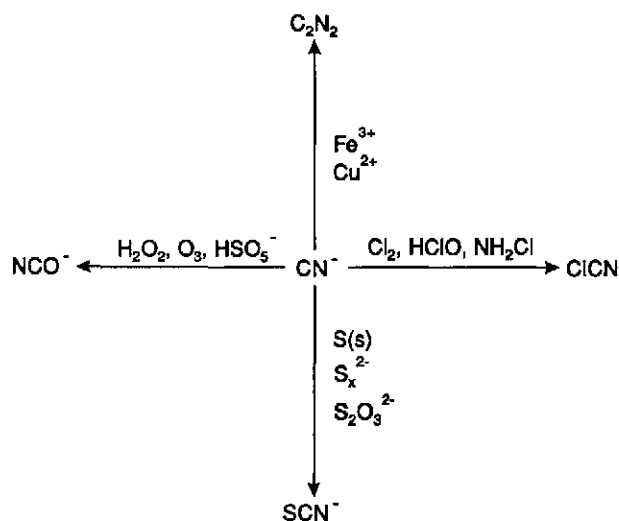
Hydrogen Peroxide

The uncatalyzed oxidation of CN^- by H_2O_2 is reported to be very slow, but no kinetic data were located. A simultaneous reaction of CN^- with H_2O_2 and $\text{S}_2\text{O}_3^{2-}$ proceeds at an observable rate, to yield SCN^- and SO_4^{2-} (5). Hydrogen peroxide oxidation of CN^- is catalyzed by trace metals, e.g., copper or iron, such that its rate makes this reaction industrially feasible (6-7).

Ozone

There is much literature on the CN^- - O_3 reaction (8-13). In practice, the rate of this reaction is limited by mass transfer of O_3 from the gas phase to the solution (8-9). Techniques for the study of fast reactions were employed primarily by Gurol and others (10-13) to study the rate and mechanism. The deduced rate law was

Figure 7-1



Oxidation of free cyanide.

$$d[\text{Z}]/dt = -k[\text{Z}]K_a(K_a + [\text{H}^+])^{-1}[\text{O}_3],$$

where $[\text{Z}] = [\text{CN}^-] + [\text{HCN}]$,

and K_a = acidity constant of HCN , about $10^{-9}M$.

The rate constant k is on the order of $10^5 M^{-1} \cdot s^{-1}$ at 200 to 25°C . Molecular HCN reacts much more slowly than CN^- with O_3 . In alkaline solution, catalysis of O_3 decomposition by OH^- competes with reaction with CN^- . The CN^- - O_3 reaction is catalyzed by copper species (11-13).

Peroxomonosulfate: The Sulfur Dioxide and Air Process

Oxidation of CN^- by O_2 in the presence of SO_2 is in use industrially as the INCO SO_2 -air process (14-15). It is thought that SO_2 and O_2 in the alkaline slurry first react to form a peroxy species, probably HOOSO_3^- , which oxidizes CN^- . The literature search revealed no published kinetics studies.

Oxygen

The oxidation of CN^- by O_2 is observable, but no systematic kinetic study has been published. Observations by Silver (16) showed CO_3^{2-} buildup in air-exposed KCN solutions. He made observations at 30° and 70°C on the decomposition of KCN solutions in the absence or presence of air and light. His results indicated accelerated oxidation in the presence of light. The rate increased with

Figure 7-2

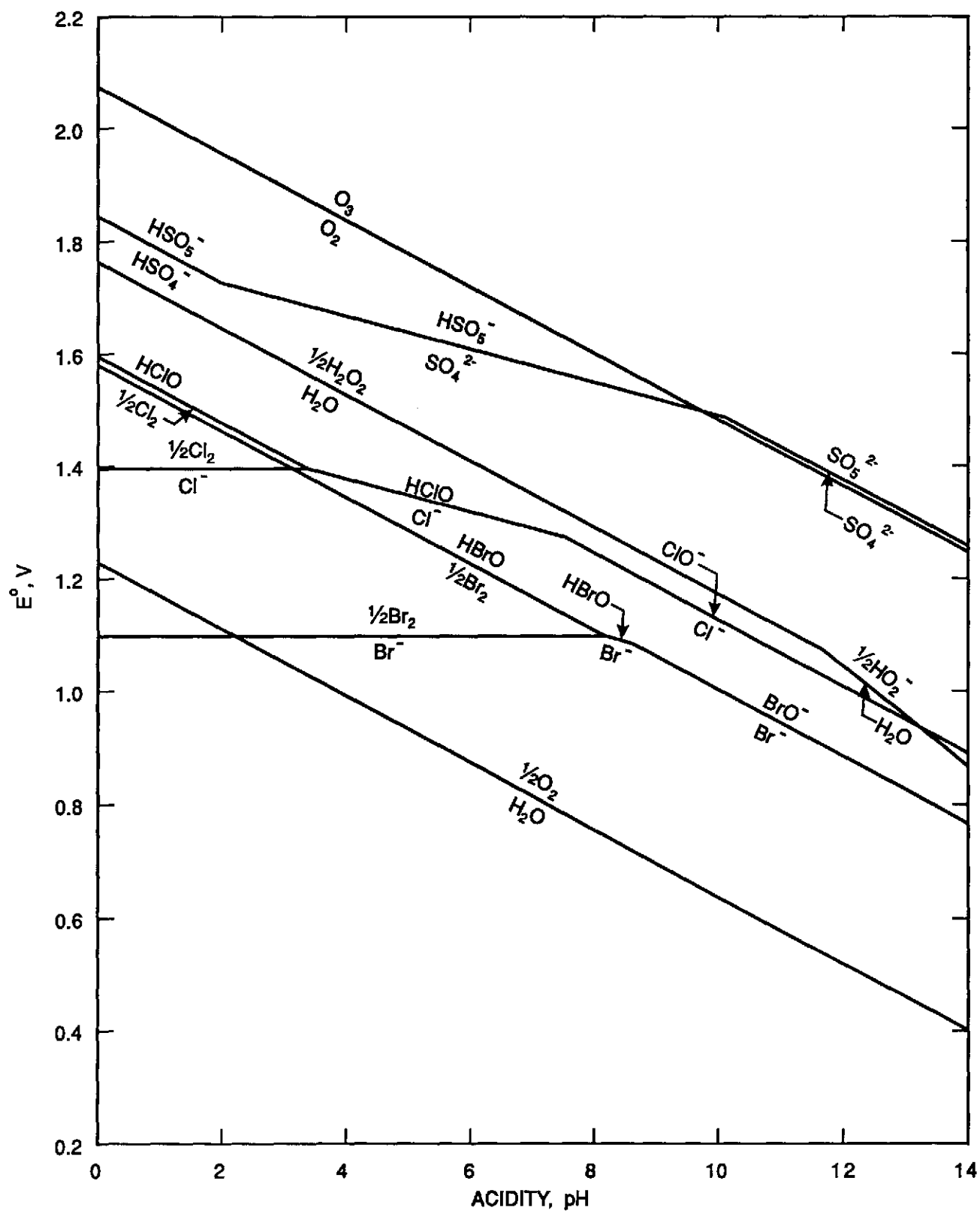
*Eh-pH diagrams for oxidants.*

Table 7-1.-Oxidation reactions of free cyanide and derived species

Substrate	Oxidant	Reaction	$\Delta_r G^\circ$, 25° C kJ·mol ⁻¹ substrate ¹
CN ⁻	O ₂	2CN ⁻ + O ₂ --> 2NCO ⁻	-270
	H ₂ O ₂	CN ⁻ + H ₂ O ₂ --> NCO ⁻ + H ₂ O	-373
	O ₃	CN ⁻ + O ₃ --> NCO ⁻ + O ₂	-444
	ClO ⁻	CN ⁻ + ClO ⁻ --> NCO ⁻ + Cl ⁻	-364
SCN ⁻	O ₂	SCN ⁻ + 2O ₂ + 2OH ⁻ --> NCO ⁻ + SO ₄ ²⁻ + H ₂ O	-857
	H ₂ O ₂	SCN ⁻ + 4H ₂ O ₂ + 2OH ⁻ --> NCO ⁻ + SO ₄ ²⁻ + 5H ₂ O	-1,270
	O ₃	SCN ⁻ + 4O ₃ + 2OH ⁻ --> NCO ⁻ + SO ₄ ²⁻ + 4O ₂ + H ₂ O	-1,553
	ClO ⁻	SCN ⁻ + 4ClO ⁻ + 2OH ⁻ --> NCO ⁻ + SO ₄ ²⁻ + 4Cl ⁻ + H ₂ O	-1,235
NCO ⁻	O ₃	2NCO ⁻ + 3O ₃ + OH ⁻ --> 2CO ₃ ²⁻ + N ₂ + 3O ₂ + H ₂ O	-653
	ClO ⁻	2NCO ⁻ + 3ClO ⁻ + 2OH ⁻ --> 2CO ₃ ²⁻ + N ₂ + 3Cl ⁻ + H ₂ O	-533

¹Calculated from data in tables B-1 and C-1.

Table 7-2.-Conversion of free cyanide to thiocyanate

Reaction	$\Delta_r G^\circ$, 25° C kJ·mol ⁻¹ CN ⁻
CN ⁻ + (1/8)S ₈ (s) --> SCN ⁻	-80
CN ⁻ + S ₂ O ₃ ²⁻ --> SCN ⁻ + SO ₃ ²⁻	-43
CN ⁻ + S _x ²⁻ --> SCN ⁻ + S _{x-1} ²⁻	-76 (x = 5) -72 (x = 4) -61 (x = 3)

time at 30° C, but decreased with time at 70° C. Apparently, oxidation by O₂ is catalyzed by impurities, very possibly iron cyanide complexes. If it is assumed that the reaction is uncatalyzed and of second order, the oxidation rate law is

$$r = k[p(\text{O}_2)][\text{CN}^-],$$

where $p(\text{O}_2)$ = ambient O₂ partial pressure,

and $k < 10^{-2} (\text{mol} \cdot \text{L}^{-1})^{-1} \cdot \text{Pa}^{-1} \cdot \text{s}^{-1}$ at 30° C.

Oxidation of CN⁻ by O₂ has been reported to be catalyzed by activated carbon (17-18). In a representative experiment at pH 10.2 with 0.008M NaCN containing 25 g·L⁻¹ of activated carbon, during 48 h at 20° C, about 40 pct of the CN⁻ was lost by oxidation to NCO⁻. In the absence of activated carbon, the loss of CN⁻ was about 5 pct, attributed to volatilization of HCN. Assuming that the loss of CN⁻ as NCO⁻ was due to oxidation by atmospheric O₂, and that the rate law is

$$r = k'[p(\text{O}_2)][\text{CN}^-][\text{C}],$$

a value of $6 \times 10^{-7} (\text{mol} \cdot \text{L}^{-1})^{-1} \cdot \text{Pa}^{-1} (\text{g} \cdot \text{L}^{-1} \text{ C})^{-1} \cdot \text{s}^{-1}$ is obtained for the rate constant k' at 20° C.

Copper has been reported to catalyze the oxidation of CN⁻ by O₂ on activated carbon (19).

Hypochlorite

The reaction of CN⁻ with ClO⁻/HClO to form ClCN is very fast and is substantially complete in the time required to mix the reactants (20). The ClCN formed is subsequently hydrolyzed to NCO⁻ (see below). This reaction is widely used for cyanide removal (21), and there is abundant literature on its industrial use. Gerritsen and Margerum (22) recently studied the reaction by spectrophotometric observation of ClO⁻ consumption using rapid-reaction techniques at 25° C and ionic strength 1.0M. The derived rate law was

$$\begin{aligned} d[\text{CN}^-]/dt &= d[\text{ClO}^-]/dt \\ &= -(k_1 + k_2[\text{OH}^-]^{-1})[\text{CN}^-][\text{ClO}^-], \end{aligned}$$

where $k_1 = 310M^{-1} \cdot \text{s}^{-1}$

and $k_2 = 583 \text{ s}^{-1}$.

From these data the half-life of free CN⁻ is calculated as 2.2 s in the presence of $1 \times 10^{-3}M$ excess ClO⁻ at pH 11. This result agrees with the rapid rate observed in practice. An earlier investigation of this reaction (23) gave discordant results and has been criticized (22).

Oxidation of Cyanide to Cyanogen

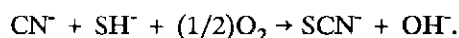
Oxidation of CN⁻ to NC-CN occurs only in acid solutions with different oxidants. Consequently, formation of NC-CN is not expected during normal precious metals mining or closure operations, in which solutions are alkaline. However, contact of cyanide-bearing solutions with acid mine drainage or with acidic process or waste solutions could result in generation of NC-CN as well as HCN. Probably the best known instance of the formation of NC-CN is the reaction of CN⁻/HCN with Cu(II) species (24-25),



Oxidation of CN⁻/HCN to NC-CN also occurs with Fe(III) species, including $[\text{Fe}(\text{CN})_6]^{3-}$ (24-25). Reaction of CN⁻/HCN with Mn(III) or Mn(IV) oxides, MnO₂, Cr(VI), or V(V) in acid solutions may yield C₂N₂.

Oxidation of Cyanide to Thiocyanate

The formation of SCN⁻ in cyanide leach solutions is attributed to the reaction of CN⁻ with solid sulfur or dissolved S_x²⁻, or S₂O₃²⁻ formed by oxidation of sulfide minerals, e.g., by dissolved O₂. A simplified reaction equation is



Sulfur

The reaction of CN⁻ with S₈ (the most common molecular form of sulfur) was studied in water-methanol H₂O-CH₃OH mixtures, 80 to 100 pct CH₃OH, at 4° to 25° C (26). The reaction is first order each in CN⁻ and S₈, with a second-order rate constant of 8 to 34M⁻¹·s⁻¹ over the reported ranges of temperature and solvent composition.

Polysulfides

The reaction of CN⁻ with S_x²⁻ (x = 2 to 6) was studied at 25° C in 0.1M carbonate buffers and reported to be of nonintegral order (27),

$$d[\text{Z}]/dt = -k[\text{Z}]^x[\text{S}_x^{2-}]^y,$$

where $[\text{Z}] = [\text{CN}^-] + [\text{HCN}]$.

The values of x and y varied from 1.34 and 0.85, respectively, at pH 8.2, to 0.49 and 0.78, respectively, at pH 12.0. The value of k ranged from 0.0025M⁻¹·s⁻¹ at pH 8.2 to 0.014M⁻¹·s⁻¹ at pH 12.0. This study was a statistical investigation rather than a systematic effort to determine precisely the rate-limiting elementary steps and mechanism

as a function of solution composition. At initial concentrations of 0.01M each of CN^- and S as polysulfide, 50 pct of the CN^- would be converted to SCN^- in several hours and 99 pct in a few weeks at 25° C.

Thiosulfate

The reaction of CN^- with $\text{S}_2\text{O}_3^{2-}$ is first order in each reactant (28). At zero ionic strength, the second-order rate constant varies from $1.2 \times 10^{-5} \text{M}^{-1} \cdot \text{s}^{-1}$ at 25° C to $3.6 \times 10^{-4} \text{M}^{-1} \cdot \text{s}^{-1}$ at 90° C. The rate constants are 2 to 3 times higher at ionic strength 0.1 M. Data for the $\text{CN}^-/\text{S}_2\text{O}_3^{2-}$ reaction are given in table F-1 and figure 7-3. The reaction was reported to be strongly catalyzed by copper compounds, but no data were published. At initial concentrations of 0.01M each of CN^- and $\text{S}_2\text{O}_3^{2-}$, 50 pct of the CN^- would be converted to SCN^- in about 3 months and 99 pct in about 30 years at 25° C and zero ionic strength. This reaction is treated as an example in chapter 12.

Oxidation of Thiocyanate

As a rule, the oxidants that oxidize CN^- to NCO^- also oxidize SCN^- . As described below, oxidation of SCN^- usually results first in conversion to SO_4^{2-} and CN^-/HCN . The CN^-/HCN is then oxidized by more of the oxidant.

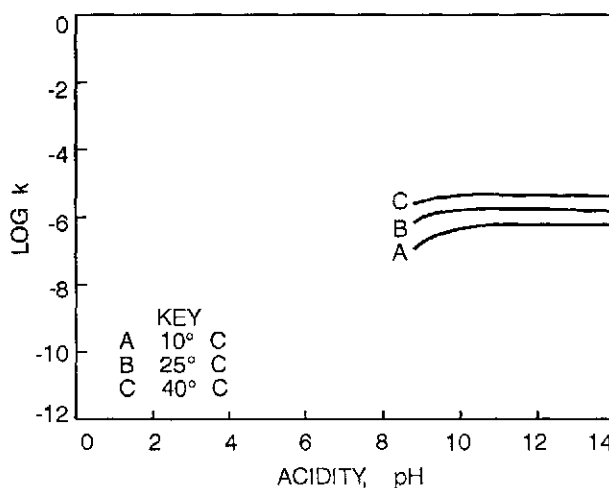
Hydrogen Peroxide

Oxidation of SCN^- by H_2O_2 was studied by Wilson and Harris (29-30). The data are presented in table F-2 and figure 7-4. At pH 4 to 11, the products are SO_4^{2-} and NCO^- ; the rate law is first order each in SCN^- and H_2O_2 . At pH above 11, the rate decreases markedly; this is attributed to deprotonation of H_2O_2 to HO_2^- . At pH below 2, the products are HSO_4^- and HCN , and HCN has an inhibitory effect on the rate. The initial rate is first order each in SCN^- , H_2O_2 , and H^+ . The kinetic complications in acid solution involve formation of $\text{S}(\text{CN})_2$, which undergoes further reactions (31-32). The $\text{SCN}^-/\text{H}_2\text{O}_2$ reaction is catalyzed by copper and possibly by iron (29-30, 33). The first step in SCN^- oxidation by H_2O_2 is the formation of "hypothiocyanite," OSCN^- , which has been characterized by ultraviolet spectroscopy; the acid HOSCN has a pK_a of about 5 (34).

Ozone

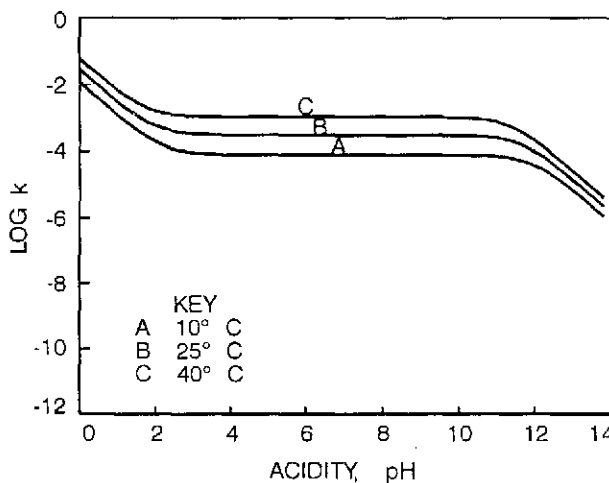
Thiocyanate is oxidized by O_3 very rapidly, at a rate limited by mass transfer of O_3 from gas phase to solution (35). This reaction appears to be faster than the CN^-/O_3 reaction, judging by reported detection of CN^- as an intermediate. No rate constants were reported for this

Figure 7-3



Log rate constant ($\log k$) versus pH for reaction of cyanide with thiosulfate.

Figure 7-4



Log k versus pH for reaction of thiocyanate with hydrogen peroxide.

reaction. For the assumed second-order reaction, the rate constant has been estimated as on the order of $10^6 (\text{mol} \cdot \text{L}^{-1})^{-1} \cdot \text{s}^{-1}$ at ambient temperatures (35).

Peroxomonosulfate

No information was located on the oxidation of SCN^- by HOOSO_3^- . The rate of this reaction may be comparable to the rate of oxidation of SCN^- by H_2O_2 .

Oxygen

Oxidation of SCN^- by O_2 is extremely slow at ambient temperatures (29). No information on catalysis of this reaction and no kinetic data were found. Some Cu(II) species might catalyze the reaction of SCN^- with O_2 .

Hypochlorite

The oxidation of SCN^- by ClO^- is expected to be very fast; no kinetic studies were located.

Other Oxidants; Mechanism of Thiocyanate Oxidations

In the oxidation of SCN^- by other oxygen-containing oxidants, e.g., BrO_3^- (36), IO_3^- (37), $\text{S}_2\text{O}_8^{2-}$ (38), HSO_5^- (39), HNO_2 (40), or HNO_3 (40), HCN or CN^- is observed as a product or indicated as an intermediate. Cyanide formation also occurs in the oxidation of SCN^- by H_2O_2 (29-30) or O_3 (35), and may occur in oxidation by HSO_5^- or ClO^- . All of the data are consistent with attack of the oxidant on the sulfur atom of SCN^- . In proposed mechanisms, the first-formed intermediate species OSCN^- reacts with more oxidant to form O_2SCN^- and O_3SCN^- . These species rapidly decompose to sulfur oxide species and CN^-/HCN .

Any of the oxidants used to oxidize CN^-/HCN will also oxidize SCN^- , and the latter reaction may proceed faster than the former. The reaction of SCN^- with different oxidants is known or expected to result in liberation of CN^-/HCN , because the oxidant attacks the sulfur atom in preference to the carbon atom in SCN^- . Consequently, oxidation of SCN^- should be conducted with sufficient oxidant and enough time to ensure the oxidation of the liberated CN^- or HCN . In the cases of O_3 or ClO^- , the reactions with CN^- are very fast. With H_2O_2 and HOOSO_3^- , additional reaction time may be required.

Proposals to treat cyanide wastes by conversion to SCN^- are of questionable efficacy because of the possibility of liberation of CN^-/HCN in the oxidation of SCN^- in the environment.

Oxidation of Cyanate

Strong oxidants oxidize NCO^- to other products, generally reported or assumed to be CO_3^{2-} and N_2 . As described below, the actual reaction is not always that simple.

Ozone

Cyanate is oxidized by O_3 to CO_3^{2-} , N_2 , and NO_3^- . Assuming second-order kinetics, the rate constant at 20°C is

estimated to be of the order of $10^3\text{M}^{-1}\cdot\text{s}^{-1}$, which is much slower than the CN^- - O_3 reaction (35). In practice, the reaction rate is limited by mass transfer of O_3 from the gas phase to the solution. Details concerning the formation of NO_3^- in this reaction have not been reported.

Hypochlorite

Cyanate is oxidized by ClO^- to CO_3^{2-} and N_2 ; with excess ClO^- , NO_3^- has been reported as an accessory product. Three investigations of this reaction have been published. Lister (20, 41) investigated the reaction by monitoring the concentrations of NCO^- and ClO^- at pH 13 to 14, ionic strength 2.2M , and 50° to 75°C . He reported the rate law

$$-d[\text{NCO}^-]/dt = k'[\text{NCO}^-][\text{R}][\text{OH}^-]^{-1}.$$

Extrapolation of his data to 25°C gives $k' = 6.2 \times 10^{-8}\text{s}^{-1}$. If the rate law is expressed in terms of hydrogen ion concentration,

$$-d[\text{NCO}^-]/dt = k[\text{NCO}^-][\text{R}][\text{H}^+],$$

where $[\text{R}] = [\text{ClO}^-] + [\text{HClO}]$.

By using the relationship $k = k'/K_w$ where $K_w = [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14}$ (appendix C), one obtains $k = 6.2 \times 10^6\text{M}^{-2}\cdot\text{s}^{-1}$.

Teo and Tan (42) monitored the concentrations of NCO^- and ClO^-/HClO at pH 8.6 to 10, 27° to 50°C , and unstated ionic strength. They obtained the same rate law, with $k = 4.8 \times 10^8\text{M}^{-2}\cdot\text{s}^{-1}$ at 25°C . This value is nearly 80 times higher than the value derived from Lister's data.

Mapstone and Thorn (23) monitored nitrogen evolution at pH 9 to 10 and 18°C . They reported the reaction as first order each in concentrations of NCO^- and ClO^- , but did not report pH dependence. Their value of k , derived assuming a mean pH of 9.5, agrees, perhaps fortuitously, within a factor of 2 with the data of Teo and Tan extrapolated to 18°C .

The disagreement among the quoted investigators is attributed to the following:

1. All of the investigators reported induction periods before the evolution of N_2 occurred.
2. The reaction is not precisely stoichiometric. Most of the investigators detected formation of NO_3^- , especially when excess ClO^- was used.
3. The $\text{ClO}^-:\text{NCO}^- = 3:2$ stoichiometry indicates a complex reaction mechanism.

Given all of these considerations, the investigators may not have all monitored the same reaction.

Peroxomonosulfate

No data on the oxidation of NCO^- by HSO_5^{2-} were located. Thermodynamically, the oxidant strength of HSO_5^{2-} or SO_5^{2-} is comparable to ClO^- and O_3 , as shown in figure 7-2. Reaction of NCO^- with $\text{HSO}_5\text{SO}_5^{2-}$ is possible, but would be hindered by electrostatic repulsion of the reactants.

Hydrogen Peroxide

No information on the oxidation of NCO^- by H_2O_2 was located. Thermodynamically, $\text{H}_2\text{O}_2/\text{HO}_2^-$ is as strong an oxidant as ClO^- , as shown in figure 7-2, so reaction of NCO^- with $\text{H}_2\text{O}_2/\text{HO}_2^-$ is certainly possible.

Possible Mechanisms for Cyanate Oxidation

Lister (41) speculated that HClO attacks NCO^- to form an intermediate such as Cl-NH-CO_2^- , followed by further rapid oxidation by ClO^-/HClO . Teo and Tan (42) proposed a ClO^-/HClO -catalyzed hydrolysis of NCO^- to NH_4^+ and CO_3^{2-} , followed by reaction of $\text{NH}_4^+/\text{NH}_3$ with ClO^-/HClO ; this mechanism disagrees with their observed rate law.

Attack of the oxidant on the nitrogen atom is also a reasonable hypothesis and may give a species that would hydrolyze to CO_2 and an oxidized nitrogen species, perhaps hydroxylamine (NH_2OH) with O_3 , or monochloramine (NH_2Cl) with ClO^- . The oxidized nitrogen species would then react with more oxidant to produce N_2 or more highly oxidized species, ultimately resulting in formation of NO_3^- .

ADDITION, EXCHANGE, AND SUBSTITUTION REACTIONS OF CARBON(II) SPECIES

Carbon(II) is represented by CN^-/HCN , i.e., $\{\text{HCN}\}$, and species derived by addition, exchange, and hydrolysis reactions. These reactions are described in this section and schematized in figures 7-5 and 7-6.

Addition Reactions

Free $\{\text{CN}^- \}$ undergoes addition reactions that constitute the major routes for its nonoxidative removal. The addition reactions of $\{\text{CN}^- \}$ are schematized in figure 7-5 and discussed in the following paragraphs.

Cyanide and Water

Cyanide undergoes addition of H_2O to yield formamide, $\{\text{HCON}\}$, which hydrolyzes to $\{\text{HCOO}\}$ at a faster rate (see below) (43-44). This observation agrees with the rule that amides R-CO-NH_2 hydrolyze to carboxylates, R-CO_2^-

faster than nitriles R-CN undergo addition of H_2O to form R-CO-NH_2 (45, pp. 1004-1010; 46). Sanchez and others (44) studied the reaction of $\{\text{HCN}\}$ with H_2O . The rate data are given in table F-3 and figure 7-7. The reaction rate is independent of pH at $\text{pH} > 10$, where the half-life of $\{\text{HCN}\}$ varies from about 80 years at 0°C to about 120 days at 40°C . The reaction rate decreases at $\text{pH} < 10$, then increases again in acid solution (47). The observations of Silver (16) regarding $\{\text{HCN}\}$ hydrolysis agree semiquantitatively with the results of Sanchez and others (44).

Hydrolysis of $\{\text{HCN}\}$ to $\{\text{HCOO}\}$ is one of a number of pathways by which $\{\text{HCN}\}$ is lost or degraded in industrial operations or the environment. Pathways of loss or degradation of $\{\text{HCN}\}$ are summarized at the end of this chapter.

Cyanide and Ammonia

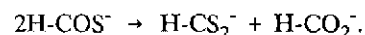
The reaction of $\{\text{HCN}\}$ with NH_3 to yield formamidine, $\{\text{HCNN}\}$, was observed by Oro and Kimball (43) and studied briefly by Sanchez and others (44). At 30° to 60°C and pH 7.1 to 9.6, and periods up to 14 days, no more than 0.4 pct conversion of $\{\text{HCN}\}$ to $\{\text{HCNN}\}$ occurred in solutions 1M in CN^- and 3M in NH_3 . Hydrolysis of $\{\text{HCNN}\}$ to $\{\text{HCON}\}$ proceeds at a similar or faster rate, which limits the concentration of $\{\text{HCNN}\}$.

Cyanide and Sulfide

The reaction of $\{\text{HCN}\}$ with $\text{H}_2\text{S}/\text{SH}^-$ to yield thioformamide, $\{\text{HCSN}\}$ is known (48), but no kinetic data were located. Analogous reactions of other nitriles R-CN are known (49, p. 443).

Exchange Reactions Involving Ammonia and Sulfide

In solutions containing both NH_3 and $\text{H}_2\text{S}/\text{SH}^-$, $\{\text{HCNN}\}$, $\{\text{HCSN}\}$, $\{\text{HCSS}\}$, $\{\text{HCON}\}$, and $\{\text{HCOS}\}$ may undergo exchange reactions. No information on such reactions was located, aside from an unsubstantiated statement that dithioformate, $\{\text{HCSS}\}$, forms via a redistribution reaction of thioformate, $\{\text{HCOS}\}$ (50),



Exchange reactions are known for organic analogs (49, pp. 428, 443, 454; 51, pp. 719, 736, 749). They include

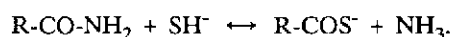
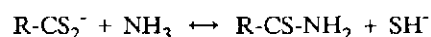
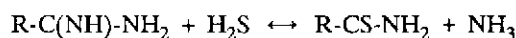
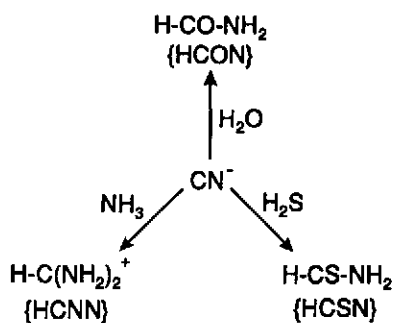
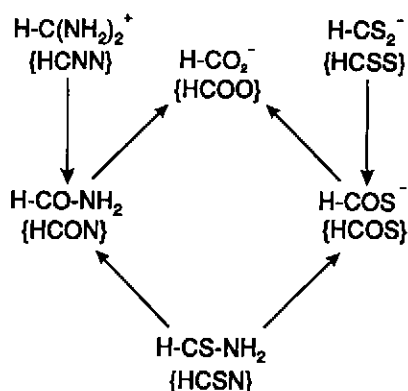


Figure 7-5



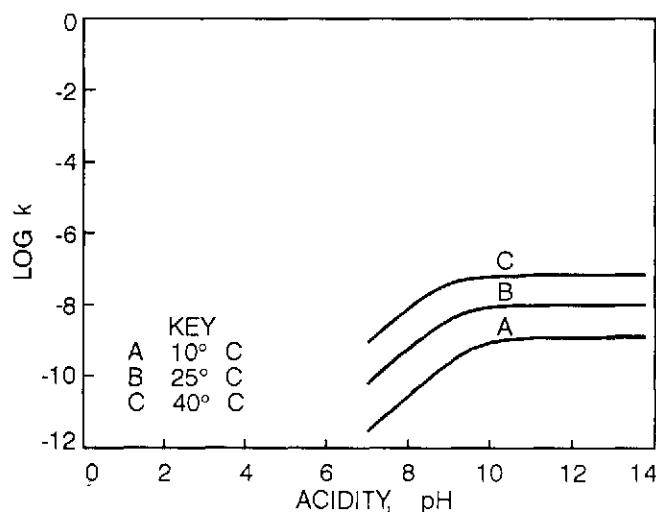
Addition reactions of free cyanide.

Figure 7-6



Hydrolysis reactions of carbon(II) species.

Figure 7-7



Log *k* versus pH for addition of water to cyanide.

The failure to observe {HCOS} in the hydrolysis of {HCSN} may have been due to the presence of NH₃ in the reaction solution (44). At the low concentrations of NH₃ and H₂S/SH⁻ in process and impounded solutions, such exchange reactions are not expected to be significant.

Hydrolysis Reactions

The products of the addition reactions of {HCN} undergo hydrolysis and are thereby finally converted to {HCOO}. These reactions are discussed in this section and schematized in figure 7-5.

Formamidine

The hydrolysis of {HCNN} gives {HCON}. Sanchez and others (44) report brief observations that suggest a half-life at 30° C of 7 to 14 days at pH 7.1, to 2 to 4 h at pH 9.5. As a rule, amidines R-C(NH)-NH₂ hydrolyze to R-CO-NH₂ much faster than R-CO-NH₂ hydrolyzes to R-CO₂⁻ (45, p. 498; 46). Acetamidine (R = CH₃) hydrolyzes to acetamide (CH₃CONH₂) rapidly in water at 25° C (46).

Thioformamide

Sanchez and others (44) report that the main product of hydrolysis of {HCSN} is {HCON}; formation of {HCOS} was not observed. Their brief observations indicate a half-life at 30° C of 3 days at pH 8.5. For comparison, organic thioamides R-CS-NH₂, e.g., thioacetamide (R = CH₃), hydrolyze to both R-CO-NH₂ and R-COS⁻ (49, p. 448; 52-53). The relative amounts of products depend on temperature and pH. With acetamide, hydrolysis to R-CO-NH₂ predominates in acid solution, and hydrolysis to R-COS⁻ predominates in basic solution (49, pp. 448; 52-54). It is possible that {HCOS} forms in the hydrolysis of {HCSN} under other conditions than Sanchez and others (44) studied.

Dithioformate

No information was located on the rate of hydrolysis of {HCSS}. The organic analogs R-CS₂⁻ hydrolyze slowly (52, pp. 719, 732, 750). Oxidation by O₂ or other oxidants may compete with hydrolysis (51, pp. 723, 750). Dithioformate in solution as its alkali metal salts forms complexes with heavy metal ions, so hydrolysis is not readily catalyzed by heavy metal cations (54); contrast the behavior of {HCOS} (see below).

Formamide

The hydrolysis of {HCON} to {HCOO} and NH₃ was studied at 80° C (55) and at 25° to 50° C (56-57). The

results from Salem and Sidahmed (56-57) are given in table F-4 and figure 7-8. At pH 11, the half-life of {HCON} varies from about 50 days at 0° C to about 1.5 days at 40° C. The half-life for addition of H₂O to CN⁻ is much longer than that for hydrolysis of {HCON}, being longer by factors of 600 and 80 at 0° and 40° C, respectively. Consequently, {HCON} does not accumulate during the conversion of CN⁻ to {HCOO⁻}. These results parallel the trends observed for organic analogs (45, pp. 1004-1010; 46, 52). The rate constants calculated for 80° C from the data of Salem and Sidahmed (56-57) differ from those of Hine and others (55) by 3 and 30 pct, respectively, for acid and alkaline hydrolysis.

Thioformate

No data on the hydrolysis of {HCOS} were located. Organic analogs R-COS⁻ hydrolyze slowly in acidic or basic solutions (51, pp. 719, 732, 750; 52, 58-59); half-lives are months at 70° C at pH 2 to 10. Thioformate in solution as its alkali metal salts reacts with heavy metal cations to precipitate the metal sulfides, which indicates catalyzed hydrolysis (54). Oxidation by O₂ or other oxidants may compete with hydrolysis (51, pp. 723, 750), though it too is slow, as no oxidation was detected in solutions of thioacetic acid (CH₃-CO-SH) in 7 days at room temperature (60).

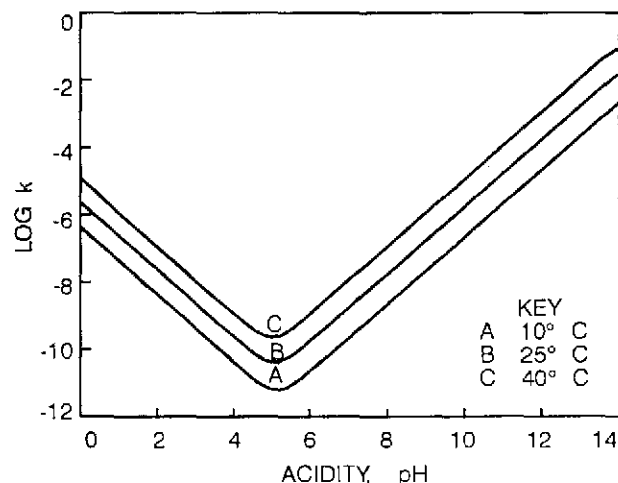
ADDITION, EXCHANGE, AND SUBSTITUTION REACTIONS OF CARBON(III) SPECIES

Carbon(III) is represented by {NCCN} and species derived from it by addition, exchange, and hydrolysis reactions. Disproportionation reactions also occur with formation of equimolar quantities of C(II) and C(IV) species. Insofar as {NCCN} is formed by oxidation of {HCN} only in acid solutions, the species described in this section are not likely to be encountered in normal precious metals operations. Contact of cyanide solutions with acidic solutions such as acid mine drainage may result in formation of {NCCN} via oxidation by Fe(III) or Cu(II), e.g., and hence the species derived from it described below. Cyanogen is unstable at all pH values with respect to disproportionation to CN⁻/HCN and NCO⁻ as shown in figure E-3.

Addition Reactions

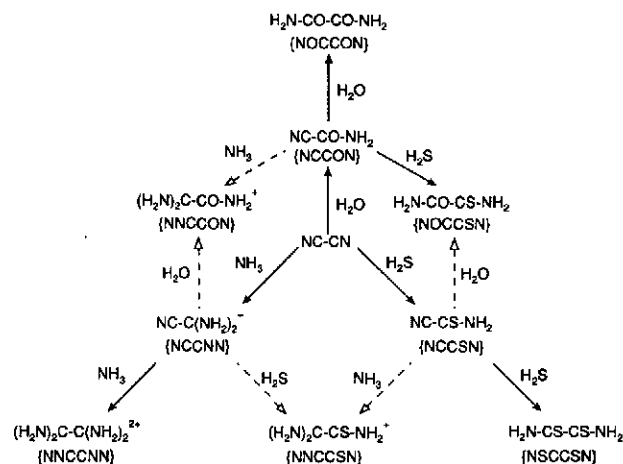
The addition reactions of {NCCN} are schematized in figure 7-9 and discussed in the following paragraphs. Since {NCCN} has two CN groups, the possible reaction products are more numerous than with {HCN}. Addition of one molecule of H₂O, NH₃, or H₂S results in formation of species {NCCNX}, which undergo addition of a second

Figure 7-8



Log k versus pH for hydrolysis of formamide.

Figure 7-9



Addition reactions of cyanogen.

molecule of reagent to form {YNCCNX}, where X and Y represent oxygen, nitrogen, or sulfur.

Cyanogen and Water

Cyanogen disproportionates rapidly to CN⁻ and NCO⁻ in basic solution, in part via addition of H₂O to form cyanoformamide, {NCCON} (24, 61-62). The rate was observed to vary directly with OH⁻ concentration at pH 10 to 12 (62). The data are given in table F-5 and figure 7-10. The half-life of {NCCN} varies from about 2 s at 0° C to about 0.07 s at 40° C, at pH 11.0.

Addition of water to {NCCN} in acid solution gives {NCCON}, which in turn undergoes addition of a second

molecule of H_2O to yield oxamide, $\{\text{NOCCON}\}$ (24, 61-62). With dilute acid solutions, $\text{pH} > 0$, $\{\text{NCCON}\}$ is isolable (61). In concentrated HCl solution, e.g., formation of $\{\text{NOCCON}\}$ is fast, and $\{\text{NCCON}\}$ cannot be isolated (24, 61). Kinetic data for addition of H_2O to $\{\text{NCCN}\}$ in acid solution were not located.

In alkaline solution, $\{\text{NCCON}\}$ disproportionates to CN^- and NCO^- at a rate independent of pH at $\text{pH} > 11$ (62). The data are given in table F-6 and figure 7-11. At $\text{pH} 11.0$ the half-life of NC-CO-NH^- varies from about 70 s at 0°C to about 0.3 s at 40°C .

Cyanogen and Ammonia

In liquid NH_3 , $\{\text{NCCN}\}$ undergoes addition of NH_3 . Cyanoformamidine, $\{\text{NCCNN}\}$, and oxamidine, $\{\text{NNCCNN}\}$, are isolable, depending on reaction conditions (63-64). No data are available concerning the formation of $\{\text{NCCNN}\}$ and $\{\text{NNCCNN}\}$ in the reaction of $\{\text{NCCN}\}$ with aqueous NH_3 . In concentrated aqueous solutions of organic amines, the organic oxamidines are formed rapidly. The oxamidines are isolable, but the intermediate cyanoformamides were not observed (65).

Cyanogen and Sulfides

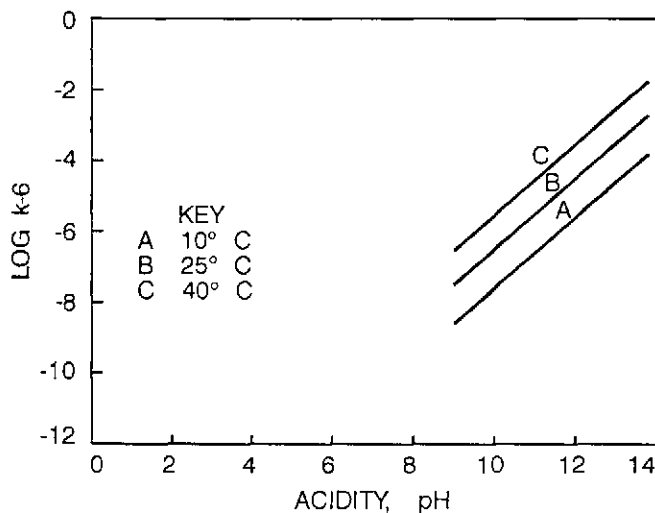
In aqueous solution, $\{\text{NCCN}\}$ reacts rapidly with H_2S to form dithiooxamide, $\{\text{NSCCSN}\}$ (24, 61). The intermediate cyanthioformamide, $\{\text{NCCSN}\}$, was not observed, possibly because of the low solubility of $\{\text{NSCCSN}\}$. The analogous reactions of $\{\text{NCCN}\}$ with thiols R-SH are known (66).

Reactions of Cyanoformamide

The species $\{\text{NCCON}\}$, $\{\text{NCCSN}\}$, and $\{\text{NCCNN}\}$ are reactive. They are known or thought to undergo addition or disproportionation reactions, as schematized in figure 7-12. The disproportionation of $\{\text{NCCON}\}$ was discussed above in connection with the addition of H_2O to $\{\text{NCCN}\}$. Cyanoformamide undergoes addition of H_2S to form thiooxamide, $\{\text{NSCCON}\}$ (61), and probably undergoes addition of NH_3 to form amidinoformamide, $\{\text{NNCCON}\}$. Other possible but undemonstrated addition reactions to give $\{\text{NNCCON}\}$, $\{\text{NSCCON}\}$, and amidinothioformamide, $\{\text{NNCCSN}\}$, are shown in figure 7-12.

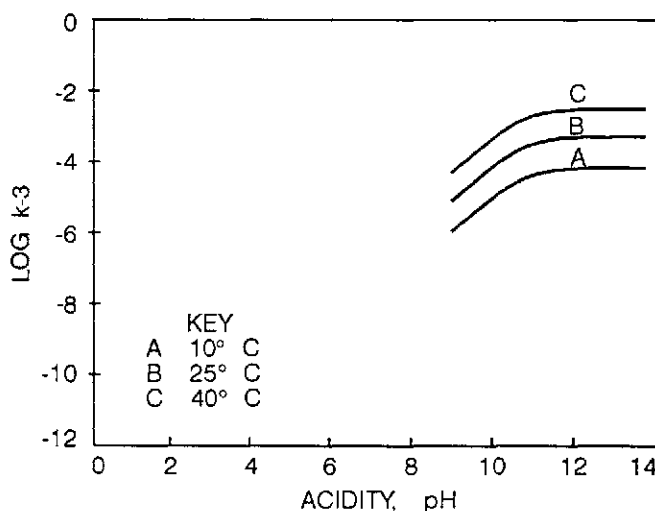
Cyanoformamide in warm water disproportionates to $\{\text{HCN}\}$ and HNCO , which hydrolyzes to CO_2 and NH_3 (see below) (61). The disproportionation of $\{\text{NCCON}\}$ in basic solution is described above. The species $\{\text{NCCSN}\}$ and $\{\text{NCCNN}\}$ may also disproportionate to $\{\text{HCN}\}$ and SCN^- and cyanamide, $\{\text{NCN}\}$, respectively; no data were located. These reactions are also schematized in figure 7-12.

Figure 7-10



Log k versus pH for addition of water to cyanogen.

Figure 7-11

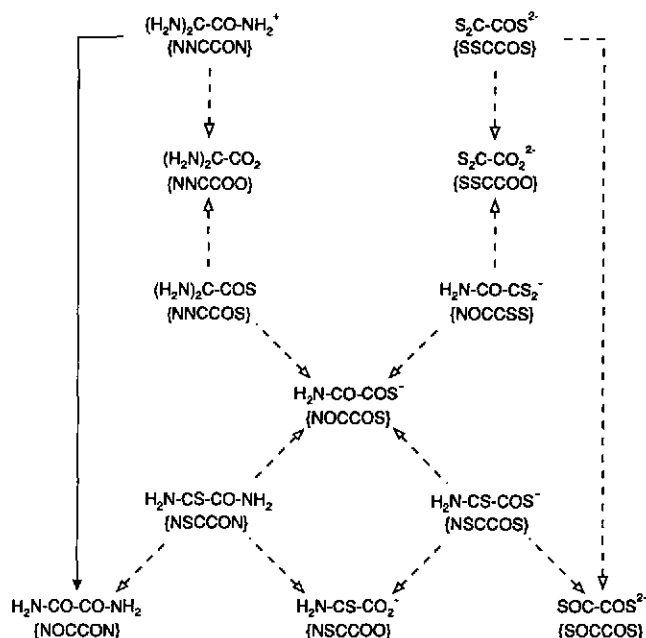


Log k versus pH for disproportionation of cyanoformamide.

Exchange Reactions Involving Ammonia and Sulfide

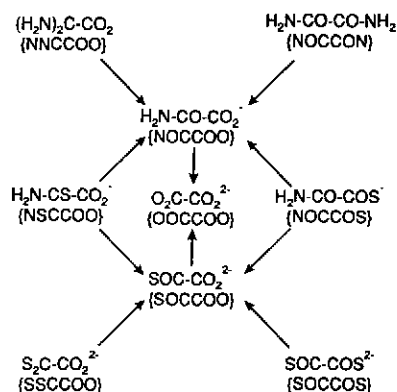
In solutions containing both NH_3 and $\text{H}_2\text{S}/\text{SH}^-$, the species formed in addition and substitution reactions of $\{\text{NCCN}\}$ may undergo exchange reactions. No information on such reactions was located. Such exchange reactions are known for organic analogs (66-69). At the low concentrations of NH_3 and $\text{H}_2\text{S}/\text{SH}^-$ in process and impounded solutions, the extent of such reactions is expected to be negligible.

Figure 7-14



Hydrolysis reactions of carbon(III) species with three nitrogen or sulfur atoms.

Figure 7-15



Hydrolysis reactions of carbon(III) species with two nitrogen or sulfur atoms.

Species with Two Sulfur Atoms Bound to the Same Carbon Atom

These species, {YXCCSS}, may form via redistribution reactions of {YXCCOS}. As with R-CS₂⁻, described above under hydrolysis of C(II) species, hydrolysis and oxidation are expected to compete. No kinetic data were located. The syntheses of 1,1-dithiooxalate, {O2CCSS}, trithiooxalate, {SOCCSS}, and tetrathiooxalate, {SSCCSS}, were conducted in an inert atmosphere (71-72).

Species With One Oxygen Atom and One Nitrogen Atom Bound to the Same Carbon Atom

These species are amides, {YXCCON}. They are known or expected to hydrolyze slowly to {YXCCOO}. The most important members of this group are oxamide, {NOCCON}, and oxamic acid, {NOCCOO}. Kinetic data for the hydrolysis of these species have been published (73-75). The successive hydrolyses {NOCCON} → {NOCCOO} → {O2CCOO} was studied by Packer and others (73) in hot acid solution and by Voortman and others (74-75) alkaline solution at 0° to 60° C and in hot acid solution. The data are given in tables F-7 and F-8 and in figures 7-16 and 7-17. The respective half-lives at pH 11.0 vary from about 2 days and 120 days at 0° C to about 5 h and 4 days at 40° C.

Species With One Oxygen Atom and One Sulfur Atom Bound to the Same Carbon Atom

For these species, {YXCCOS}, analogous to R-COS⁻ described above, hydrolysis and oxidation are expected to compete. Thiooxalate, {O2CCOS}, was prepared under an inert atmosphere (71). Fast hydrolysis at pH < 2 was reported for 1,2-dithiooxalate, {SOCCOS} (76).

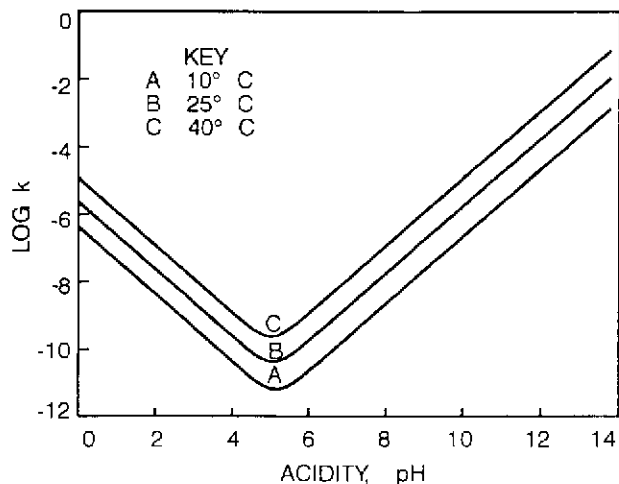
ADDITION, EXCHANGE, AND SUBSTITUTION REACTIONS OF CARBON(IV) SPECIES

Carbon(IV) is represented by C1CN and NCO⁻ and species derived by addition, exchange, hydrolysis, and substitution reactions. The oxidation of CN⁻ by chlorine oxidants such as ClO⁻ gives C1CN, and oxidation by oxygen oxidants such as H₂O₂, O₃, and HOOSO₃⁻ gives NCO⁻. Thus C1CN and NCO⁻ are important intermediates in the oxidative destruction of CN⁻, and the species derived by addition, exchange, hydrolysis, and substitution reactions are of interest.

Reactions of Cyanogen Halides

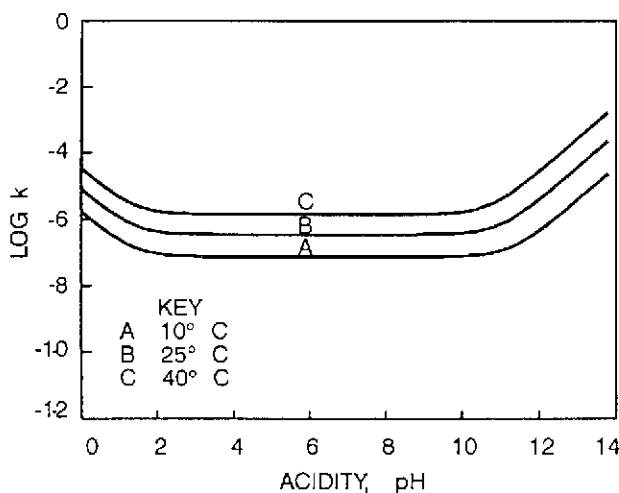
The cyanogen halides form when {HCN} reacts with halogens or hypohalites. In cyanide destruction by hypochlorite oxidation, C1CN is the primary product. Bromine or hypobromite oxidation of {HCN} gives BrCN. The cyanogen halides undergo substitution reactions with H₂O, NH₃, or H₂S/SH⁻, to form NCO⁻, H₂N₂CN, and SCN⁻, respectively. A conceivable mechanism is addition of the reagent to cyanogen halide, followed by rapid elimination of hydrogen halide. These reactions are described in this section and schematized in figure 7-18.

Figure 7-16



Log k versus pH for hydrolysis of oxamide.

Figure 7-17



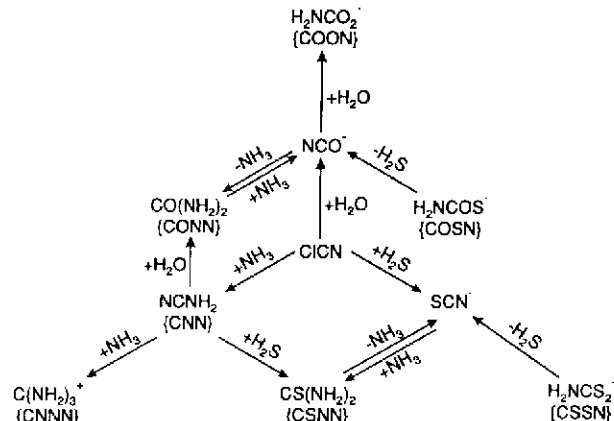
Log k versus pH for hydrolysis of oxamic acid.

Cyanogen Chloride and Water

Cyanogen chloride, ClCN , hydrolyzes to NCO^- in alkaline solution (77-80). The data are presented in table F-9 and figure 7-19. At pH above 6, the rate is proportional to OH^- concentration. At pH 11.0, the half-life varies from about 4 h at 0° C to about 4 s at 40° C. Hydrolysis of ClCN is catalyzed by CO_3^{2-} , PO_4^{3-} , H_2O_2 , Cl_2 , and ClO^- (79-80); the data are incomplete.

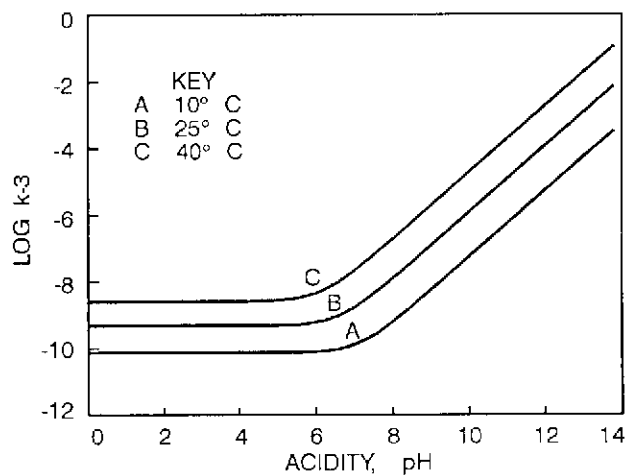
Cyanate, formed directly as an oxidation product of CN^- or via hydrolysis of ClCN , is the most important intermediate in the oxidative destruction of CN^- . Its hydrolysis to NH_3 and HCO_3^- is described below.

Figure 7-18



Substitution reactions of cyanogen chloride and subsequent addition reactions.

Figure 7-19



Log k versus pH for hydrolysis of cyanogen chloride.

The hydrolysis of BrCN proceeds similarly to that of ClCN but about 1 power of 10 slower (81). The data are incomplete.

Cyanogen Chloride and Ammonia

The reaction of ClCN with aqueous NH_3 to form H_2NCN was reported to be no faster than its hydrolysis to NCO^- with $10^{-4}M$ to $10^{-3}M$ reactants at pH 8 and unspecified room temperature (77). No systematic study was located. However, a more recent study of ClCN substitution reactions with different amines, including hydroxylamine (NH_2OH), hydrazine (N_2H_4), and methylamine (CH_3NH_2),

reports fast reactions at 25° C and pH 4 to 6, with second-order rate constants in the range 0.2 to 60 ($\text{mol} \cdot \text{L}^{-1}$)⁻¹·s⁻¹ (80).

Cyanogen Chloride and Sulfide

The reaction of ClCN with SH⁻ to form NCS⁻ is quantitative in 0.5 h at unspecified room temperature (77). In practice, ClCN would be generated via the oxidation of {HCN} with ClO⁻, and sulfides would be oxidized simultaneously. Formation of SCN⁻ from ClCN is therefore unlikely; further, any SCN⁻ present would also be rapidly oxidized by ClO⁻.

Other Addition Reactions of Carbon(IV) Species

Figure 7-18 also shows species that would be expected to form by further addition reactions of NCO⁻, H₂NCN, and NCS⁻. As shown there and described below, some of those species, on the contrary, undergo the reverse of those addition reactions.

Cyanamide and Water

Cyanamide, {CNN}, undergoes addition of H₂O to form urea, {CONN} (82-84). The data are given in table F-10 and figure 7-20. The rate is independent of pH at pH above 11 (82). At pH 11.0 the half-life varies from about 2 years at 0° C to about 4 days at 40° C. Only at concentrations above 10⁻²M does dimerization of {CNN} to NC-N=C(NH₂)₂ become significant (82). The hydrolysis of {CNN} is catalyzed by manganese or iron oxides (85-86). Data for hydrolysis in acid solution (83-84), studied in different temperature ranges, grossly disagree when processed to calculate rate constants from 0° to 90° C. Possibly the mechanism changes with temperature; the formation of H₃NCN⁺ is also a factor.

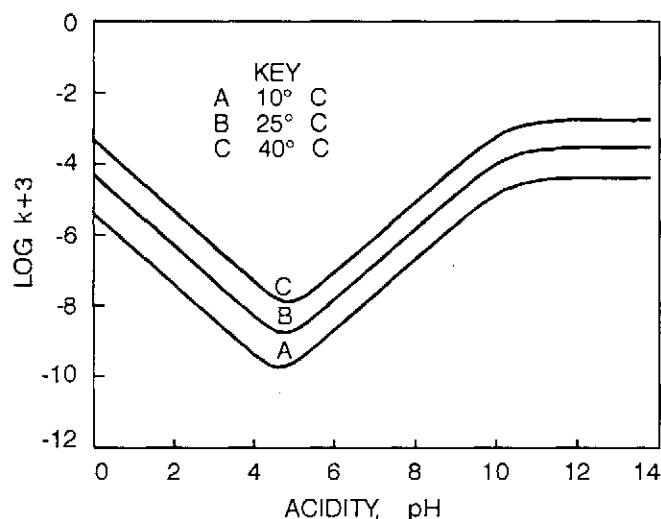
Cyanamide and Ammonia

The reaction of {CNN} with NH₃ to form guanidine, {CINN}, is well known (45, pp. 1098-1099). Usually an ammonium salt is the reagent, and the guanidinium salt is the product. No kinetic data for this reaction in aqueous solution were located.

Cyanamide and Sulfide

The reaction of {CNN} with H₂S/SH⁻ to form thiourea, {CSNN}, is well known (49, p. 456); kinetic data were also published (87).

Figure 7-20



Log *k* versus pH for addition of water to cyanamide.

Thiocyanate and Water

The hydrolysis of SCN⁻ to H₂S, NH₄⁺, and CO₂ proceeds only in strongly acid solutions (pH < 1) (88). The mechanism may involve hydrolysis to HNCO (cyanic acid) and H₂S, followed by hydrolysis of HNCO to NH₄⁺ and CO₂, rather than addition of H₂O to form thiocarbamate, {COSN}. Destruction of SCN⁻ is therefore best accomplished by oxidation (see above).

Thiocyanate and Ammonia

The well-known reaction of SCN⁻ with NH₄⁺ to form {CSNN} proceeds in concentrated solutions, especially at higher temperatures (89, pp. 334, 342).

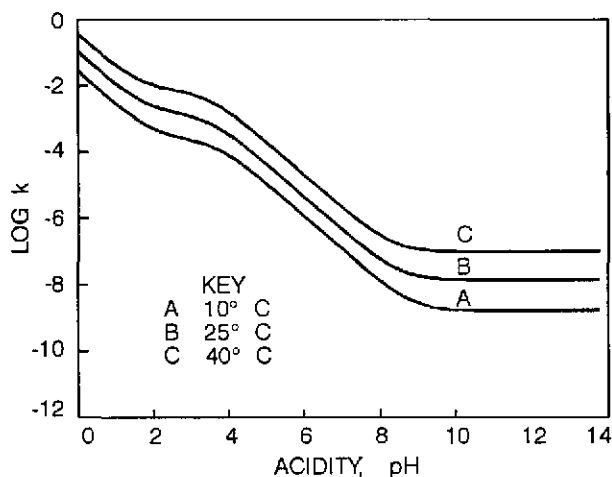
Thiocyanate and Sulfide

The reaction of SCN⁻ with H₂S/SH⁻ to form dithiocarbamate, {CSSN}, does not occur; on the contrary, the reverse of this reaction, decomposition of {CSSN} to SCN⁻ and SH⁻, occurs in alkaline solution (90-91). Dithiocarbamate is made by the addition of NH₃ to CS₂ in alkaline solution; this reaction is reversed in acid solution (90, 92).

Cyanate and Water

The addition reaction of NCO⁻ with H₂O gives carbamate, {COON}, which in turn hydrolyzes much faster to NH₃ and {COOO} (see below). The data are given in

Figure 7-21

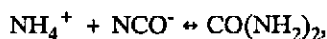
Log *k* versus pH for addition of water to cyanate.

tables F-11 and F-12 and figure 7-21. The rate of disappearance of NCO^- is independent of pH at $\text{pH} > 10$ (20, 93-95). The reaction in alkaline solution is catalyzed by product HCO_3^- (95). In the presence of Ca^{2+} to precipitate carbonate species, the half-life of NCO^- varies from about 50 years at 0°C to about 70 days at 40°C at $\text{pH} 11.0$. In the presence of a constant concentration of $0.010M \text{HCO}_3^-$ ($\text{pH} 8$ to 9), the half-life of NCO^- varies from about 1.7 years at 0°C to about 14 days at 40°C . At higher pH values, these half-lives would be increased by factors corresponding to the fraction of carbonate present as HCO_3^- . At $\text{pH} 11.0$ this factor is about 5.

Hydrolysis of NCO^- may be subject to competition from other reactions, such as oxidation to N_2 and CO_3^{2-} , which consume NCO^- in industrial processes or the environment. Pathways for the degradation of NCO^- are summarized in connection with loss and degradation of CN^- at the end of this chapter.

Cyanate and Ammonia

The well-known reaction of NCO^- with NH_4^+ to form $\{\text{CONN}\}$, proceeds in concentrated solutions, especially at higher temperatures (89, pp. 334, 342; 93). For the equilibrium of $\{\text{CONN}\}$ with NH_4^+ and NCO^- ,



log *K* is +4.7, calculated from Gibbs energy data in tables B-1 and C-1. Kinetic data for the formation of $\{\text{CONN}\}$ from NH_4^+ and NCO^- are given in table F-13 (93).

Cyanate and Sulfide

The reaction of NCO^- with $\text{H}_2\text{S}/\text{SH}^-$ to form $\{\text{COSN}\}$ does not occur; on the contrary, the reverse of this reaction, decomposition of $\{\text{COSN}\}$ to NCO^- and SH^- , occurs in alkaline solution (96). Thiocarbamate is made by the addition of NH_3 to COS in alkaline solution; this reaction is reversed in acid solution (96).

Exchange Reactions Involving Ammonia and Sulfide

In solutions containing both NH_3 and $\text{H}_2\text{S}/\text{SH}^-$, the species formed in addition and substitution reactions of ClCN may undergo exchange reactions. Species such as $\{\text{COSN}\}$, $\{\text{CSSN}\}$, and $\{\text{CSSS}\}$ (trithiocarbonate) could conceivably form. As stated above for C(II) and C(III) species, such reactions are unlikely to be significant at the low concentrations of the reactants in process solutions.

Hydrolysis Reactions

The species formed in the addition and exchange reactions described in the preceding section undergo hydrolysis. The final product is $\{\text{COOO}\}$. These reactions are described below and schematized in figure 7-22.

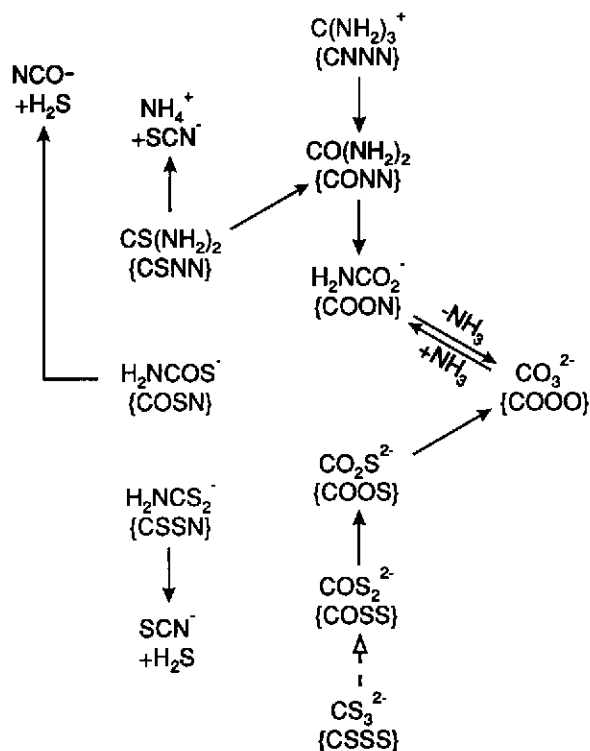
Guanidine

The hydrolysis of $\{\text{CNNN}\}$ proceeds at an observable rate in hot alkaline solutions (97-98), but not in hot neutral or acid solutions (97). Homer and Alwis (97) report that $\{\text{CONN}\}$ is the product at 15° to 70°C ; Eloranta (98) obtained $\{\text{COOO}\}$ and NH_3 at 130° to 135°C and did not detect $\{\text{CONN}\}$. At the temperatures employed by Eloranta, the hydrolysis of $\{\text{CONN}\}$ may have proceeded faster than that of $\{\text{CNNN}\}$. The investigation of Homer and Alwis appears more systematic, and includes comparison with hydrolyses of related substrates. The data are given in table F-14 and figure 7-23.

Thiourea

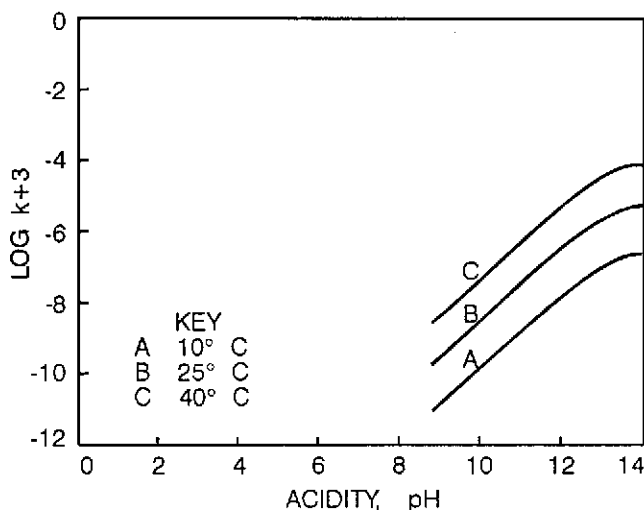
At $\text{pH} < 8$, $\{\text{CSNN}\}$ decomposes to SCN^- and NH_4^+ (88). At $\text{pH} > 12$, $\{\text{CSNN}\}$ hydrolyzes to SH^- and presumably $\text{OC}(\text{NH}_2)_2$ (99). The data are shown in table F-15 and figure 7-24. At $\text{pH} 11.0$ the half-life of $\{\text{CSNN}\}$ varies from about 1,400 years at 0°C to about 20 years at 40°C .

Figure 7-22



Hydrolysis reactions of carbon(IV) species.

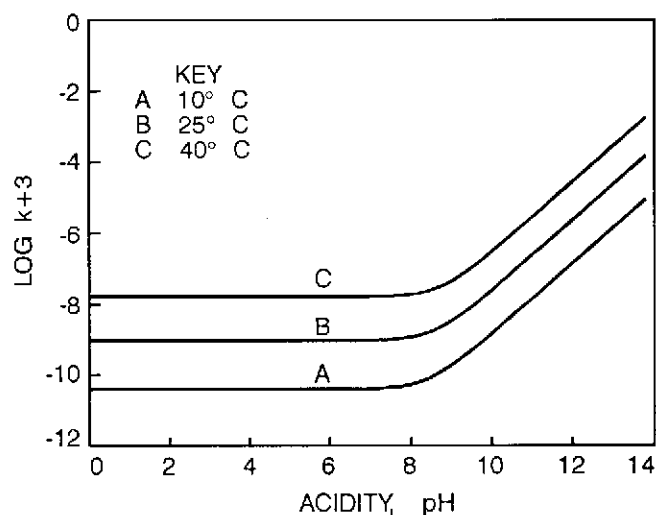
Figure 7-23

Log k versus pH for hydrolysis of guanidinium ion.

Dithiocarbamate

The elimination reactions mentioned above probably compete with the hydrolysis of {CSSN} to NH_4^+ , CO_2 , and H_2S (93-94).

Figure 7-24

Log k versus pH for decomposition of thiourea.

Trithiocarbonate

Trithiocarbonate, {CSSS}, presumably hydrolyzes to {COOO} via dithiocarbonate, {COSS}, but no data were located. It decomposes rapidly to CS_2 and H_2S in acid solution (100-101). It readily undergoes oxidation by O_2 and other oxidants (100); these reactions presumably compete with hydrolysis.

Urea

The hydrolysis of {CONN} proceeds to NH_3 and {COOO} (83, 102-103), presumably via the intermediate {COON}, which hydrolyzes much faster (104-105) (see below). The data are given in table F-16 and figure 7-25. The rate of hydrolysis of {CONN} is independent of pH at pH below 12, where its half-life varies from about 5,000 years at 0° C to 2.5 years at 40° C.

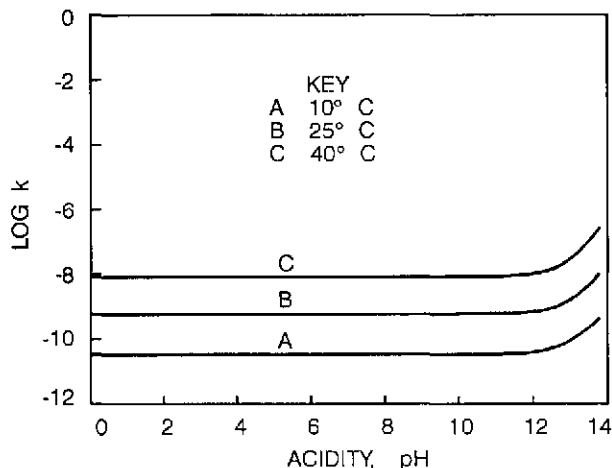
Thiocarbamate

The elimination reactions mentioned above probably compete with the hydrolysis of {COSN} to NH_4^+ , CO_2 , and H_2S (96).

Dithiocarbonate

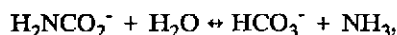
Dithiocarbonate, {COSS}, hydrolyzes to {COOO} and SH^- (101) with a half-life of 50 h in 5M NaOH at 25° C; the hydrolysis is faster at lower alkalinity.

Figure 7-25

Log *k* versus pH for hydrolysis of urea.

Carbamate

The equilibrium of {COON} with NH₃ and HCO₃⁻ is rapid (minutes):



for which the equilibrium constant $K = 0.5$ at 25° C (104-105). This equilibrium is significant only at pH 9 to 10, where HCO₃⁻ and NH₃ are the predominant species in carbonate and ammonia solutions, respectively. The kinetic data were insufficient to elucidate a rate equation.

Thiocarbonate

Thiocarbonate, {COOS}, rapidly hydrolyzes to {COOO} and SH⁻ (108) with a half-life of 5 min in 5M NaOH at 25° C; the hydrolysis is faster at lower alkalinity.

SUMMARY OF REACTIONS OF FREE CYANIDE AND DERIVED SPECIES

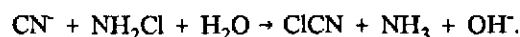
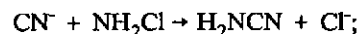
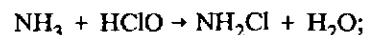
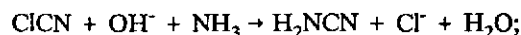
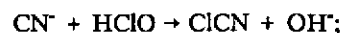
Redox Reactions

The oxidations of {HCN} and derived species by ClO⁻ and O₃ are as a rule very fast, and are complete in seconds to minutes. Oxidations by H₂O₂ are generally slower, and require minutes to hours. Insufficient data were located for oxidations by HOOSO₃⁻, the presumed intermediate in the SO₂-air process. Oxidations by O₂ are usually very slow and require days to years, unless catalysis occurs.

Water Addition and Hydrolysis Reactions

The water addition and hydrolysis reactions of {HCN}, {NCCN}, and ClCN are the most important reactions that

remove these species, besides oxidation reactions. The end products of the water addition and hydrolysis reactions are respectively {HCOO}, {OOCOO}, and {COOO}. These reactions proceed with widely differing pH-dependent rates. A summary of reaction standard Gibbs energy changes and substrate half-lives at pH 11.0 is given in table 7-3. The correlation of standard Gibbs energy change and reaction rate is poor. The most slowly reacting species are {HCN}, {CNNN}, {CONN}, and {CSNN}. The formation of {CNNN}, {CONN}, and {CSNN} would be expected to require the presence of {CNN}, which could form via the oxidation of {HCN} in the presence of NH₃ by ClO⁻/HClO:



As described above, {CNN} reacts with H₂O, NH₃ and H₂S/SH⁻ to form {CONN}, {CNNN} and {CSNN}, respectively. With the oxygen oxidants H₂O₂, O₃, and HOOSO₃⁻, CN⁻ is converted to NCO⁻, and no {CNN} is formed. Reaction of NCO⁻ with NH₃ gives {CONN}, but there are no reactions of NCO⁻ that form {CNNN} or {CSNN}.

Other Reactions

Addition Reactions With Ammonia and Sulfide

Where NH₃ and H₂S/SH⁻ are present in solutions as a result of hydrolysis reactions or reactions of sulfide minerals, addition reactions of {HCN} and derived species with these reactants may occur. The species thus formed hydrolyze at different rates. Sulfur-containing species also undergo oxidation by O₂ or other oxidants. Volatilization of NH₃ and H₂S and oxidation of sulfides compete with addition reactions.

Exchange Reactions

Exchange reactions of nitrogen- and sulfur-containing species with NH₃ and H₂S/SH⁻ are known to occur, but are not likely to be significant at the low concentrations prevailing in process and impounded solutions. Volatilization of NH₃ and H₂S and oxidation of sulfides compete with exchange reactions.

Table 7-3.-Water addition hydrolysis and reactions of free cyanide and derived and related species

Reaction	$\Delta_r G^\circ$, 25° C kJ·mol ⁻¹ substrate	Approximate reactant half-life ¹ at pH 11.0	
		0° C	40° C
$\text{CN}^- + 2\text{H}_2\text{O} \rightarrow \text{H-CO-NH}_2 + \text{OH}^-$	-36	80 years	120 days
$\text{H-CO-NH}_2 + \text{OH}^- \rightarrow \text{HCO}_2^- + \text{NH}_3$	-39	50 days	1.5 days
$\text{H-C}(\text{NH}_2)_2^+ + \text{OH}^- \rightarrow \text{H-CO-NH}_2 + \text{NH}_3$	N	days	hours
$\text{H-CS-NH}_2 + \text{OH}^- \rightarrow \text{H-CO-NH}_2 + \text{SH}^-$	N	days	hours
$\text{NC-CN} + \text{OH}^- \rightarrow \text{NC-CO-NH}^-$	N	3 s	0.10 s
$\text{NC-CN} + 2\text{OH}^- \rightarrow \text{CN}^- + \text{NCO}^- + \text{H}_2\text{O}$	-149	9 s	0.2 s
$\text{NC-CO-NH}^- + \text{OH}^- \rightarrow \text{CN}^- + \text{NCO}^- + \text{H}_2\text{O}$	N	1.1 min	0.3s
$\text{NC-CO-NH}^- + 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{N-CO-CO-NH}_2 + \text{OH}^-$	N	months	days
$\text{H}_2\text{N-CO-CO-NH}_2 + \text{OH}^- \rightarrow \text{H}_2\text{N-CO-CO}_2^- + \text{NH}_3$	-35	2 days	5 h
$\text{H}_2\text{N-CO-CO}_2^- + \text{OH}^- \rightarrow \text{C}_2\text{O}_4^{2-} + \text{NH}_3$	-49	120 days	40 days
$\text{NC-C}(\text{NH}_2)_2^+ + 3\text{OH}^- \rightarrow \text{CN}^- + \text{HNCN}^- + 3\text{H}_2\text{O}$	N	minutes	seconds
$\text{NC-C}(\text{NH}_2)_2^+ + 2\text{OH}^- \rightarrow \text{NC-CO-NH}^- + \text{NH}_3 + \text{H}_2\text{O}$	N	days	hours
$\text{C}_2(\text{NH}_2)_4^{2+} + 2\text{OH}^- \rightarrow \text{H}_2\text{N-CO-CO-NH}_2 + 2\text{NH}_3$	N	days	hours
$\text{NC-CS-NH}^- + \text{OH}^- \rightarrow \text{CN}^- + \text{SCN}^- + \text{H}_2\text{O}$	N	minutes	seconds
$\text{NC-CS-NH}^- + \text{OH}^- \rightarrow \text{NC-CO-NH}^- + \text{SH}^-$	N	days	hours
$\text{H}_2\text{N-CS-CS-NH}_2 + \text{OH}^- \rightarrow \text{H}_2\text{N-CS-CO-NH}_2 + \text{SH}^-$	N	days	hours
$\text{H}_2\text{N-CS-CO-NH}_2 + \text{OH}^- \rightarrow \text{H}_2\text{N-CO-CO-NH}_2 + \text{SH}^-$	N	days	hours
$\text{ClCN} + 2\text{OH}^- \rightarrow \text{NCO}^- + \text{Cl}^- + \text{H}_2\text{O}$	-282	4 h	4 s
$\text{NCO}^- + \text{H}_2\text{O} \rightarrow \text{H}_2\text{N-CO}_2^-$	-44	50 years	70 days
$\text{H}_2\text{N-CO}_2^- + \text{OH}^- \rightarrow \text{CO}_3^{2-} + \text{NH}_3$	-19	minutes	seconds
$\text{HNCN}^- + 2\text{H}_2\text{O} \rightarrow \text{CO}(\text{NH}_2)_2 + \text{OH}^-$	-71	2 years	4 days
$\text{C}(\text{NH}_2)_3^+ + \text{OH}^- \rightarrow \text{CO}(\text{NH}_2)_2 + \text{NH}_3$	-60	150 years	1 year
$\text{CO}(\text{NH}_2)_2 + \text{OH}^- \rightarrow \text{H}_2\text{N-CO}_2^- + \text{NH}_3$	-44	5,000 years	2.5 years
$\text{CS}(\text{NH}_2)_2 + \text{OH}^- \rightarrow \text{CO}(\text{NH}_2)_2 + \text{SH}^-$	-52	1,400 years	22 years
$\text{CS}(\text{NH}_2)_2 + \text{OH}^- \rightarrow \text{NCS}^- + \text{NH}_3 + \text{H}_2\text{O}$	-32	6×10^6 years	1,300 years

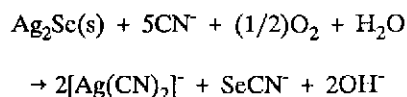
N No data.

¹Entries without numbers are rough estimates obtained from data for analogous reactions.

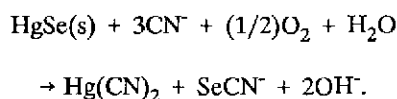
SELENIUM IN CYANIDE PROCESS SOLUTIONS

Selenium occurs in precious metals ores and can be leached by cyanidation. In ores, selenium can exist in minerals that include heavy-metal selenides, metal selenites and selenates, and native selenium. The dissolution of elemental selenium in cyanide solutions to form selenocyanate, (SeCN^-), is well known and parallels the analogous dissolution of elemental sulfur to form SCN^- .

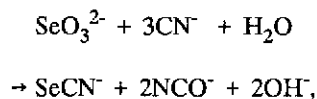
In cyanide leach solutions, heavy-metal selenide minerals can dissolve in the presence of air and form SeCN^- ; the heavy metal can dissolve as cyanide complexes (Zn , Cd , Hg , Cu , Ag , Ni , Co , Fe) or form oxide species (Pb , Sb , Bi). For Ag_2Se and HgSe , the presumed reactions are



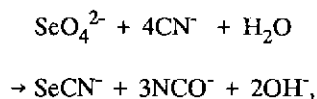
and



The alkaline cyanide solutions can leach selenite and selenate minerals to form dissolved SeO_3^{2-} and SeO_4^{2-} and metal cyanide or oxide species. From thermodynamic data (tables B-1 and C-1), CN^- is predicted to reduce SeO_3^{2-} and SeO_4^{2-} to SeCN^- ,



and



but the rates of these reactions are unknown. Equilibrium predominance area diagrams for selenium alone and in cyanide solutions are given in figures E-7 through E-9; these may be compared with the corresponding diagrams for sulfur in figures E-4 through E-6.

Little is known about the aqueous chemistry of SeCN^- . It forms insoluble salts with some heavy-metal ions and complexes with many metal ions analogous to the corresponding thiocyanate species (89, pp. 342-344). In acid solution, SeCN^- decomposes to selenium and HCN , as shown in figures E-8 and E-9, so SeCN^- may be classified

as a "weak-acid-dissociable" (WAD) cyanide. No information was located concerning oxidation of SeCN^- . As is the case with SCN^- , oxidants may attack the Se atom preferentially, with the formation of selenium oxide species and CN^-/HCN .

CYANIDE DEGRADATION IN INDUSTRIAL PROCESSES

From data on industrial cyanide losses (17-18) and a review of the fate of cyanide in the environment (106), the pathways for loss or degradation of CN^- are

- Volatilization of HCN , e.g., via acidification by atmospheric CO_2 [$\text{CN}^- + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{HCN} + \text{HCO}_3^-$].
- Oxidation to NCO^- , and hydrolysis of NCO^- to CO_3^{2-} and NH_3 or oxidation to N_2 and CO_3^{2-} .
- Oxidation to $\text{H}_2\text{N}_2\text{CN}$ in the presence of NH_3 .
- Reaction with sulfur species to form SCN^- .
- Complexation or precipitation by metals such as iron and copper.
- Hydrolysis to HCO_2^- and NH_3 .
- Adsorption on carbon, clays, soils, or biomass.
- Biodegradation.

Adams (17-18) studied cyanide losses in gold process solutions as a function of the concentration of suspended activated carbon. Data were given for a solution composition typical for carbon adsorption of gold, 0.008M NaCN at a pH of 10.2 and a temperature of 20° C, dosed with 25 g·L⁻¹ of fresh activated carbon. The data are not very consistent, but they indicate that the loss of CN^- from solution after 48 h was distributed approximately as follows:

Oxidized to NCO^-	35 pct
Volatilized as HCN	5 pct
Adsorbed on carbon	25 pct
Hydrolyzed to HCO_2^- and NH_3	0 pct
Total	65 pct

The fate of the other 35 pct of CN^- was not reported. In control experiments without carbon, the total loss of CN^- , which was attributed to volatilization of HCN , was about 5 pct. As described above under cyanide oxidation, activated carbon catalyzes the oxidation of CN^- to NCO^- by O_2 . There was a loss of about 10 pct of the NCO^- , which was assumed to be due to hydrolysis to CO_3^{2-} and NH_3 . The rate data given above for the hydrolysis of NCO^- led to a predicted time for hydrolysis of 10 pct of the NCO^- , which is 1 to 2 powers of 10 longer than that observed by Adams, so catalysis of the hydrolysis of NCO^- by activated carbon is indicated. No formation of HCO_2^- was reported; this is consistent with the rate data described above, which

give a time of roughly 300 days for conversion of 1 pct of CN^- to HCO_2^- .

The engineering details of industrial practice for cyanide destruction and studies of the degradation of CN^- at closed mining and processing sites have been adequately reviewed elsewhere (107-108) and are not discussed further in this publication.

REFERENCES²

1. Jones, R. A. Y. *Physical and Mechanistic Organic Chemistry*. Cambridge Univ. Press, 1979, pp. 62-72.
2. Hammett, L. P. *Physical Organic Chemistry. Reaction Rates, Equilibria, and Mechanisms*. McGraw-Hill, 2nd ed., 1970, pp. 315-342.
3. Bunnett, J. F. *From Kinetic Data to Reaction Mechanism*. Ch. in *Investigation of Rates and Mechanisms of Reactions, Part I*, ed. by C. F. Bernasconi. Wiley, 4th ed., v. VI, 1986, pp. 285-288.
4. Cohen, E. R., and B. N. Taylor. The 1986 CODATA Recommended Values of the Fundamental Physical Constants. *J. Phys. Chem. Ref. Data*, v. 6, 1988, pp. 1795-1803.
5. Schiller, J. E. A New Reaction of Cyanide With Peroxide and Thiosulfate at pH 7-9. *Inorg. Chem.*, v. 26, 1987, pp. 948-950.
6. Knorre, H., and A. Griffiths. Cyanide Detoxification With Hydrogen Peroxide Using the Degussa Process. Paper in *Cyanide and the Environment*, ed. by D. Van Zyl (Proc. Conf., Tucson, AZ, Dec. 11-14, 1984). CO State Univ., Fort Collins, CO, v. 2, 1985, pp. 519-530.
7. Ahsan, W. Q., A. Griffiths, and E. P. Jucevic. Detoxification of Spent Heaps With Hydrogen Peroxide. Ch. in *Gold Forum on Technology and Practices, World Gold '89*, ed. by R. B. Bhappu and R. J. Harden. Soc. Min., Metall., Explor., AIME, 1989, pp. 270-272.
8. Rowley, W. J., and F. D. Otto. Ozonation of Cyanide With Emphasis on Gold Mill Wastewaters. *Can. J. Chem. Eng.*, v. 58, 1980, pp. 646-653.
9. Zeevalkink, J. A., D. C. Visser, P. Arnoldy, and C. Boelhouwer. Mechanism and Kinetics of Cyanide Ozonation in Water. *Water Res.*, v. 14, 1980, pp. 1375-1385.
10. Gurol, M. D., W. M. Bremen, and T. E. Holden. Oxidation of Cyanides in Industrial Wastewater by Ozone. Paper in *Cyanide and the Environment*, ed. by D. Van Zyl, (Proc. Conf., Tucson, AZ, Dec. 11-14, 1984). CO State Univ., Fort Collins, CO, v. 2, 1985, pp. 341-361.
11. _____. Oxidation of Cyanides in Industrial Wastewaters by Ozone. *Environ. Proc.*, v. 4, No. 1, 1985, pp. 46-51.
12. Gurol, M. D., and W. M. Bremen. Kinetics and Mechanism of Ozonation of Free Cyanide Species in Water. *Environ. Sci. Technol.*, v. 19, 1985, pp. 804-809.
13. Gurol, M. D., and T. E. Holden. The Effect of Copper and Iron Complexation on Removal of Cyanide by Ozone. *Ind. Eng. Chem. Res.*, v. 27, 1988, pp. 1157-1162.
14. Lewis, A. New INCO Tech Process Attacks Toxic Cyanides. *Eng. Min. J.*, v. 185, No. 7, 1984, pp. 52-54.
15. Devuyt, E. A., B. R. Conard, G. Robbins, and R. Vergunst. INCO SO_2 -Air Cyanide Removal Process Update. Ch. in *Gold Forum on Technology and Practices, World Gold '89*, ed. by R. B. Bhappu, and R. J. Harden. Soc. Min., Metall., Explor., AIME, 1989, pp. 353-356.
16. Silver, H. G. Chemical Behavior of the Components of the $KCN/KAu(CN)_2$ Electroplating System. *J. Electrochem. Soc.*, v. 115, 1968, pp. 26C-32C.
17. Adams, M. D. The Chemical Behavior of Cyanide in the Extraction of Gold. 1. Kinetics of Cyanide Loss in the Presence and Absence of Activated Carbon. *J. S. Afr. Inst. Min. Metall.*, v. 90, 1990, pp. 37-44.
18. _____. The Chemical Behavior of Cyanide in the Extraction of Gold. 2. Mechanism of Cyanide Loss in the Carbon-in-Pulp Process. *J. S. Afr. Inst. Min. Metall.*, v. 90, 1990, pp. 67-73.
19. Weber, W. J., Jr., and O. Corapcioglu. Catalytic Oxidation of Cyanides. Proc. 36th Waste Conf., 1981, pp. 500-508; *Chem. Abstr.*, v. 96, 1982, No. 186706v.
20. Lister, M. W. Some Observation on Cyanic Acid and Cyanates. *Can. J. Chem.*, v. 33, 1955, pp. 426-440.
21. Jenks, W. R. Cyanides. Ch. in *Kirk-Othmer Encyclopedia of Chemical Technology*. Wiley, 3rd ed., v. 7, 1979, pp. 316-317.
22. Gerritsen, C. M., and D. W. Margerum. Nonmetal Redox Kinetics: Hypochlorite and Hypochlorous Acid Reactions With Cyanide. *Inorg. Chem.*, v. 29, 1990, pp. 2757-2762.
23. Mapstone, G. E., and B. R. Thorn. The Hypochlorite Oxidation of Cyanide and Cyanate. *J. Appl. Chem. Biotechnol.*, v. 28, 1978, pp. 135-143.
24. Brotherton, T. K., and J. W. Lynn. The Synthesis and Chemistry of Cyanogen. *Chem. Rev.*, v. 59, 1959, pp. 841-883.
25. Sharpe, A. G. The Chemistry of Cyano Complexes of the Transition Metals. Academic, 1976, pp. 114, 271.
26. Bartlett, P. D., and R. E. Davis. Reactions of Elemental Sulfur. II. The Reaction of Alkali Cyanides With Sulfur, and Some Single-Sulfur Transfer Reactions. *J. Am. Chem. Soc.*, v. 80, 1958, pp. 2513-2516.
27. Luthy R. G., and S. G. Bruce, Jr. Kinetics of Reaction of Cyanide and Reduced Sulfur Species in Aqueous Solution. *Environ. Sci. Technol.*, v. 13, 1979, pp. 1481-1487.
28. Davis, R. E. Displacement Reactions at the Sulfur Atom. III. The Reaction of Cyanide With Thiosulfate. *J. Phys. Chem.*, v. 66, 1962, pp. 956-957.
29. Wilson, I. R., and G. M. Harris. The Oxidation of Thiocyanate Ion by Hydrogen Peroxide. I. The pH-Independent Reaction. *J. Am. Chem. Soc.*, v. 82, 1960, pp. 4515-4517.
30. _____. The Oxidation of Thiocyanate Ion by Hydrogen Peroxide. II. The Acid-Catalyzed Reaction. *J. Am. Chem. Soc.*, v. 83, 1961, pp. 286-289.
31. Kitching, W., R. H. Smith, and I. R. Wilson. Kinetics of the Decomposition of Sulphur Dicyanide in Aqueous Solution. *Aust. J. Chem.*, v. 15, 1962, pp. 211-217.
32. Kerr, D. F., and I. R. Wilson. Reaction of Sulphur Dicyanide With Thiocyanate Ion. *J. Chem. Soc., Dalton Trans.*, 1973, pp. 459-461.
33. Orban, M. Oscillations and Bistability in the $Cu(II)$ -Catalyzed Reaction Between H_2O_2 and $KSCN$. *J. Am. Chem. Soc.*, v. 108, 1986, pp. 6893-6898.
34. Tenovuo, J., K. M. Pruitt, B. Mansson-Rahemtulla, P. Harrington, and D. C. Baldone. Products of Thiocyanate Peroxidation: Properties and Reaction Mechanisms. *Biochem. et Biophys. Acta*, v. 870, 1986, pp. 377-384.
35. Layne, M. E., P. C. Singer, and M. I. Lidwin. Ozonation of Thiocyanate. Paper in *Cyanide and the Environment*, ed. by D. Van Zyl, (Proc. Conf., Tucson, AZ, Dec. 11-14, 1984). CO State Univ., Fort Collins, CO, v. 2, 1985, pp. 433-455.
36. Radhakrishnamurti, P. S., S. A. Misra, and J. K. Panda. Kinetics and Mechanism of Oxidation of Thiocyanate by Bromate and Chloramine-T in Acid and Alkaline Media. *Indian J. Chem.*, v. 20A, 1981, pp. 459-461.
37. Gauguin, R. Oxidation of Thiocyanate by Iodate. *Anal. Chim. Acta*, v. 3, 1949, pp. 272-276.
38. Balej, J., and J. Vondrak. (Oxidation of Thiocyanates by Peroxydisulfates in Aqueous Solution.) *Collect. Czech. Chem. Commun.*, v. 26, 1961, pp. 1251-1261; *Chem. Abstr.*, v. 55, 1961, No. 15205g.

²A title in parentheses is a translation from the language in which the work was published.

39. Smith, R. H., and I. R. Wilson. The Mechanism of the Oxidation of Thiocyanate Ion by Peroxomonosulphate in Aqueous Solution. II. Kinetics of the Reaction. *Aust. J. Chem.*, v. 19, 1966, pp. 1365-1375.
40. Hughes, M. N., E. D. Phillips, G. Stedman, and P. A. E. Whincup. Oxidation of Metal Thiocyanates by Nitric and Nitrous Acids. Part II. Kinetics. *J. Chem. Soc. A.*, 1969, pp. 1148-1151.
41. Lister, M. W. The Reaction Between Cyanate and Hypochlorite. *Can. J. Chem.*, v. 34, 1956, pp. 489-501.
42. Teo, W. K., and T. C. Tan. Hypochlorite Oxidation of Cyanate Under Mildly Alkaline Conditions. *Water Res.*, v. 21, 1987, pp. 677-682.
43. Oro, J., and A. P. Kimball. Synthesis of Purines Under Possible Primitive Earth Conditions. II. Purine Intermediates From Hydrogen Cyanide. *Arch. Biochem. Biophys.*, v. 96, 1962, pp. 293-313.
44. Sanchez, R. A., J. P. Ferris, and L. E. Orgel. Studies in Prebiotic Synthesis. II. Synthesis of Purine Precursors and Amino Acids From Aqueous Hydrogen Cyanide. *J. Mol. Biol.*, v. 30, 1968, pp. 223-253.
45. Barton, D. B., and W. D. Ollis (eds.). *Comprehensive Organic Chemistry—The Synthesis and Reactions of Organic Compounds*. Pergamon, v. 2, 1979.
46. Patai, S. (ed.). *The Chemistry of Amidines and Imidates*. Wiley-Interscience, 1975, p. 350.
47. Khorkin, A. A., O. N. Temkin, and R. M. Flid. Kinetics of the Acid Hydrolysis of Hydrocyanic Acid. *Russ. J. Phys. Chem. (Engl. Transl.)*, v. 41, 1967, pp. 150-152.
48. Tull, R., and L. M. Weinstock. A New Synthesis of Thioformamide. *Angew. Chem., Int. Ed. Engl.*, v. 8, 1969, pp. 278-279.
49. Barton, D. B., and W. D. Ollis (eds.). *Comprehensive Organic Chemistry—The Synthesis and Reactions of Organic Compounds*. Pergamon, v. 3, 1979.
50. Engler, R., and G. Gattow. Untersuchungen Ueber Thioameisensaure 1. Darstellung und Eigenschaften von Monothioformiaten und Monothioameisensaure (Investigation of Thioformic Acids. 1. Preparation and Properties of Monothioformates and Monothioformic Acid). *Z. Anorg. Allg. Chem.*, v. 388, 1972, pp. 78-88.
51. Patai, S. (ed.). *The Chemistry of Carboxylic Acids and Esters*. Wiley-Interscience, 1969.
52. Peeters, O. M., and C. J. de Ranter. Pathways in Thioacetamide Hydrolysis in Aqueous Acid: Detection by Kinetic Analysis. *J. Chem. Soc., Perkin Trans. II*, 1974, pp. 1832-1835.
53. —. Kinetics of the Hydrolysis of Thioacetamide in Alkaline Solution. *J. Chem. Soc., Perkin Trans. II*, 1976, pp. 1062-1065.
54. Engler, R., G. Gattow, and M. Draeger. Untersuchungen ueber Thioameisensaure. 2. Darstellung und Eigenschaften von Dithioformiaten (Investigation of Thioformic Acids. 1. Preparation and Properties of Dithioformates). *Z. Anorg. Allg. Chem.*, v. 388, 1972, pp. 229-237.
55. Hine, J., R. S. M. King, W. R. Midden, and A. Sinha. Hydrolysis of Formamide at 80° C and pH 1-9. *J. Org. Chem.*, v. 46, 1981, pp. 3186-3189.
56. Salem, I. M., and S. M. Sidahmed. Solvent Effect on the Kinetic Study of the Alkaline Hydrolysis of Formamide in Acetone-Water Mixtures. *J. Chin. Chem. Soc. (Taipei)*, v. 32, 1985, pp. 451-456; *Chem. Abstr.*, v. 106, 1987, No. 66547x.
57. —. The Acid Hydrolysis of Formamide in Water-Acetone Mixtures. *Egypt. J. Chem.*, v. 29, 1986, pp. 521-528; *Chem. Abstr.*, v. 111, 1989, No. 6642t.
58. Cefola, M., S. Peter, P. S. Gentile, and A. V. Celiano. Rate of Hydrolysis of Thiolacetic Acid in Basic Solutions. *Talanta*, v. 9, 1962, pp. 537-542.
59. Hipkin, J., and D. P. N. Satchell. The Spontaneous and Acid-Catalyzed Hydrolysis of Thiolcarboxylic Acids. *Tetrahedron*, v. 21, 1965, pp. 835-842.
60. Sunner, S., and I. Wadsoe. The Heat of Hydrolysis of Thiolacetic acid. *Trans. Faraday Soc.*, v. 53, 1957, pp. 455-459.
61. Welcher, R. P., M. E. Castellion, and V. P. Wystrach. The Preparation and Reactions of 1-Cyanoformamide. *J. Am. Chem. Soc.*, v. 81, 1959, pp. 2541-2547.
62. Wang, Y. L., H. D. Lee, M. W. Beach, and D. W. Margerum. Kinetics of Base Hydrolysis of Cyanogen and 1-Cyanoformamide. *Inorg. Chem.*, v. 26, 1987, pp. 2444-2449.
63. Ito, M. (C-Cyanoformamidine Salts). *Jpn. Pat.* 74 20,182, May 23, 1974, *Chem. Abstr.*, v. 82, 1975, No. 30983h.
64. —. (Oxamidine Phosphate). *Jpn. Pat.* 72 42,819, Oct. 28, 1972, *Chem. Abstr.*, v. 78, 1973, No. 57800a.
65. Woodburn, H. M., B. A. Morehead, and C. M. Chih. The Reaction of Cyanogen With Organic Compounds. II. Primary Aliphatic Amines. *J. Org. Chem.*, v. 15, 1950, pp. 535-540.
66. Woodburn, H. M., and C. E. Sroog. The Reaction of Cyanogen with Organic Compounds. V. Mercaptans. *J. Org. Chem.*, v. 17, 1952, pp. 371-378.
67. Woodburn, H. M., W. Platek, and E. L. Graminski. The Chemistry of Oxamidines. II. Reaction with Hydrogen Sulfide. *J. Org. Chem.*, v. 23, 1958, pp. 319-322.
68. Yoshimura, J., K. Fujimori, Y. Sugiyama, and H. Ando. Syntheses of N-Substituted Carbamimidoylformic Acids. *Bull. Chem. Soc. Jpn.*, v. 44, 1971, pp. 3131-3136.
69. Kibbel, H. U., B. Lampe, S. Schuett, and F. Tesch. Aminocarbonylthioformate—Darstellung und Reactionen (Aminocarbonylthioformates—Preparation and Reactions). *Z. Anorg. Allg. Chem.*, v. 480, 1981, pp. 186-192.
70. Ractz, R., and H. Schroeder. Products From Reaction of Hydrazine and Thiooxamic Acid and Their Conversion Into Heterocyclic Compounds. *J. Org. Chem.*, v. 23, 1958, pp. 1931-1934.
71. Stork, W., and R. Mattes. Alkali Metal Salts of Monothio-, 1,1-Dithio-, and 1,1,2-Trithiooxalic Acid. *Angew. Chem. Int. Ed. Engl.*, v. 14, 1975, pp. 436-437.
72. Reynolds, J. R., F. E. Karasz, C. P. Lillya, and J. C. W. Chien. Electrically Conducting Transition Metal Complexes of Tetrathiooxalate. *J. Chem. Soc., Chem. Commun.*, 1985, pp. 268-269.
73. Packer, J., A. L. Thomson, and J. Vaughan. The Hydrolysis of Amides of Dibasic Acids. Part II. The Acid Hydrolysis of Oxamide and Oxamic Acid. *J. Chem. Soc.*, 1952, pp. 4516-4518.
74. Voortman, U., P. Crooy, and A. Bruylants. Etude Cinetique de l'Hydrolyse des Amides. X. Hydrolyse Acide des Diamides (Kinetic Studies of Amide Hydrolysis. X. Acid Hydrolysis of Diamides). *Bull. Soc. Chim. Belg.*, v. 73, 1964, pp. 241-254.
75. Voortman, U., P. Crooy, A. Bruylants, and C. Baczyński. Etude Cinetique de l'Hydrolyse des Amides. XII. Hydrolyse Alcalin de l'Oxamide, de la Malonamide, de la Fumaramide, et de la Maleamide (Kinetic Studies of Amide Hydrolysis. XII. Alkaline Hydrolysis of Oxamide, Malonamide, Fumaramide, and Maleamide). *Bull. Soc. Chim. Belg.*, v. 73, 1964, pp. 753-767.
76. Pilipenko, A. T., and N. N. Maslei. (The Acid Properties of Dithiooxalic Acid and the Stability in Time of Potassium Dithiooxalate Solutions.) *Ukr. Khim. Zh.*, v. 33, 1967, pp. 831-833; *Chem. Abstr.*, v. 68, 1968, No. 6920n.
77. Price, C. C., T. E. Larson, K. M. Beck, F. C. Harrington, L. C. Smith and I. Stephanoff. Hydrolysis and Chlorinolysis of Cyanogen Chloride. *J. Am. Chem. Soc.*, v. 69, 1947, pp. 1640-1644.
78. Lister, M. W. Some Observations on the Hydrolysis of Cyanogen Chloride. *Can. J. Chem.*, v. 35, 1957, pp. 736-739.
79. Bailey, P. L., and E. Bishop. Hydrolysis of Cyanogen Chloride. *J. Chem. Soc., Dalton Trans.*, 1973, pp. 912-916.
80. Edwards, J. O., T. E. Ersfeld, K. M. Ibne-Rasa, G. Levey, and M. Moyer. Reaction Rates for Nucleophiles With Cyanogen Chloride: Comparison With Two Other Digonal Carbon Compounds. *Int. J. Chem. Kinet.*, v. 18, 1986, pp. 165-180.
81. Griffith, R. O., R. S. Jobin, and A. McKeown. The Kinetics of Reactions of Cyanogen Halides With Bases in Aqueous Solution. *Trans. Faraday Soc.*, v. 34, 1938, pp. 316-325.
82. Golov, V. G., and M. G. Ivanov. (Behavior of Cyanamide in Aqueous Alkaline Solutions). *Tr. Khim. Khim. Tekhnol.*, v. 1, 1968, pp. 86-89; *Chem. Abstr.*, v. 70, 1968, No. 81555e.

83. Eloranta, J. The Hydrolysis of Cyanamide in Dilute Acid Solution. *Suom. Kemistil.*, v. 33B, 1960, pp. 152-155.
84. Mole, B. R., J. P. Murray, and J. G. Tillett. The Acid Hydrolysis of Cyanamide. *J. Chem. Soc.*, 1965, pp. 802-805.
85. Radaelli, L., L. Angeloni, and V. Bruno. (Hydrolysis of Cyanamide to Urea. I. Variations in the Catalytic Activity of Ferric Oxide.) *Ann. Chim. (Rome)*, v. 57, 1967, pp. 855-864; *Chem. Abstr.*, v. 67, 1967, No. 91088g.
86. Radaelli, L., and V. Bruno. (Hydrolysis of Cyanamide to Urea. II. Variations in the Catalytic Activity of Manganese Dioxide.) *Ann. Chim. (Rome)*, v. 57, 1967, pp. 865-872; *Chem. Abstr.*, v. 67, 1967, No. 91089h.
87. Kitaev, G. A., and I. T. Romanov. (Synthesis of Thiourea From Hydrogen Sulfide and Cyanamide.) *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.*, v. 19, 1976, pp. 941-943; *Chem. Abstr.*, v. 85, 1976, No. 93771v.
88. Shaw, W. H. R., and D. G. Walker. The Decomposition of Thiourea in Water Solutions. *J. Am. Chem. Soc.*, v. 78, 1956, pp. 5769-5772.
89. Greenwood, N. N., and A. Earnshaw. *Chemistry of the Elements*. Pergamon, 1984.
90. Hahnkamm, V., and G. Gattow. Untersuchungen Ueber Dithiocarbamidsaeure. 3. Alkalimetalldithiocarbamate $M[SC(S)NH_2]$ (Investigations on Dithiocarbamic Acid 3. Alkali Metal Dithiocarbamates $M[SC(S)NH_2]$). *Z. Anorg. Allg. Chem.*, v. 368, 1969, pp. 127-132.
91. Wronski, M. (Kinetics of Decomposition of Dithiocarbamates in Alkaline Solutions.) *Zesz. Nauki. Uniw. Lodz, Nauky Mat.-Przyr.*, Ser. II, No. 6, 1959, pp. 121-128; *Chem. Abstr.*, v. 55, 1961, 4113b.
92. Gattow, G., and V. Hahnkamm. Untersuchungen Ueber Dithiocarbamidsaeure. 2. Verhalten der Dithiocarbamidsaeure in Waessrigen Loesung (Investigations on Dithiocarbamic Acid. 2. Behavior of Dithiocarbamic Acid in Aqueous Solution). *Z. Anorg. Allg. Chem.*, v. 365, 1969, pp. 70-78.
93. Kemp, I. A., and G. Kohnstam. The Decomposition of Inorganic Cyanates in Water. *J. Chem. Soc.*, 1956, pp. 900-911.
94. Jensen, M. B. On the Kinetics of the Decomposition of Cyanic Acid. *Acta Chem. Scand.*, v. 12, 1958, pp. 1657-1670.
95. Jensen, M. B. On the Kinetics of the Decomposition of Cyanic Acid. II. The Carbonate Catalysis. *Acta Chem. Scand.*, v. 13, 1959, pp. 659-664.
96. Klaeser, K., and G. Gattow. Untersuchungen Ueber Monothiocarbamidsaeure. 1. Darstellung und Eigenschaften von Monothiocarbamaten (Investigations on Monothiocarbamic Acid. 1. Preparation and Properties of Monothiocarbamates). *Z. Anorg. Allg. Chem.*, v. 480, 1981, pp. 122-128.
97. Homer, R. B., and K. W. Alwis. Kinetics and Mechanism of the Alkaline Hydrolysis of Guanidine, Hexamethylguanidium Perchlorate, and Tetramethylurea. *J. Chem. Soc., Perkin Trans. II*, 1976, pp. 781-784.
98. Eloranta, J. The Alkaline Hydrolysis of Guanidine Hydrochloride. *Suo. Kemistil.*, v. 34B, 1961, pp. 107-110.
99. Marcotrigiano, G., G. Peyronel, and R. Battistuzzi. Kinetics of the Desulphuration of ^{35}S -Labelled Thiourea in Sodium Hydroxide Studied by Chromatographic Methods. *J. Chem. Soc., Perkin Trans. II*, 1972, pp. 1539-1541.
100. Ingram, G., and B. A. Toms. The Hydrolysis of Sodium Trithiocarbonate and Its Reaction With Ethanol. *J. Chem. Soc.*, 1957, pp. 4328-4344.
101. Draeger, M., and G. Gattow. Chalcogenocarbonic Acids and Their Anions. *Angew. Chem. Int. Ed. Engl.*, v. 7, 1968, pp. 868-879.
102. Shaw, W. H. R., and J. J. Bordeaux. The Decomposition of Urea in Aqueous Media. *J. Am. Chem. Soc.*, v. 77, 1955, pp. 4729-4733.
103. Lynn, K. R. Kinetics of Base-Catalyzed Hydrolysis of Urea. *J. Phys. Chem.*, v. 69, 1965, pp. 687-689.
104. Christensson, F., H. C. S. Koefoed, A. C. Petersen, and K. Rasmussen. Equilibrium Constants in the Ammonium Carbonate-Carbamate System. The Acid Dissociation Constant of Carbamic Acid. *Acta Chem. Scand.*, v. 32A, 1978, pp. 15-17.
105. Claude, B. Hydrolyse et Thermochemie de Quelques Carbamates (Hydrolysis and Thermochemistry of Some Carbamates). *Rev. Chim. Miner.*, v. 2, 1965, pp. 327-338.
106. Huiatt, J. L., J. E. Kerrigan, F. A. Olson, and G. L. Potter (eds.). *Workshop on Cyanide From Mineral Processing*. *UT Min. Miner. Resour. Res. Inst.*, 1982, pp. 4-1 to 4-20.
107. Ritcey, G. M. *Tailings Management—Problems and Solutions in the Mining Industry*. Elsevier, 1979, pp. 604-649.
108. Smith, A., and T. Mudder. *The Chemistry and Treatment of Cyanidation Wastes*. Mining Journal Books, London, 1991, 345 pp.

CHAPTER 8.—REACTIONS OF METAL CYANIDE SPECIES

INTRODUCTION

The role of the cyanide chemistry of precious metals and associated accessory elements in the operation and closure of precious metals mines is the heart of this publication. The precious metals and accessory elements differ greatly in the formation and reactions of cyanide species, and this complicates the environmental fate and toxicity of cyanide. Chemical data on the formation and reactions of metal cyanide species are therefore critical to understanding and managing the environmental fate of cyanides.

This chapter discusses the chemistry of the metal cyanide complexes pertinent to mining, processing, and closure operations. Modern nomenclature, which is described in chapter 2, is used throughout. Much of the information is derived from a monograph by Sharpe (1),¹ or from thermodynamic data (2-4) that are detailed in appendix D. Additional information was obtained from primary sources as specified below.

The metals Zn, Cd, Hg, Cu, Ag, Au, Ni, Co, Fe, Mn, Cr, V, and Ti are discussed individually in the sections below after an initial overview. The subject of mixtures of metals in cyanide solutions is treated in chapter 10. The cyanides of the remaining elements are surveyed in chapter 3. All six platinum-group metals and Mo, W, and Re also form strong cyanide complexes (1). These are not discussed here because the reactions involved are slow and complex, few thermodynamic or kinetic data are available, and these metals are rarely reported in precious metals cyanide leaching operations.

The discussion in this chapter is limited to thermal, i.e., nonphotochemical, reactions. Photochemical reactions are discussed in chapter 9. As seen in the subsequent discussion, there is not much literature on the oxidative destruction of metal cyanide species.

OVERVIEW AND CLASSIFICATION OF METAL CYANIDE SPECIES

In terms of equilibrium constants for their formation, many metal cyanide complexes are stronger than metal complexes with most other ligands, even ethylenediaminetetraacetate ($H_4\text{edta}$) and related reagents (2-4). Some pertinent data are shown in table 8-1, which gives the formation constants for dissolved metal complexes with CN^- , OH^- , $(\text{edta})^{4-}$, and $(\text{nta})^{3-}$ (nitrilotriacetate), and solid metal sulfides and oxide compounds. Calculations with the data in table 8-1 show that most metal oxide compounds and even some metal sulfides are soluble in alkali-metal cyanide solutions.

The reactions of the metal cyanide species with acids are of major importance. Metal cyanide species differ widely in their reactivity with acids to liberate HCN. As outlined in chapter 2, metals have been classified with respect to the reactivity of their cyanide complexes with acids as "weak-acid-dissociable" (WAD) or "non-weak-acid-dissociable" (non-WAD). As noted, this classification is oversimplified, and some metals are more accurately classified as "partially WAD." The details of the reactions of metal cyanide species with acids are described below and subsequently summarized.

Also of major importance are the reactions of metal cyanide species with oxidants, e.g., hypochlorite (ClO^-), hydrogen peroxide (H_2O_2), and ozone (O_3). This oxidation chemistry is likewise discussed in the following sections and subsequently summarized.

Finally, two more sections discuss removal of metals from cyanide solutions by cementation and consider the complexing of metals by other ligands in the absence of sufficient CN^- .

ZINC, CADMIUM, AND MERCURY

Reactions involving the cyanide complexes of Zn, Cd, and Hg are nearly all fast. The water solubilities of the binary cyanides $\text{M}(\text{CN})_2$ with $\text{M} = \text{Zn, Cd, or Hg}$, are 3×10^{-5} , 0.1, and 0.4M, respectively, at 25° C. In solutions 0.01M in free CN^- , typical of precious metals leaching conditions, Zn, Cd, and Hg each exist as their soluble tetracyanommetallates $[\text{M}(\text{CN})_4]^{2-}$. Acids totally and rapidly decompose the zinc and cadmium cyanide complexes to liberate HCN. Anionic $\text{Hg}(\text{II})$ cyanide complexes are decomposed by acid to soluble $\text{Hg}(\text{CN})_2$, which is thermodynamically so stable that its decomposition by acid requires the presence of a strong ligand, precipitant, or oxidant, e.g., I^- , H_2S , or Cl_2 . Soluble sulfides convert all of the Zn, Cd, and Hg cyanide complexes to the insoluble metal sulfides at all pH values with liberation of free CN^-/HCN .

Reaction of $\text{Hg}(\text{I})$ compounds with CN^- results in disproportionation to metallic mercury and $\text{Hg}(\text{II})$ cyanide complexes.

Mercury (II) cyanide forms complexes with other metal cyanide complexes, e.g., the hexacyanoferrates (II) and (III), $[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{Fe}(\text{CN})_6]^{3-}$. The log K (rate constant) values for the 1:1 complexes with the hexacyanoferrates are both about 2 (5).

Stable $\text{Hg}(\text{II})$ species with both CN^- and O^{2-} , OH^- , Cl^- , and SCN^- (thiocyanate) are known; data are compiled in table D-5. The cyanide oxide $\text{Hg}_2\text{O}(\text{CN})_2$ is less soluble in water, $4 \times 10^{-3}\text{M}$ at 25° C, than $\text{Hg}(\text{CN})_2$. Mercury(II) cyanide forms complexes with other heavy-metal salts, in which it functions like an organic nitrile.

¹Italic numbers in parentheses refer to items in the list of references at the end of this chapter.

Table 8-1.—Comparison of stability constants of metal complexes with cyanide and other ligands

M^{q+}	$M(CN)_n^{q-n}$		M oxide		$MS_{q/2}$, $\log K^1$	$M(edta)^{q-4}$, $\log K^2$	$M(nta)_2^{q-6}$, $\log K^2$
	n	Log K	Formula	Log K			
Zn(II)	4	19.6	ZnO	16.7	25.4	16.5	14.2
Cd(II)	4	17.9	Cd(OH) ₂	14.4	28.1	16.5	14.4
Hg(II)	4	39.0	HgO	25.4	53.2	21.5	³ 14.3
Cu(I)	3	27.0	CuO _{0.5}	14.7	23.6	N	N
Ag(I)	2	20.5	AgO _{0.5}	7.7	25.0	7.2	³ 5.4
Cu(II)	4	22.6	CuO	20.4	37.4	18.8	17.5
Ni(II)	4	30.2	Ni(OH) ₂	17.2	24.1	18.4	16.3
Co(II)	5	23.	Co(OH) ₂	15.7	23.2	16.4	14.3
Fe(II)	6	35.4	Fe(OH) ₂	15.2	17.7	14.3	12.8
Mn(II)	6	10.	Mn(OH) ₂	12.8	14.0	13.9	10.9
Co(III)	6	73.	CoO(OH)	48.5	X	41.4	N
Fe(III)	6	42.3	FeO(OH)	41.7	X	25.1	24.3
Mn(III)	6	35.	MnO(OH)	42.2	X	25.3	N
Cr(III)	6	33.	CrO _{1.5} · xH ₂ O	32.	14.6	23.4	N

N No data.

X Compound does not exist.

¹Reaction $M^{q+} + (q/2)SH^- + (q/2)OH^- \rightarrow MS_{q/2} + (q/2)H_2O$.

²Ionic strength 0.1M.

³1:1 complex.

Note.—Data for cyanides, sulfides, and oxides are from appendix D; data for other ligands are from Martell and Smith (2-4); edta = ethylenediamine tetraacetate; nta = nitrilotriacetate. Values are at 25° C and zero ionic strength unless stated otherwise.

Most of the foregoing information in this section is illustrated in the equilibrium predominance area diagrams (EPAD) in figures E-10 through E-74 in appendix E.

Zinc and cadmium cyanide complexes are decomposed via hydrolysis of CN⁻ to metal hydroxides, ammonia (NH₃), and formate (HCO₂⁻) at 150° to 200° C (6-7). They undergo oxidative destruction by ClO⁻ (8-9; 10, p. 204), H₂O₂ in the presence of copper catalyst (10, p. 239), SO₂/air in the presence of copper catalyst (10, pp. 303-304), O₃ (11-12), or ClO₂ (13) to metal oxide products and cyanate (NCO⁻). Detailed systematic kinetics studies of these reactions have not been published. No literature on the oxidative destruction of mercury cyanide complexes was located. Cyanide complexes of mercury have been treated with metallic copper to cement mercury, and the resulting copper cyanide solution has been oxidized with H₂O₂ (16).

COPPER, SILVER, AND GOLD

Reactions involving the cyanide complexes of Cu, Ag, and Au in the 1+ oxidation state are usually fast. The binary cyanides, MCN with M = Cu, Ag, or Au, are all very insoluble in water. In solutions 0.01M in free CN⁻ under precious metals leaching conditions, Cu, Ag, and Au exist only in the 1+ oxidation state and form the soluble complexes [Cu(CN)₃]²⁻, [Ag(CN)₂]⁻, and [Au(CN)₂]⁻, respectively. The [Cu(CN)₂]⁻ complex predominates only at free CN⁻ concentrations below about 10⁻⁵M. At free CN⁻ concentrations above 0.01M to 0.1M, [Cu(CN)₄]³⁻, [Ag(CN)₃]²⁻, and [Ag(CN)₄]³⁻ predominate. The anionic cyanide complexes of copper and silver are rapidly decomposed by acids to the insoluble binary cyanides. For gold, this reaction is incomplete (15). Decomposition of

the binary cyanides MCN by acids requires a strong complexing or oxidizing agent, e.g., I or Cl₂. Soluble sulfides precipitate silver sulfide (Ag₂S) from solutions of its anionic cyanide complexes but do not react with the anionic Cu(I) or Au(I) cyanide complexes. However, H₂S reacts with Cu(I) cyanides to form copper sulfide (Cu₂S) and hydrogen cyanide (HCN) at pH below 8.

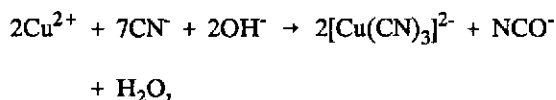
Few stable complexes containing both CN⁻ and other inorganic ligands appear to exist for Cu(I) or Ag(I). The species [Ag(OH)(CN)]⁻ exists in alkaline solutions (see appendix D). Complexes of Cu(I), Ag(I), and Au(I) with both CN⁻ and S₂O₃²⁻ (thiosulfate) have been reported (16). The extent to which Au(I) forms complexes such as Au(CN)L, where L is a different inorganic ligand, has been little investigated. Only the iodocyanaurate(I), [Au(CN)I]⁻ was reported recently (17). However, judging by the log K data for this species and data for similar Hg(II) species (table D-5), species such as [Au(CN)Cl]⁻ and [Au(CN)(SCN)]⁻ may exist in solutions depleted of CN⁻.

Most of the foregoing information in this section is illustrated in the EPAD in figures E-75 through E-94 and E-101 through E-140.

Copper(II) cyanide complexes are unstable with respect to reduction of Cu(II). Cyanide rapidly reduces Cu(II) to Cu(I), and is itself oxidized to cyanogen (C₂N₂ in acid solution or to NCO⁻ in basic solution. When Cu(II) is added to excess alkaline cyanide solution, the violet [Cu(CN)₄]²⁻ forms transiently (18-19). For the reaction



log K = +15.5 at 25° C. For the reaction



log K = +93.4 at 25° C. The log K values for these reactions are so large that there is no known complexing agent for Cu(II) that will prevent the reduction of Cu(II) by CN⁻ (2-4); see tables 8-1, D-6, and D-7. However, CuCN and solutions of Cu(I) cyanide complexes with mole ratio CN⁻ to Cu(I) < 3 in the presence of NH₃ or organic amines undergo slow oxidation by atmospheric O₂ to form ternary complexes that are polymeric cyanocuprate(I) salts of Cu(II) complexes with NH₃ or organic amine (1, 20). The complex [Cu(edta)]²⁻ reacts with CN⁻ to form [Cu(edta)(CN)]³⁻ with a log K value of about +4 (21). However, this complex undergoes significant decomposition during 1 day. Although Cu(II) is readily reduced by free CN⁻, reduction by complexed CN⁻ in [Cu(CN)₃]²⁻ or [Cu(CN)₃]²⁻ appears to be slow.

Reactions of Au(III) complexes are generally slow. The colorless tetracyanoaurate(III), [Au(CN)₄]⁻, can be formed by reaction of Au(III) compounds with CN⁻. It is not decomposed by acids; the solid acid H[Au(CN)₄]·xH₂O can be isolated. Gold(III) complexes with both CN⁻ and other ligands, e.g., [Au(CN)₂Cl]⁻. Data for such species are compiled in table D-10. The [Au(CN)₄]⁻ species is reported to form by anodic oxidation in cyanide gold-plating baths, but has not been reported to form during gold leaching. It can be reduced to [Au(CN)₂]⁻ by N₂H₄ (22).

The cyanide complexes of copper are decomposed via hydrolysis of the CN⁻ to copper oxides, NH₃, and HCO₂⁻ at 150° to 200° C (6). They undergo oxidative destruction by ClO⁻ (8-9; 10, p. 204), H₂O₂ (10, p. 239), SO₂/air (10, pp. 303-304), O₃ (12-13, 23), or ClO₂ (chlorine dioxide) (13), to metal oxide products and NCO⁻. Detailed systematic kinetics studies of these reactions have not been published. Oxygen is reported to oxidize Cu(I) cyanide complexes in the presence of activated carbon (24).

Silver cyanide complexes are incompletely destroyed by ClO⁻ (8-9) but are reported to be completely destroyed by O₃ (11). No information on the oxidation of silver cyanide species by H₂O₂ or SO₂/air was located. Reaction of silver cyanide complexes with metallic copper to cement silver, followed by H₂O₂ oxidation of the copper cyanide species was reported (14).

Gold cyanide complexes are reported to precipitate AuCN on reaction with O₃ (11). No data were located regarding the reactions of gold cyanide species with other oxidants.

NICKEL

Reactions of Ni(II) complexes are usually fast. The only important nickel species in dilute cyanide solutions is the orange-yellow tetracyanonickelate(II), [Ni(CN)₄]²⁻. The kinetics of formation of [Ni(CN)₄]²⁻ from Ni²⁺ and CN⁻, and the total decomposition of [Ni(CN)₄]²⁻ by acid with liberation of HCN, both of which are rapid, have been studied (25-28). Researchers studying the latter (25-26) inferred the formation of protonated species, e.g., [HNi(CN)₄]⁻, but in a subsequent reinvestigation, the data were interpreted without formation of protonated species (27). The acid H₂[Ni(CN)₄] is not isolable and is probably strong, i.e., completely dissociated. Intermediate species such as [Ni(CN)₃]⁻ are evidently not stable and disproportionate to Ni²⁺ and [Ni(CN)₄]²⁻.

In solutions with free CN⁻ exceeding 1M, [Ni(CN)₄]²⁻ is incompletely converted to orange-red pentacyanonickelate(II), [Ni(CN)₅]³⁻.

Examples of relatively slow reactions of Ni(II) are the reactions of CN⁻ with Ni(II) complexes of polyamines, e.g., triethylenetetramine, or aminopolycarboxylates, e.g., edta.

The reverse reactions of $[\text{Ni}(\text{CN})_4]^{2-}$ with such ligands, which occur in nearly neutral solutions, are also slow.

The addition of soluble sulfides to $[\text{Ni}(\text{CN})_4]^{2-}$ solutions does not precipitate NiS.

Most of the foregoing information in this section is illustrated in the EPAD in figures E-141 through E-162.

Cyanide complexes of Ni(I) and Ni(0) are known, but their preparation requires strongly reducing conditions, and they are very readily oxidized. Thus, they are not expected to occur in hydrometallurgical processes.

Nickel(III) cyanide complexes are reported to occur as unstable intermediates in the oxidation of $[\text{Ni}(\text{CN})_4]^{2-}$ by Cl_2 or HClO (29).

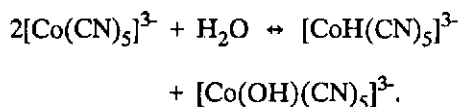
Tetracyanonickelate(II) decomposes via hydrolysis of the CN^- to $\text{Ni}(\text{OH})_2$, NH_3 , and HCO_2^- at 150° to 200°C (6,30-31). It is also oxidized by ClO^- (9; 10, p. 204), H_2O_2 in the presence of copper catalyst (10, p. 239), SO_2/air in the presence of copper catalyst (10, pp. 303-304), or O_3 (11-12, 23), but not by ClO_2 (13). The reaction with ClO^- is slower than the corresponding reactions with the zinc and cadmium cyanide complexes. The reaction of $[\text{Ni}(\text{CN})_4]^{2-}$ with O_3 is reported to be fast. Detailed systematic kinetics studies of these reactions have not been published.

Recently, a reaction of $[\text{Ni}(\text{CN})_4]^{2-}$ in a polysulfide solution to form a Ni(II) polysulfide complex, $[\text{Ni}(\text{S}_4)_2]^{2-}$, was reported (32). The reaction occurred in minutes at room temperature. The fate of the CN^- was not stated, but presumably the CN^- was converted to SCN^- .

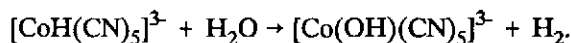
COBALT

Reactions of Co(II) complexes are usually fast; reactions of Co(III) complexes are usually slow. The cyanide chemistry of cobalt is unusual in that Co(II) cyanide complexes are very easily oxidized to Co(III) cyanide complexes, so that in mining and metallurgical situations, cobalt minerals leached by cyanide solutions will be rapidly oxidized by air to Co(III).

Reaction of Co^{2+} with CN^- in the absence of oxygen gives olive-green pentacyanocobaltate(II), $[\text{Co}(\text{CN})_5]^{3-}$, which is in equilibrium with a violet dimer $[\text{Co}_2(\text{CN})_{10}]^{6-}$. This complex reacts with H_2O to give an equilibrium involving the colorless hydridopentacyanocobaltate(III), $[\text{CoH}(\text{CN})_5]^{3-}$, and the yellow hydroxopentacyanocobaltate(III), $[\text{Co}(\text{OH})(\text{CN})_5]^{3-}$:



The hydrido complex is readily oxidized by O_2 . It also reacts slowly with water:



Pentacyanocobaltate(II) also reacts rapidly with O_2 to form the intermediate superoxopentacyanocobaltate(III) $[\text{Co}(\text{CN})_5(\text{O}_2)]^{3-}$, which hydrolyzes to $[\text{Co}(\text{OH})(\text{CN})_5]^{3-}$ or forms hexacyanocobaltate(III), $[\text{Co}(\text{CN})_6]^{3-}$ if free CN^- is present. Pentacyanocobaltate(II) is rapidly and completely decomposed by acids, with liberation of HCN (33).

The pale yellow hexacyanocobaltate(III) is a very inert species; the free acid $\text{H}_3[\text{Co}(\text{CN})_6]$ is stable and isolable as a soluble solid. The only known means of decomposition of $[\text{Co}(\text{CN})_6]^{3-}$ in aqueous solution is by photochemistry, which is described in chapter 9.

The chemistry of the yellow $[\text{Co}(\text{OH})(\text{CN})_5]^{3-}$ and $[\text{Co}(\text{H}_2\text{O})(\text{CN})_5]^{2-}$ derived by protonation (pH below 9) has not been adequately investigated. There is evidence that these complexes slowly polymerize at moderate concentrations, perhaps in a way similar to that of the corresponding ion complexes (see below). Aquopentacyanocobaltate(III) undergoes substitution of the water by CN^- , Cl^- , NH_3 , NCS^- , or other species, and the kinetics of many of these reactions have been determined (34-37). Data are presented in table 8-2. These reactions are catalyzed by $[\text{Co}(\text{CN})_5]^{3-}$, the presence of which requires the absence of O_2 .

Tetracyano and tricyano complexes of Co(III) have been obtained photochemically (38-39) (see chapter 9). These species polymerize to unidentified products unless their concentrations are below $10^{-3}M$.

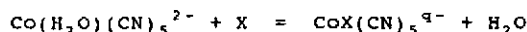
Hexacyanocobaltate(III) is not destroyed by ClO^- (10, p.204), O_3 (11-12) or ClO_2 (13). The only known routes to destruction of Co(III) cyanide species are photochemical reactions, which are discussed in chapter 9.

IRON

Although the reactions of most Fe(II) and Fe(III) complexes are fast, the reactions of Fe(II) and Fe(III) cyanide complexes are usually slow. The light-yellow hexacyanoferrate(II) (ferrocyanide), $[\text{Fe}(\text{CN})_6]^{4-}$, and deep yellow to red-orange hexacyanoferrate(III) (ferricyanide), $[\text{Fe}(\text{CN})_6]^{3-}$, are among the best known of all metal cyanide complexes. They are both thermodynamically unstable with respect to decomposition by acids; however the rates of decomposition by acid are so slow that the free acids $\text{H}_4[\text{Fe}(\text{CN})_6]$ and $\text{H}_3[\text{Fe}(\text{CN})_6]$ are isolable as soluble solids.

Table 8-2.-Substitution reactions of pentacyanocobaltates(III)

(All data at 40° C and ionic strength 1.0M)



$$\text{Forward rate: } -d[\text{Co}(\text{H}_2\text{O})(\text{CN})_5^{2-}]/dt = k_f[\text{Co}(\text{H}_2\text{O})(\text{CN})_5^{2-}][\text{X}]$$

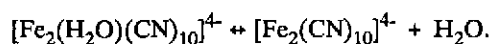
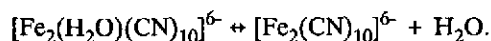
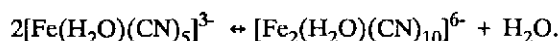
$$\text{Reverse rate: } -d[\text{CoX}(\text{CN})_5^{q-}]/dt = k_r[\text{CoX}(\text{CN})_5^{q-}]$$

X	$k_f, \text{M}^{-1} \text{s}^{-1}$	k_r, s^{-1}	References
CN ⁻	1.2×10^{-4}	N	34
Cl	5.5×10^{-4}	4.5×10^{-4}	36
NH ₃	2.1×10^{-4}	N	37
NCS ⁻	6.3×10^{-4}	3.7×10^{-7}	34-35

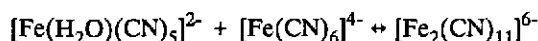
N No data.

Reaction of iron salts with CN⁻ in aqueous solution cannot be stopped at any intermediate soluble complexes; the hexacyanoferrates are always formed. The reaction of Fe(II) salts with CN⁻ to form [Fe(CN)₆]⁴⁻ is rapid, and [Fe(CN)₆]⁴⁻ can be oxidized to [Fe(CN)₆]³⁻ at a rate which depends on pH and the oxidant used. The reaction of Fe(III) salts with CN⁻ does not as readily form [Fe(CN)₆]³⁻ because hydrous Fe(III) oxide forms first because of the high pH. The hydrous Fe(III) oxide reacts slowly with CN⁻ to form [Fe(CN)₆]⁴⁻ as well as [Fe(CN)₆]³⁻, because CN⁻ slowly reduces the Fe(III) species. From thermodynamic data, reaction of Fe(III) salts with CN⁻ in acid solution should yield Fe(II) and C₂N₂, but this reaction seems not to have been documented.

The yellow, hydroxypentacyanoferrates and aquopentacyanoferrates, [Fe(OH)(CN)₅]³⁻, [Fe(H₂O)(CN)₅]³⁻, and [Fe(H₂O)(CN)₅]²⁻, are obtainable only by photochemistry so far as is known (see chapter 9). The complexes [Fe(H₂O)(CN)₅]³⁻ and [Fe(H₂O)(CN)₅]²⁻ are deprotonated to the respective hydroxo complexes above pH about 14 and pH about 9, respectively. These complexes exist in slow equilibria via condensation reactions to form the aquodecacyanodiferrates and decacyanodiferrates:



They also react with the hexacyanoferrates to form the undecacyanoferrates; e.g.,

+ H₂O.

Most of the dinuclear complexes, namely with two Fe(II), one Fe(II) and one Fe(III), or two Fe(III), are known. However, characterization of their solution chemistry has not been sufficiently elucidated, and spectroscopic data from different authors disagree (see chapter 5). The oxodecacyanodiferrates, [Fe₂O(CN)₁₀]⁴⁻, may also exist, in analogy with a manganese analog mentioned below.

Published equilibrium data for the dinuclear iron cyanide species disagree (40-45); for this reason the dinuclear species were not included in the thermodynamic data in appendix D. Figures 8-1 and 8-2 summarize the relationships among the iron cyanide species. Rough but self-consistent values of pertinent equilibrium constants and reduction potentials are given in figures 8-1 and 8-2. Despite the limited accuracy of the data, it may be concluded that the pentacyanoferrate species and their condensation products are all unstable with respect to redistribution to hexacyanoferrates and iron cyanide precipitates. Consequently, they would not appear on EPAD and figures E-165, E-167, and E-168 represent true equilibrium conditions.

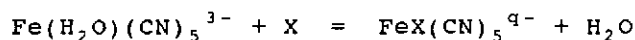
The aquopentacyanoferrates undergo substitution of H₂O by other reagents, e.g., CN⁻, NH₃, SO₃²⁻; the kinetics of several such reactions have been studied (42, 46-54). Some data for [Fe(H₂O)(CN)₅]³⁻ are compiled in table 8-3. Similar reactions of [Fe(H₂O)(CN)₅]²⁻ are much slower and subject to catalysis by [Fe(H₂O)(CN)₅]³⁻ (48, 50, 54); this fact was not realized in earlier work (46).

A few substitution or addition reactions of dinuclear iron cyanide species with reagents of no metallurgical interest have been studied (41, 43, 55).

The aquopentacyanoferrates both decompose to the respective hexacyanoferrates and cationic iron species, which cause precipitates to form (56-57).

Table 8-3.--Substitution reactions of pentacyanoferrates(II)

(All data at 25° C and ionic strength 1.0M)

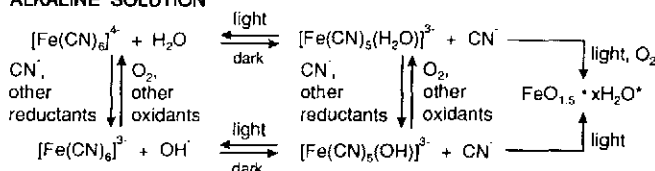
Forward rate: $-\text{d}[\text{Fe}(\text{H}_2\text{O})(\text{CN})_5^{3-}]/\text{dt} = k_f[\text{Fe}(\text{H}_2\text{O})(\text{CN})_5^{3-}][\text{X}]$ Reverse rate: $-\text{d}[\text{FeX}(\text{CN})_5^{q-}]/\text{dt} = k_r[\text{FeX}(\text{CN})_5^{q-}]$

X	$k_f, \text{M}^{-1} \text{s}^{-1}$	k_r, s^{-1}	References
CN^-	1.5	$3. \times 10^{-8}$	53
NH_3	1.9×10^2	1.8×10^{-2}	47-48, 51-52
SO_3^{2-}	3.3	1.3×10^{-3}	42, 49

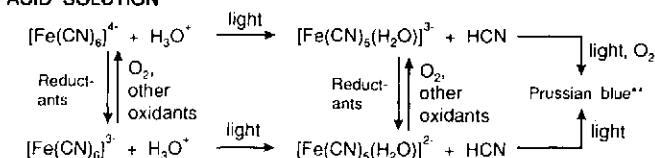
¹ Ionic strength 0.015M.

Figure 8-1

ALKALINE SOLUTION

* + $\text{CN}^-, \text{NCO}^-$ (? via Fe(III) species, O_2 ?)

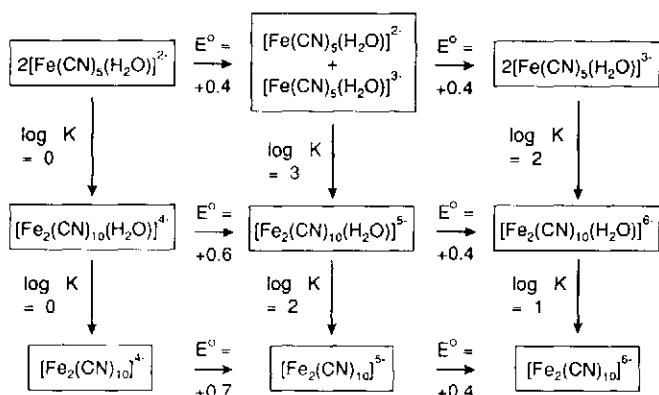
ACID SOLUTION



** + $\text{HCN}, \text{C}_2\text{N}_2$ (? via Fe(III) species; hydrolyzes?),
 NCO^- (? via Fe(III) species, $\rightarrow \text{CO}_2 + \text{NH}_4^+$)

Formation of aquodecacyanoferrate and decacyanoferrate species.

Figure 8-2



Formation of undecacyanoferrate species.

Oxidation of $[\text{Fe}(\text{CN})_6]^{4-}$ to $[\text{Fe}(\text{CN})_6]^{3-}$ by HClO (58), ClO_2^- (59), H_2O_2 (60), and O_2 (61) has recently been studied. Hydrogen peroxide reduces $[\text{Fe}(\text{CN})_6]^{3-}$ to $[\text{Fe}(\text{CN})_6]^{4-}$ in basic solution, but oxidizes $[\text{Fe}(\text{CN})_6]^{4-}$ to $[\text{Fe}(\text{CN})_6]^{3-}$ in acid solution. The oxidation of $[\text{Fe}(\text{H}_2\text{O})(\text{CN})_5]^{2+}$ to $[\text{Fe}(\text{H}_2\text{O})(\text{CN})_5]^{3+}$ by H_2O_2 (62) and O_2 (63) has been studied. The reaction with O_2 is catalyzed by Fe^{2+} .

Free cyanide reduces $[\text{Fe}(\text{CN})_6]^{3-}$ to $[\text{Fe}(\text{CN})_6]^{4-}$ slowly; the reaction is strongly catalyzed by copper and has a complex mechanism (64-65).

The hexacyanoferrates decompose to iron oxides, NH_3 , and HCO_2^- (CN^- hydrolysis) at 150-200° C (6). Destructive oxidation by ClO^- (10, p. 204), O_3 (11-12), or ClO_2 (13) is nonexistent or slow in the absence of ultraviolet irradiation. It is reported that BrO^- destructively oxidizes $[\text{Fe}(\text{CN})_6]^{3-}$ at 75° C; ClO^- is much less effective (66). Effective destruction of iron cyanide species requires photochemical reactions; these are discussed in chapter 9.

Much of the published kinetic, equilibrium, and spectroscopic data for iron cyanide complexes, especially the aquopentacyano and dinuclear complexes, contain conflicting results. These have been attributed to failure to allow for the condensation reactions (40, 56, 67-68), failure to protect against oxidation by O_2 (56, 63, 67) catalysis effects (48, 50, 63), unstable or impure reagents (40-41, 51, 68), spectrophotometric observations limited to only one wavelength (69), and failure to protect against photochemical reactions (60, 67, 69).

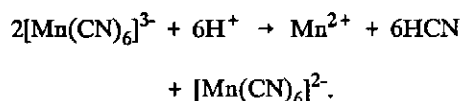
MANGANESE

The chemistry of cyanide complexes of manganese, especially in aqueous solution, has not been adequately characterized. Reactions of Mn(II) complexes are generally fast. Some of the solid salts of hexacyanomanganate(II), $[\text{Mn}(\text{CN})_6]^{4-}$, are blue to violet, but whether this

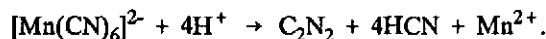
species exists in solutions of Mn^{2+} and CN^- has not been definitively demonstrated. Manganese(II) cyanide complexes are totally and rapidly decomposed by acids with liberation of HCN , therefore they fall in the WAD classification.

Solutions of Mn^{2+} and CN^- are oxidizable, e.g., by O_2 , to Mn(III) cyanide complexes. Potassium hexacyanomanganate(III), $\text{K}_3[\text{Mn}(\text{CN})_6]$, is a well-known red salt; its dilute aqueous solution decomposes, precipitating hydrous manganese oxides. Hydroxocyanomanganates or oxocyanomanganates exist; reddish-brown oxodecacyanodimanganate(III), $[\text{Mn}_2\text{O}(\text{CN})_{10}]^{6-}$ has been characterized in the solid state. Published data on the solution chemistry of manganese cyanide complexes are contradictory and show that the system is complex, with hydrolysis and disproportionation reactions occurring (70-77). A dinuclear complex, presumably $[\text{Mn}_2\text{O}(\text{CN})_{10}]^{6-}$, was reported to be oxidizable in two one-electron steps to Mn(III)Mn(IV) and Mn(IV)₂ species; the oxidized species undergo reduction by CN^- to the Mn(III)₂ species (75).

Addition of acid (pH 0 to 1) to solutions of $[\text{Mn}(\text{CN})_6]^{3-}$ results in decomposition in minutes to Mn^{2+} , HCN , and the unstable hexacyanomanganate(IV), $[\text{Mn}(\text{CN})_6]^{2-}$ (76-77).



At pH 0 to 1, $[\text{Mn}(\text{CN})_6]^{2-}$ decomposes in hours to C_2N_2 , HCN , and Mn^{2+} (79):



The reaction is catalyzed by product Mn^{2+} . At higher pH values, $[\text{Mn}(\text{CN})_6]^{3-}$ and $[\text{Mn}(\text{CN})_6]^{2-}$ hydrolyze to manganese oxides. Accordingly, the Mn(III) and Mn(IV) cyanide complexes may be classified as WAD.

In solution, MnO_4^- is rapidly reduced by CN^- to form manganese cyanide complexes.

The oxidation of cyanomanganates to MnO_2 and NCO^- by O_2 has not been demonstrated. Considering that MnO_2 is thermodynamically capable of oxidizing CN^- , manganese oxides may possibly catalyze the oxidation of CN^- by O_2 . As noted above, the Mn(IV)-containing dinuclear cyanide complexes oxidize CN^- (75). No literature was located that specifically addressed oxidative destruction of manganese cyanide complexes.

CHROMIUM

Reactions of Cr(III) complexes are usually slow. Chromium(III) cyanide complexes are formed along with

hydrous Cr_2O_3 when Cr(III) salts react with CN^- . The yellow hexacyanochromate(III), $[\text{Cr}(\text{CN})_6]^{3-}$, is decomposed to hydrous Cr_2O_3 in hot solutions. It is decomposed completely by acids with liberation of HCN , but at a rate slow enough to permit characterization of the intermediate aquocyno or hydroxocyno complexes (78). Accordingly, Cr(III) cyanide species may be classified as WAD, but complete decomposition requires days at 25° C and pH 2 (78-79). These reactions are catalyzed by Cr(II), which requires the absence of O_2 (80).

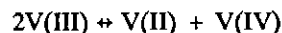
Chromium(II) cyanide complexes, e.g. hexacyanochromate(II), $[\text{Cr}(\text{CN})_6]^{4-}$, exist only under strongly reducing conditions in the absence of O_2 (81).

A Cr(IV) peroxocyno complex, $[\text{Cr}(\text{O}_2)_2(\text{CN})_3]^{3-}$, is known in the solid state, but practically nothing is known about its solution chemistry.

The only information located on nonphotochemical oxidative destruction of chromium cyanide complexes was an unsubstantiated claim that H_2O_2 oxidizes Cr(III) cyanide complexes to CrO_4^{2-} in alkaline solution (82). Photochemical reactions that destroy Cr(III) cyanide species are discussed in chapter 9.

VANADIUM

Reactions of vanadium complexes are generally fast. Vanadium forms cyanide complexes in the 2+, 3+, and 4+ oxidation states. The yellow-brown hexacyanovanadate(II), $[\text{V}(\text{CN})_6]^{4-}$, the red heptacyanovanadate(III), $[\text{V}(\text{CN})_7]^{3-}$, and the green oxopentacyanovanadate(IV), $[\text{VO}(\text{CN})_5]^{3-}$, have been characterized in the solid state. Their solution chemistry is complex because disproportionation equilibria occur (83):



At least one other complex of unknown composition exists in cyanovanadate solutions (83). The reactivity of the cyanovanadates with acids has not been documented, and no thermodynamic data exist. If the cyanovanadates fit the trend of lower stability of cyanide complexes of transition metals on moving leftward in the periodic table, they are probably all WAD. Cyanide concentrations above 1M are required to maintain $[\text{V}(\text{CN})_7]^{3-}$ in solution (83).

The V(II) and V(III) cyanide complexes are readily oxidized by O_2 to V(IV) species (83). Vanadium(IV) in alkaline solution is easily oxidized by O_2 to vanadates(V); the same is probably true of V(IV) cyanide species. Vanadium(V) appears not to form cyanide complexes. Whether vanadate(V) and cyanide form cyanovanadate(IV) species via a redox reaction has not been investigated. Such a reaction, if it occurs, coupled with reoxidation of the cyanovanadate(IV) species by O_2 , would constitute a vanadium-catalyzed oxidation of CN^- by O_2 .

TITANIUM

Attempts to obtain cyanotitanates from aqueous solutions give only hydrous oxides. Complex salts, e.g., $\text{Cs}_4\text{Ti}(\text{CN})_7$, were reported to be obtained in nonaqueous preparations, but they are decomposed by water (84).

SUMMARY OF METAL CYANIDE DESTRUCTION REACTIONS

The reactivity of metal cyanide species toward different reagents that may decompose them was discussed in the preceding sections. This section provides a summary of the nonoxidative and oxidative reactions that decompose metal cyanide species.

Nonoxidative Reactions

The reactivity of metal cyanide complexes toward decomposition by reagents that are not oxidants is summarized in table 8-4. In table 8-4, reactions with acids and sulfides are compiled and the metal cyanide complexes are classified as WAD, partially WAD (part-WAD), or non-WAD. No other common or inexpensive precipitants or complexing agents are listed, because they do not react with the metal cyanide complexes. Even ethylenediaminetetraacetate, one of the strongest complexing agents, does not displace CN^- from metal cyanide complexes in alkaline solution, as shown by calculations with the data in table 8-1.

From table 8-4, the thermodynamic data in appendix D, and the EPAD in appendix E, a more accurate classification is as follows:

WAD: Zn, Cd, Ni, Mn, Cr.

Partially WAD: Hg, Cu, Ag, Au(I).

Non-WAD: Au(III), Co, Fe.

The diagrams in appendix E clearly illustrate the distinction between WAD and partially WAD metal cyanide species. Compare, e.g., figures E-11, E-33, E-54, E-75, E-101, E-122, and E-142. These are pM-pH diagrams that show the predominant species at a free cyanide activity of $10^{-5}M$ for Zn, Cd, Hg, Cu(I), Ag, Au(I), and Ni, respectively. At pH below 6, the predominant species of the respective metals are Zn^{2+} , Cd^{2+} , $\text{Hg}(\text{CN})_2(\text{aq})$, $\text{CuCN}(\text{s})$, $[\text{Ag}(\text{CN})_2]^-$ and $\text{AgCN}(\text{s})$, $[\text{Au}(\text{CN})_2]^-$ and $\text{AuCN}(\text{s})$, and Ni^{2+} .

Some metal cyanide complexes are so stable that alkaline sulfides do not precipitate the metal sulfide; this is the case for Cu, Au, Ni, Co, and Fe. For copper and nickel, the metal sulfides and HCN are obtained at pH below 7

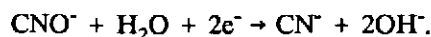
by using H_2S . For Mn(II) and Mn(III), sulfides are expected to precipitate MnS ; Mn(III) is reduced. Chromium(III) sulfide is not formed even from Cr^{3+} and sulfides, so its formation from chromium cyanide species is not expected. Equilibrium predominance area diagrams for metal cyanide species in the presence of sulfide are given in figures E-18, E-40, E-61, E-81, E-108, and E-149.

Oxidative Reactions

Table 8-5 summarizes reactions for the oxidative destruction of metal cyanide species. Many of the entries are predictions based on thermodynamic data. The reactions involve oxidation of CN^- to NCO^- , which in turn hydrolyzes slowly to CO_3^{2-} and NH_3 or may be further oxidized to CO_3^{2-} and N_2 , as discussed in chapter 7. In most cases, the metal product is known or expected to be an oxide species. The oxidative destruction of cyanide complexes of Zn, Cd, Cu, Ag, and Ni has been studied by different investigators. In nearly all of the published reports, the evident objective was practical utility (8-9, 11-14). Knowledge of the oxidation of metal cyanide species is inadequate. The published reports claim depletion of CN^- from the solution, but say little or nothing about residual CN^- in precipitated metal-containing products. The literature search revealed no fundamental systematic kinetic and mechanism studies of oxidative metal-cyanide destruction reactions. A knowledge of the mechanisms of these reactions is needed to achieve a sufficient understanding of the fate of metal cyanide species in the environment and to design more effective cyanide destruction technology.

Possible Formation of Fulminates

Strong cyanide complexes, e.g., of Hg, Ag, and Au, may possibly react with strong oxidants by attack on the nitrogen atom of the CN group, with formation of fulminate (CNO^-) complexes. In such strong cyanide complexes, the carbon atom, being strongly bonded to the metal ion, is not readily accessible to attack. An estimated value of the standard Gibbs energy of formation of CNO^- (table B-1), combined with the value for CN^- , yields an estimated standard reduction potential of $E^\circ = +0.45 \text{ V}$ for the half-reaction



The value of E° for this half-reaction allows the possibility that strong oxidants such as ClO^- or O_3 may oxidize metal cyanide species to the metal fulminate species:

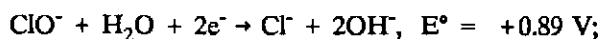


Table 8-4.-Nonoxidative decomposition of metal cyanide species

Metal	Reagent in dilute aqueous solution				Classification
	H ₂ SO ₄	HCl	Na ₂ S	H ₂ S	
Zn(II)	Zn ²⁺	Zn ²⁺	ZnS	ZnS	WAD
Cd(II)	Cd ²⁺	Cd ²⁺	CdS	CdS	WAD
Hg(II)	Hg(CN) ₂	¹ HgCl ₂	HgS	HgS	part-WAD
Cu(I)	CuCN(s)	CuCN(s)	NR	Cu ₂ S	part-WAD
Ag(I)	AgCN(s)	AgCl(s)	Ag ₂ S	Ag ₂ S	part-WAD
Au(I)	AuCN(s)	AuCN(s)	NR	NR	part-WAD
Ni(II)	Ni ²⁺	Ni ²⁺	NR	NiS	WAD
Co(III)	NR	NR	NR	NR	non-WAD
Fe(II)	NR	NR	NR	NR	non-WAD
Fe(III)	NR	NR	(²)	(²)	non-WAD
Mn(II)	Mn ²⁺	Mn ²⁺	MnS	MnS	WAD
Mn(III)	³ Mn ²⁺	³ Mn ²⁺	MnS	MnS	WAD
Cr(III)	Cr ³⁺	Cr ³⁺	NR	NR	WAD

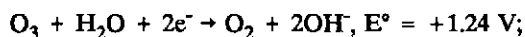
NR No reaction.

¹Reaction may be incomplete.

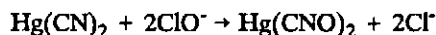
²[Fe(CN)₆]³⁻ reduced to [Fe(CN)₆]⁴⁻.

³C₂N₂ also formed.

Note.—Cu(II) is not included because it is reduced rapidly to Cu(I) by CN⁻. Co(II) is not included because it is oxidized rapidly to Co(III) by O₂ in the presence of CN⁻.



from data in table B-1. This creates the possibility of explosive reaction products, especially if the solutions become concentrated, e.g.,



None of the publications concerning the oxidation of metal cyanide species consider the possible formation of fulminates, so this matter deserves investigation.

CEMENTATION OF METALS FROM CYANIDE SOLUTIONS

The cementation of metals is often a suitable technique for removing metals from cyanide solutions. The best-known instance is the Merrill-Crowe process, in which

zinc dust is used to cement gold and silver from de-aerated cyanide pregnant solutions. Mercury, if present in such solutions, is also cemented. Table 8-6 lists standard reduction potentials for metal cyanide species. It shows that zinc could in theory also cement Cd, Cu, Ni, and Co from cyanide solutions. The reduction potentials are very negative, so that exclusion of O₂ may be required. The kinetically very inert [Co(CN)₆]³⁻ and [Fe(CN)₆]⁴⁻ may not react with metallic zinc.

Cementation with zinc would convert the partially WAD cyanide complexes of Hg, Cu, and Ag to metallic Hg, Cu, and Ag and the WAD zinc cyanide species. The latter are more readily destroyed with oxidants or treated with Na₂S to remove zinc as ZnS and regenerate NaCN.

Cementation of mercury and silver from cyanide solutions with copper and subsequent destruction of the copper cyanide species with H₂O₂ was reported (14).

Table 8-5.—Oxidative decomposition of metal cyanide species

Metal	Reagent in dilute alkaline solution			
	NaClO	¹ H ₂ O ₂	O ₃	¹ HOOSO ₃ ⁻
Zn(II)	Zn(OH) ₂	Zn(OH) ₂	Zn(OH) ₂	Zn(OH) ₂
Cd(II)	Cd(OH) ₂	Cd(OH) ₂	Cd(OH) ₂	Cd(OH) ₂
Hg(II)	HgO?	HgO?	HgO?	HgO?
Cu(I)	Cu(OH) ₂	Cu(OH) ₂	Cu(OH) ₂	Cu(OH) ₂
Ag(I)	AgCl?	AgO _x ?	AgO _x ?	AgO _x ?
Au(I)	AuCN?	AuCN?	AuCN	AuCN?
Ni(II)	NiO _x	NiO _x ?	NiO _x	NiO _x
Co(III)	NR	NR	NR	NR
Fe(II)	(²)	NR	(²)	(²)
Fe(III)	NR	(³)	NR	NR
Mn(II)	MnO _x ? ⁴	MnO _x ? ⁴	MnO _x ? ⁴	MnO _x ? ⁴
Mn(III)	MnO _x ?	MnO _x ?	MnO _x ?	MnO _x ?
Cr(III)	CrO ₄ ²⁻ ?	CrO ₄ ²⁻ ?	CrO ₄ ²⁻ ?	CrO ₄ ²⁻ ?

NR No reaction.

¹With Cu catalyst.²[Fe(CN)₆]⁴⁻ oxidized to [Fe(CN)₆]³⁻.³[Fe(CN)₆]³⁻ reduced to [Fe(CN)₆]⁴⁻.⁴Probably via [Mn(CN)₆]³⁻.

Note.—Question marks after entries denote uncertainty about expected products or rates of reaction. Cu(II) is not included because it is reduced rapidly to Cu(I) by CN⁻. Co(II) is not included because it is oxidized rapidly to Co(III) by O₂ in the presence of CN⁻.)

REACTION OF METAL CYANIDE SPECIES WITH SULFUR OR POLYSULFIDES

The reactions of metal cyanide species with sulfur or polysulfides to form metal sulfides and SCN⁻ provide an alternative route to the decomposition of metal cyanide species. The reactions of free CN⁻ with sulfur and polysulfides are discussed in chapter 7. For the reaction



log K = 14.0 from standard Gibbs energy data in tables B-1 and C-1. This value of log K is sufficiently high that S(s)

or polysulfide ions S_p²⁻ (p = 2 to 6) should react with metal cyanide species to form the metal sulfide and SCN⁻. Data for several such reactions are compiled in table 8-7, which gives values of log K divided by n, the number of CN⁻ on the left side of the equation or of SCN⁻ on the right side. The values of (log K)/n range from 10.2 to 22.9, so all of the reactions are thermodynamically capable of proceeding to completion. For the kinetically inert cobalt and iron cyanide complexes, the reactions with polysulfide ions or sulfur are not expected to proceed at an observable rate except possibly by photochemical action. The reaction of [Ni(CN)₄]²⁻ with polysulfide (32) to form a Ni(II) polysulfide complex was mentioned above.

Table 8-6.--Standard reduction potentials of metal cyanide species at 25° C

(Values are calculated from data in tables in appendix D)

Half-reaction (X = CN)	E°
$\text{ZnX}_4^{2-} + 2\text{e}^- \rightarrow \text{Zn(s)} + 4\text{X}^-$	-1.34
$\text{CdX}_4^{2-} + 2\text{e}^- \rightarrow \text{Cd(s)} + 4\text{X}^-$	- .93
$\text{HgX}_2 + 2\text{e}^- \rightarrow \text{Hg(l)} + 2\text{X}^-$	- .12
$\text{HgX}_4^{2-} + 2\text{e}^- \rightarrow \text{Hg(l)} + 4\text{X}^-$	- .30
$\text{CuX(s)} + \text{e}^- \rightarrow \text{Cu(s)} + \text{X}^-$	- .65
$\text{CuX}_3^{2-} + \text{e}^- \rightarrow \text{Cu(s)} + 3\text{X}^-$	-1.09
$\text{CuX}_4^{3-} + \text{e}^- \rightarrow \text{Cu(s)} + 4\text{X}^-$	-1.18
$\text{CuX}_4^{2-} + \text{e}^- \rightarrow \text{CuX}_4^{3-}$	+ .54
$\text{AgX(s)} + \text{e}^- \rightarrow \text{Ag(s)} + \text{X}^-$	- .13
$\text{AgX}_2^- + \text{e}^- \rightarrow \text{Ag(s)} + 2\text{X}^-$	- .41
$\text{AuX}_2^- + \text{e}^- \rightarrow \text{Au(s)} + 2\text{X}^-$	- .49
$\text{AuX}_4^- + 2\text{e}^- \rightarrow \text{AuX}_2^- + 2\text{X}^-$	+ .10
$\text{NiX}_4^- + 2\text{e}^- \rightarrow \text{Ni(s)} + 4\text{X}^-$	-1.12
$\text{CoX}_5^{3-} + 2\text{e}^- \rightarrow \text{Co(s)} + 5\text{X}^-$	- .97
$\text{CoX}_6^{3-} + \text{e}^- \rightarrow \text{CoX}_5^{3-} + \text{X}^-$	-1.08
$\text{FeX}_6^{4-} + 2\text{e}^- \rightarrow \text{Fe(s)} + 6\text{X}^-$	-1.52
$\text{FeX}_6^{3-} + \text{e}^- \rightarrow \text{FeX}_6^{4-}$	+ .36
$\text{MnX}_6^{4-} + 2\text{e}^- \rightarrow \text{Mn(s)} + 6\text{X}^-$	-1.49
$\text{MnX}_6^{3-} + \text{e}^- \rightarrow \text{MnX}_6^{4-}$	+ .07
$\text{MnX}_6^{2-} + \text{e}^- \rightarrow \text{MnX}_6^{3-}$	+1.52
$\text{CrX}_6^{4-} + 2\text{e}^- \rightarrow \text{Cr(s)} + 6\text{X}^-$	-1.45
$\text{CrX}_6^{3-} + \text{e}^- \rightarrow \text{CrX}_6^{4-}$	-1.39
$\text{TlX}_2^+ + 2\text{e}^- \rightarrow \text{Tl}^+ + 2\text{X}^-$	+ .35
$\text{TlX}_4^- + 2\text{e}^- \rightarrow \text{Tl}^+ + 4\text{X}^-$	+ .09

Polysulfide complexes of many metals have been reported recently, but in no other case was a metal cyanide species used in the preparation.

OCCURRENCE OF OTHER METAL COMPLEXES IN CYANIDE PROCESS SOLUTIONS

Accessory species that may act as ligands and form complexes with metal ions exist in cyanide solutions. If the solutions contain metals in excess of the available CN^- , e.g., when oxidants are added to destroy CN^- , metal ions remaining in solution may be complexed by accessory species or OH^- . Important accessory species likely to occur in cyanide solutions are as follows, classified by source:

- Hydrolysis or oxidation of CN^- : NH_3 , SCN^- .
- Minerals: SH^- , $\text{S}_2\text{O}_3^{2-}$, SO_4^{2-} , Cl^- .
- Reagents: Cl^- , SO_4^{2-} .

As described in chapter 4, if the concentration of a free ligand in a solution of a metal ion exceeds a certain value, the metal ion will exist predominantly in the form of complexes with that ligand. Simply, in a reaction



for which the equilibrium constant is

$$K = [\text{ML}]/[\text{M}][\text{L}],$$

the concentration $[\text{L}]_{\min}$ of free ligand L above which the predominant metal species will be the complex ML is given by

$$\text{pL}_{\min} = -\log [\text{L}]_{\min} = \log K.$$

Values of $\text{pL}_{\min}$ for the ligands listed above with different metal ions are compiled in table 8-8. The values in table 8-8 are all relative to unhydrolyzed metal ions, so at pH values at which the metal ions are hydrolyzed, higher ligand concentrations are required to compete with OH^- and form complexes. Consequently, the values in table 8-8 are conservative when applied to alkaline solutions, but can still be used to indicate the possibility of the predominance of soluble metal complexes with accessory ligands. For a simple example, consider a solution depleted in CN^- contains trace heavy metals and $1 \times 10^{-5}M$ $\text{S}_2\text{O}_3^{2-}$, i.e., $\text{L} = \text{S}_2\text{O}_3^{2-}$, and $\text{pL} = -\log [\text{L}] = 5.0$. Table 8-8 shows that Hg^{2+} , Cu^+ , Ag^+ , and Au^+ have $\text{pL}_{\min}$ for $\text{S}_2\text{O}_3^{2-}$ complexes above 5.0, and $\text{S}_2\text{O}_3^{2-}$ complexes would predominate except at high pH values where OH^- would compete with $\text{S}_2\text{O}_3^{2-}$.

Table 8-7.--Reactions of free cyanide and metal cyanide species with polysulfide ions or sulfur

Reaction	(log K)/n ¹
$S(s) + CN^- \rightarrow SCN^-$	14.0
$Zn(CN)_2(s) + S_3^{2-} \rightarrow ZnS(s) + 2SCN^-$	17.6
$[Zn(CN)_4]^{2-} + S_5^{2-} \rightarrow ZnS(s) + 4SCN^-$	14.3
$Cd(CN)_2 + S_3^{2-} \rightarrow CdS(s) + 2SCN^-$	21.2
$[Cd(CN)_4]^{2-} + S_5^{2-} \rightarrow CdS(s) + 4SCN^-$	15.4
$Hg(CN)_2 + S_3^{2-} \rightarrow HgS(s) + 2SCN^-$	22.9
$[Hg(CN)_4]^{2-} + S_5^{2-} \rightarrow HgS(s) + 4SCN^-$	16.4
$2CuCN(s) + S_3^{2-} \rightarrow Cu_2S(s) + 2SCN^-$	16.9
$2[Cu(CN)_2]^- + S_5^{2-} \rightarrow Cu_2S(s) + 4SCN^-$	13.8
$2[Cu(CN)_3]^{2-} + S_5^{2-} + 2S(s) \rightarrow Cu_2S(s) + 6SCN^-$	12.1
$2AgCN(s) + S_3^{2-} \rightarrow Ag_2S(s) + 2SCN^-$	22.0
$2[Ag(CN)_2]^- + S_5^{2-} \rightarrow Ag_2S(s) + 4SCN^-$	15.1
$2AuCN(s) + S_3^{2-} \rightarrow Au_2S(s) + 2SCN^-$	15.1
$2[Au(CN)_2]^- + S_5^{2-} \rightarrow Au_2S(s) + 4SCN^-$	11.5
$Ni(CN)_2(s) + S_3^{2-} \rightarrow NiS(s) + 2SCN^-$	15.0
$[Ni(CN)_4]^{2-} + S_5^{2-} \rightarrow NiS(s) + 4SCN^-$	11.3
$[Co(CN)_6]^{3-} + (1/2)S_4^{2-} + S_5^{2-} \rightarrow CoS(s) + 6SCN^-$	11.2
$[Fe(CN)_6]^{4-} + S_5^{2-} + 2S(s) \rightarrow FeS(s) + 6SCN^-$	10.2
$[Fe(CN)_6]^{3-} + (1/2)S_4^{2-} + S_5^{2-} \rightarrow FeS(s) + 6SCN^-$	12.3

¹calculated from data in tables B-1, C-1, and most of the tables in appendix D; n is the number of CN⁻ groups on the left side of the equation or of SCN⁻ ions on the right.

Table 8-8.-Minimum free ligand concentrations required
predominance of soluble metal complexes with the ligand

Metal ion	pL of specified ligand L (pH range)						
	CN ⁻ >9	Cl ⁻ >0	SH ⁻ >7	S ₂ O ₃ ²⁻ >2	SO ₄ ²⁻ >2	NH ₃ >9	SCN ⁻ >0
Zn ²⁺	5.6	0.5	(7)	2.4	2.3	2.4	1.3
Cd ²⁺	6.0	2.0	(8)	3.9	2.5	2.5	1.9
Hg ²⁺	17.0	6.8	(19)	(15)	2.7	(9.0)	9.2
Cu ⁺	10.8	2.8	(14)	(11)	(1)	(5.8)	(6)
Cu ²⁺	R	.2	R	R	2.3	4.0	2.3
Ag ⁺	10.2	3.3	(16)	8.7	1.3	3.6	4.8
Au ⁺	(19)	(4.6)	(20)	(18)	(1)	(10)	(8.8)
Au ³⁺	(20)	>7	R	R	(4)	>16	>11
Ni ²⁺	7.6	(.3)	N	(2)	2.3	2.7	1.8
Co ²⁺	(4.6)	(.3)	N	(2)	2.3	2.0	1.7
Co ³⁺	(12.2)	(2.1)	R	R	(4.0)	(>6)	R
Fe ²⁺	5.9	(.2)	N	(2)	2.3	1.4	1.3
Fe ³⁺	7.0	1.5	R	(4)	4.0	N	3.0
Mn ²⁺	(1.7)	(.1)	N	(2)	2.3	.9	1.2
Mn ³⁺	(5.8)	(1.8)	R	R	(4.0)	N	R
Cr ³⁺	(5.5)	(.5)	N	(4)	(4.0)	(>2)	3.1

N No data.

R Redox reaction.

Note.—All data are for 25° C and ionic strength zero, and are derived from the tables in appendix D. Data are expressed as $pL = -\log[L]$, where $[L]$ is the free ligand concentration. The approximate pH range in which the specified ligand species L is the predominant form of the free ligand is specified. Values in parentheses are estimated.

REFERENCES²

1. Sharpe, A. G. *The Chemistry of Cyano Complexes of the Transition Metals*. Academic, 1976, 302 pp.
2. Martell, A. E., and R. M. Smith. *Critical Stability Constants*. V. 1, Amino Acids. Plenum, 1974, 469 pp.
3. —. *Critical Stability Constants*. V. 5, First Supplement. Plenum, 1982, 604 pp.
4. Smith, R. M., and A. E. Martell. *Critical Stability Constants*. V. 6, Second Supplement. Plenum, 1989, 662 pp.
5. Beck, M. T., and E. Cs. Porzolt. The Interaction of Mercury(II) Cyanide With Coordinatively Saturated Inert Cyano Complexes. *J. Coord. Chem.*, v. 1, 1977, pp. 57-66.
6. Tan, T. C., and W. K. Teo. Destruction of Cyanides by Thermal Hydrolysis. *Plat. Surf. Finish.*, v. 74, 1987, No. 4, pp. 70-73.
7. Asayama, M., M. Okugawa, and R. Ishii. (Treatment of Cadmium-Plating Wastewater Containing Tetracyanocadmiate Ions.) *Japan Kokai* 73 95,368; *Appl.* 72 27,802, Mar. 17, 1972, 3 pp.; *Chem. Abstr.*, v. 80, 1974, No. 148921y.
8. Weiner, R., and Ch. Leiss. Zur Kinetik der Entgiftung Komplexer Cyanide (Kinetics of Detoxification of Complex Cyanides). *Metallberflaeche*, v. 26, 1972, No. 5, pp. 169-175.
9. Joshi, S. N. Kinetik der Umsetzung von Cyanidkomplexen mit Natriumhypochlorit in Verdunnter Alkalische Loesung (Kinetics of Decomposition of Cyanide Complexes With Sodium Hypochlorite in Dilute Alkaline Solution). *Chem. Tech.*, v. 35, 1983, p. 465.
10. Smith, A., and T. Mudder. *The Chemistry and Treatment of Cyanidation Wastes*. Mining Journal Books, London, 1991, 345 pp.
11. Fabjan, Ch., and R. Davies. Entgiftung Cyanidhaltiger Abwasser mit Ozon (Detoxification of Cyanide-containing Wastewater with Ozone). *Wasser, Luft, und Betrieb*, v. 30, 1976, No. 4, pp. 175-178.
12. Kandzas, P. F., and A. A. Mokina. (Use of Ozone for Purifying Industrial Wastewaters.) *Tr. Vses. Nauch.-Issled. Inst. Vodostabzh., Kanaliz., Gidrotekh. Sooruzhenii Inzh. Gidrotekhn.*, 1967, No. 20, pp. 40-45; *Chem. Abstr.*, v. 71, 1969, No. 33212q.
13. Belevzev, A. N., and Yu. L. Maximenko. Russian Study: Chlorine Dioxide Oxidation of Cyanides and Phenols. *Effluent Water Treat. J.*, v. 25, 1985, No. 5, pp. 171-176.
14. Sugimoto, T., N. Nishioka, and K. Mizutani. (Problems in Chemical Education. I. Decomposition of Cyanides in Heavy-Metal-Containing Wastewater.) *Kiyo-Nagoya Daigaku Kyoyobu*, Ser. B, v. 26, 1982, pp. 61-67; *Chem. Abstr.*, v. 97, 1982, No. 43672r.
15. Silver, H. G. Chemical Behavior of the Components of the KCN/KAu(CN)₂ Electroplating System. *J. Electrochem. Soc.*, v. 116, 1968, pp. 26C-32C.
16. El-Hinnawi, M. A., L. Peter, and B. Meyer. Raman Spectra of Copper(I), Silver(I), and Gold(I) Cyanides in Aqueous Solutions of Sodium Thiosulfate. *J. Raman Spectrosc.*, v. 16, 1985, pp. 272-279.
17. Belevantsev, V. I., B. I. Peshchevskii, and L. D. Tsvetodub. The Thermodynamics of Some Cyano-Complexes of Gold in Aqueous Solution. *Russ. J. Inorg. Chem. (Engl. Transl.)*, v. 32, 1987, pp. 59-61.
18. Katagiri, A., S. Yoshimura, and S. Yoshizawa. Formation Constant of the Tetracyanocuprate(II) Ion and the Mechanism of Its Decomposition. *Inorg. Chem.*, v. 20, 1981, pp. 4143-4147. Correction, *ibid.*, v. 25, 1986, p. 2278.
19. Yoshimura, S., A. Katagiri, Y. Deguchi, and S. Yoshizawa. Studies of the Anodic Oxidation of the Cyanide Ion in the Presence of the Copper Ion. IV. The Kinetics and Mechanism of the Decomposition of the Intermediate Tetracyanocuprate(II) Ion. *Bull. Chem. Soc. Jpn.*, v. 53, 1980, pp. 2437-2442.
20. Kappenstein, C., and U. Schubert. X-Ray Crystal Structure of Two New Mixed-valence Copper Cyanide Complexes: Unusual Bicoordinated Copper(I) Atoms in Polymeric Networks. *J. Chem. Soc. Chem. Commun.*, 1980, pp. 1116-1118.
21. Korse, J., L. A. Pronk, C. van Embden, G. Leurs, and P. W. F. Louwrier. Ternary Complexes of the Cu(II) and Ni(II) Chelates of EDTA and DCTA With Cyanide and Ethylenediamine. *Talanta*, v. 30, 1983, pp. 1-7.
22. Okinaka, Y., and C. Wolowodiuk. Cyanoaurate(III) Formation and Its Effect on Current Efficiency in Gold Plating. *J. Electrochem. Soc.*, v. 128, 1981, pp. 288-294.
23. Hyksova, D., Z. Sauman, and Z. Valtr. Beitrag zur Ozonolyse von Kupfer(I)- und Nickel(II)-Cyanokomplexen (Contribution to the Ozonolysis of Copper(I) and Nickel(II) Cyano Complexes). *Coll. Czechoslov. Chem. Commun.*, v. 37, 1972, pp. 1637-1644.
24. Weber, W. J., Jr., and O. Corapcioglu. Catalytic Oxidation of Cyanides. *Proc. 36th Indust. Waste Conf.*, 1981, pp. 500-508; *Chem. Abstr.*, v. 96, 1982, No. 186706v.
25. Kolski, G. B., and D. W. Margerum. Kinetics of Formation and Dissociation of Tetracyanonickelate(II). *Inorg. Chem.*, v. 7, 1968, pp. 2239-2243.
26. Crouse, W. C., and D. W. Margerum. Kinetics of Tetracyanonickelate(II) Reactions. *Inorg. Chem.*, v. 13, 1974, pp. 1437-1443.
27. Persson, H. Kinetics of Formation of the Tetracyanonickelate(II) Ion. *Acta Chem. Scand.*, v. 30A, 1976, pp. 39-42.
28. Persson, H., and C. G. Ekstroem. Kinetics of Dissociation of the Tetracyanonickelate(II) Ion. *Acta Chem. Scand.*, v. 30A, 1976, pp. 31-38.
29. Beach, M. W., and D. W. Margerum. Kinetics of Oxidation of Tetracyanonickelate(II) by Chlorine Monoxide, Chlorine, and Hypochlorous Acid and Kinetics of Chlorine Monoxide Formation. *Inorg. Chem.*, v. 29, 1990, pp. 1225-1232.
30. Asayama, M., M. Okugawa, and R. Ishii. (Heat Treatment of Wastewater Containing Tetracyanonickelate.) *Japanese Pat.* 73 00,190, May 20, 1971, 3 pp.; *Chem. Abstr.*, v. 78, 1973, No. 140205f.
31. Okugawa, M. (Treatment of a Liquid Containing a Nickel Cyanide Compound.) *Brit. UK Pat. Appl.* GB 2,076,388, JP Appl. 80/68,672, May 22, 1980, 7 pp.; *Chem. Abstr.*, v. 96, 1982, No. 91170b.
32. Udupa, K. N., and S. Sarkar. Reaction of [Ni(CN)₄]²⁻ with Polysulfide: Synthesis of [Ni(S₄)₂]²⁻ and its Reactions with Carbon Disulfide and Activated Acetylenes. *Polyhedron*, v. 6, 1987, pp. 627-631.
33. Espenson, J. H., and J. R. Pipal. A Kinetic Study of the Decomposition of Pentacyanocobaltate(II) in Perchloric Acid Solution. *Inorg. Chem.*, v. 7, 1968, pp. 1463-1465.
34. Burnett, M. G., and W. M. Gilfillan. The Mechanism and Kinetics of the Substitution of Azide, Thiocyanate, and Cyanide Ions in Aquopentacyanocobaltate(III) and Pentacyanohydroxocobaltate(III). *J. Chem. Soc. Dalton Trans.*, 1981, pp. 1578-1582.
35. Haim, A., and W. K. Wilmarth. The Pentacyano Complexes of Cobalt(III). I. Kinetics and Mechanism of the Substitution of Water in Co(CN)₅OH₂²⁻ by Azide and Thiocyanate Ions and by O¹⁸-Enriched Water. *Inorg. Chem.*, v. 1, 1962, pp. 573-582.
36. Grassi, R., A. Haim, and W. K. Wilmarth. The Pentacyano Complexes of Cobalt(III). III. Kinetics and Mechanism of the Substitution of Water in Co(CN)₅OH₂²⁻ by Iodide, Triiodide, Bromide, and Chloride Ions, and Aquation of Co(CN)₅I³⁻, Co(CN)₅Br³⁻, and Co(CN)₅Cl³⁻. *Inorg. Chem.*, v. 6, 1967, pp. 237-242.
37. Barca, R., J. Ellis, M.-S. Tsao, and W. K. Wilmarth. The Pentacyano Complexes of Cobalt(III). IV. Kinetics and Mechanism of the Substitution of Water in Co(CN)₅OH₂²⁻ by Pyridine, Ammonia, Hydrazine, and Hydrazinium Ion. *Inorg. Chem.*, v. 6, 1967, pp. 243-248.
38. Viaene, L., J. D'Olielager, and S. de Jaegere. Synthesis and Properties of Cyanoquo and Cyanohydroxo Complexes of Cobalt(III). *J. Inorg. Nucl. Chem.*, v. 37, 1975, pp. 2435-2438.
39. —. Isomerization Reactions of Tetracyanodiaquocobaltate(III). *Inorg. Chem.*, v. 14, 1975, pp. 2736-2739.
40. Davies, G., and A. R. Garafalo. Some Observations on Equilibria Involving Monomeric and Dimeric Pentacyanoiron(II) Complexes in Aqueous Solution. *Inorg. Chim. Acta*, v. 19, 1976, pp. L3-L4.

²A title in parentheses is a translation from the language in which the work was published.

41. James, A. D., and R. S. Murray. Substitution Reactions of Di- μ -cyano-bis[tetracyanoferrate(II)] in Aqueous Solution. *J. Chem. Soc. Dalton Trans.*, 1976, pp. 1182-1186.
42. Borghi, E. B., M. A. Blesa, P. J. Aymonino, and J. A. Olabe. Reactions of the Amino-, Sulfito-, and Aquo-pentacyanoferrate(II) Ions in Aqueous Solutions. *J. Inorg. Nucl. Chem.*, v. 43, 1981, pp. 1849-1854.
43. James, A. D., and R. S. Murray. Kinetics of Formation and Bridge Cleavage of Binuclear Complexes Derived From the Pentacyanoferrate(II and III) Ions in Aqueous Solution. *J. Chem. Soc. Dalton Trans.*, 1977, pp. 326-329.
44. Emschwiller, G., and C. K. Joergensen. Electron Transfer Bands of Binuclear Iron(II, III) Complexes Containing Two Cyanide Bridges. *Chem. Phys. Lett.*, v. 5, 1970, pp. 561-563.
45. Glauser, R., U. Hauser, F. Herren, A. Ludi, P. Roder, E. Schmidt, H. Siegenthaler, and F. Wenk. Mixed-valence Spectrum and Cyclic Voltammetry of Binuclear Iron Cyano Complexes. *J. Am. Chem. Soc.*, v. 95, 1973, pp. 8457-8458.
46. Espenson, J. H., and S. G. Wolenuk, Jr. Kinetics and Mechanism of Some Substitution Reactions of Pentacyanoferrate(III) Complexes. *Inorg. Chem.*, v. 11, 1972, pp. 2034-2041.
47. Toma, H. E., and J. M. Malin. Dissociation Kinetics of Pentacyanoiron(II) Complexes of Ammonia and Methylamine. *Inorg. Chem.*, v. 13, 1974, pp. 1772-1774.
48. James, A. D., R. S. Murray, and W. C. E. Higginson. Iron(II) Catalysis in Substitution Reactions of Aminopentacyano- and Aquopentacyano-ferrate(III) Ions. *J. Chem. Soc. Dalton Trans.*, 1974, pp. 1273-1278.
49. Bradic, Z., M. Pribanic, and S. Asperger. Kinetics and Mechanism of Replacements in Pentacyano(ligand)ferrate(II) Ions. *J. Chem. Soc. Dalton Trans.*, 1975, pp. 353-356.
50. James, A. D., and R. S. Murray. Kinetic and Equilibrium Studies on Iron(II) and Iron(III) Pentacyanoferrates. *J. Chem. Soc. Dalton Trans.*, 1975, pp. 1530-1533.
51. Katz, N. E., M. A. Blesa, J. A. Olabe, and P. J. Aymonino. Kinetics of Formation and Stability Constants of Aminopentacyanoferrate(II) Complexes. *Inorg. Chim. Acta*, v. 27, 1978, pp. L65-L66.
52. Katz, N. E., P. J. Aymonino, M. A. Blesa, and J. A. Olabe. Influence of Ligand-Water Interactions on the Aquation of Pentacyano(saturated amine)ferrate(II) Ions. *Inorg. Chem.*, v. 17, 1978, pp. 556-559.
53. Gaspar, V., and M. T. Beck. Kinetics of the Photoaquation of the Hexacyanoferrate(II) Ion. *Polyhedron*, v. 2, 1983, pp. 387-391.
54. Naik, R. M., and P. C. Nigam. Kinetics and Mechanism of the Reaction between 1,2-Diaminopropanetetraacetatoferrate(III) and Cyanide Ion. *Inorg. Chim. Acta*, v. 114, 1986, pp. 55-61.
55. Garafalo, A. R., and G. Davies. Kinetics and Mechanism of the Thiocyanate-Catalyzed Dissociation of $\text{Fe}_2(\text{CN})_{10}^{6-}(\text{aq})$ in Aqueous Sodium Perchlorate Solution. *Inorg. Chem.*, v. 15, 1976, pp. 1787-1790.
56. Olabe, J. A., and H. O. Zerga. Thermal Decomposition of the Pentacyanoaquoferrate(II) Ion in Aqueous Solution. *Inorg. Chem.*, v. 22, 1983, pp. 4156-4159.
57. Ronco, S. E., and P. J. Aymonino. Kinetics of the Thermal and Photochemical Decomposition of Aquopentacyanoferrate(III) in Aqueous Solution. *Transition Met. Chem. (London)*, v. 12, 1987, pp. 174-178.
58. Lee, H-F. Kinetics of the Reaction between Hypochlorous Acid and Hexacyanoferrate(II) Ion in Aqueous Solution. *J. Chem. Soc. Dalton Trans.*, 1988, pp. 273-275.
59. Khan, A. H., and W. C. E. Higginson. Kinetics of the Reaction between Chlorite and Hexacyanoferrate(II) in Aqueous Solution; Evidence for an Interfacial Redox Reaction. *J. Chem. Soc. Dalton Trans.*, 1981, pp. 2537-2543.
60. Eaton, D. R., and M. Pankratz. The Reaction of the Hexacyanoferrate(III) Ion with Hydrogen Peroxide. *Can. J. Chem.*, v. 63, 1985, pp. 793-797.
61. Asperger, S., I. Murati, and D. Pavlovic. Kinetics of Oxidation and of Catalytic Decomposition of Hexacyanoferrate(II) Ion. *J. Chem. Soc. A*, 1969, pp. 2044-2047.
62. Davies, G., and A. R. Garafalo. Stoichiometry and Kinetics of the Substitution-Controlled Oxidation of Pentacyanoaquoirron(II) Species by Hydrogen Peroxide and by *Tert*-Butyl Hydroperoxide in Aqueous Sodium Perchlorate Solution. *Inorg. Chem.*, v. 15, 1976, pp. 1101-1106.
63. Toma, H. E. Iron(II) Catalysis in the Oxidation of the Aquopentacyanoferrate(II) Complex by Molecular Oxygen. *Inorg. Chim. Acta*, v. 15, 1975, pp. 205-211.
64. Duke, F. R. Copper Catalysis in the Hexacyanoferrate(III) Oxidation of Cyanide. *Inorg. Nucl. Chem. Lett.*, v. 12, 1976, pp. 107-109.
65. Lopez-Cueto, G., and J. A. Casado-Riobo. Catalytic Effect of Copper on the Hexacyanoferrate(III) - Cyanide Redox Reaction. I. The Uncatalyzed and Catalyzed Reactions. *Talanta*, v. 26, 1979, pp. 127-132.
66. Ohura, H., Y. Kasaki, and S. Yamasaki. (The Reaction of Hexacyanoferrate(III) Ion with Hypobromite Ion in Alkaline Solution.) *Nippon Kagaku Kaishi*, 1985, pp. 2326-2330; *Chem. Abstr.*, v. 104, 1986, No. 121955q.
67. Malin, J. M., and R. C. Koch. Protonation of the Pentacyanoaquaferrate(II) Ion, $\text{Fe}(\text{CN})_5(\text{OH}_2)^{3-}(\text{aq})$. *Inorg. Chem.*, v. 17, 1978, pp. 752-754.
68. Davies, G., and A. R. Garafalo. Acidity of the Aquo Ligand in Aquopentacyanoferrate(II). *Inorg. Chem.*, v. 19, 1980, pp. 3543-3544.
69. Bell, S., G. Foster, M. W. Fuller, D. Hughes, K. F. Le Brocq, E. Leslie, and I. R. Wilson. Spectrophotometric Measurement of Rates of Hexacyanoferrate(III) Reactions. *Internat. J. Chem. Kinet.*, v. 18, 1986, pp. 651-653.
70. Chawla, I. D., and M. J. Frank. Electronic Spectra of Hexacyanomanganate(III) and Hydroxopentacyanomanganate(III) Ions in Acidic Media. *J. Inorg. Nucl. Chem.*, v. 32, 1970, pp. 555-563.
71. Lucena-Conde, F., J. Hernandez-Mendez, and G. Lopez-Cueto. (Analytical Chemistry of Elements With Uncommon Valences. XIX. Preparation, Analysis, and Comparative Qualitative Behavior of Two Manganese(III) Cyanide Complexes.) *Quim. Anal.*, v. 28, 1974, pp. 106-110; *Chem. Abstr.*, v. 81, 1974, No. 85391y.
72. Lopez-Cueto, G., and J. Hernandez-Mendez. (Analytical Chemistry of Elements With Uncommon Valences. XX. Comparative Spectrophotometric Behavior of Cyano Complexes of Manganese(III) in Different Media.) *Quim. Anal.*, v. 28, 1974, pp. 160-164; *Chem. Abstr.*, v. 81, 1974, No. 180741w.
73. Lopez-Cueto, G., J. Martin-Ruano, and F. Lucena-Conde. (Spectrophotometric Study of Hexacyanomanganate(III) in Cyanide Solution.) *Acta Salmant., Cienc.*, v. 54, 1975, pp. 27-33; *Chem. Abstr.*, v. 87, 1977, No. 92820q.
74. Trageser, G., and H. H. Eysel. On the Red and Dark "Modifications" of Hexacyanomanganate(III). *Inorg. Nucl. Chem. Lett.*, v. 14, 1978, pp. 65-70.
75. Lopez-Cueto, G., and A. Alonso-Mateos. (Coulometric Study at Controlled Potential of the Anodic Oxidation of the Binuclear Manganese(III) Cyanide Complex. II. Oxidation at +0.80 Volts Versus SCE: Faradaic Current, Kinetic Current.) *Rev. Roum. Chim.*, v. 31, 1986, pp. 237-253; *Chem. Abstr.*, v. 105, 1986, No. 87324a.
76. Trageser, G., and H. H. Eysel. Disproportionation of Hexacyanomanganate(III) into Hexacyanomanganate(IV) and Hexaquo-manganese(II) in Acidic Aqueous Solution. *Inorg. Chim. Acta*, v. 26, 1978, pp. L56-L58.
77. Lopez-Cueto, G., and C. Ubide. Fast Disproportionation of Hexacyanomanganate(III) in Acidic Solution. Formation of Hexacyanomanganate(IV) and Kinetics of its Decomposition. *Can. J. Chem.*, v. 64, 1986, pp. 2301-2304.
78. Schaap, W. B., R. Krishnamurthy, D. K. Wakefield, and W. F. Coleman. Cyanoaquochromium(III) Complexes: Isolation, Spectra, Aquation Reactions, and Kinetics. *Ch. in Coordination Chemistry: Papers Presented in Honor of Prof. J. C. Bailar, Jr.*, ed. by S. Kirschner (Proc. Symp. Univ. Illinois, Urbana, IL, June 22-25, 1969). Plenum, 1969, pp. 177-189.

79. Wakefield, D. K., and W. B. Schaap. The Rate of Aquation of 1,2,3-Tricyanotriaquochromium(III) in Acidic Aqueous Solution. *Inorg. Chem.*, v. 10, 1971, pp. 306-313.

80. Jeftic, L., and S. W. Feldberg. Chromium(II)-catalyzed Aquation of Hexacyanochromate(III) to Pentacyanomono-hydroxochromate(III). *J. Phys. Chem.*, v. 75, 1971, pp. 2381-2387.

81. Davies, G., N. Sutin, and K. O. Watkins. The Kinetics and Mechanism of the Reaction of Chromium(II) Cyanide Complexes with Hydrogen Peroxide in Aqueous Solution. *J. Am. Chem. Soc.*, v. 92, 1970, pp. 1892-1897.

82. Marchaj, A., Z. Stasicka, and D. Rehorek. Photochemical Production of Chromate(VI) Ions From Some Chromium(III) Complexes. *Polyhedron*, v. 2, 1983, p. 1281-1286.

83. Levenson, R. A., R. J. G. Dominguez, M. A. Willis, and F. R. Young, III. Characterization of Heptacyanovanadate(III). *Inorg. Chem.*, v. 13, 1974, pp. 2761-2764.

84. Nicholls, D., and T. A. Ryan. Complex Cyanides of Titanium. *Inorg. Chim. Acta*, v. 41, 1980, pp. 233-237.

CHAPTER 9.—PHOTOCHEMISTRY OF METAL CYANIDE SPECIES

INTRODUCTION

Sunlight plays an important role in environmental chemistry by initiating photochemical reactions. Sunlight is therefore an important contributor to the degradation of pollutants, including cyanides. The cyanide complexes of certain metals, namely Co, Fe, and Cr, are not rapidly decomposed by acids or destroyed by oxidants. However, the cyanide complexes of Co, Fe, and Cr undergo photochemical decomposition when irradiated with blue to near-ultraviolet light, 500 to 300 nm wavelength. Solar ultraviolet light encompasses this wavelength range and will cause photochemical decomposition of these metal cyanide complexes.

This chapter begins with a review of the principles of photochemistry, followed by presentation of photochemical information on the cyanide complexes of Co, Fe, and Cr. The chapter concludes with a brief review of the oxidation of free CN^- by O_2 , photocatalyzed by TiO_2 .

PRINCIPLES OF PHOTOCHEMISTRY

A treatise on the photochemistry of metal compounds (1) provides background information. At ambient temperatures, practically all chemical species are in their lowest energy electronic state, termed the "electronic ground state." States at higher electronic energy levels are termed "electronically excited states." A chemical species must absorb light energy to be raised from its ground state to an electronically excited state.

Photochemical reactions are chemical reactions undergone by a chemical species in an electronically excited state. To distinguish photochemical reactions from reactions of chemical species in their electronic ground states, the latter are termed "thermal reactions." Photochemical reactions are particularly important for chemical species that undergo slow thermal reactions. The products obtained in photochemical reactions are often different from the products obtained in thermal reactions. The yield of a product in a photochemical reaction is defined as the number of moles of product formed per mole of photons absorbed by the substrate, and is termed the "quantum efficiency" or "quantum yield." By definition, the maximum value of the quantum yield is 1, unless a chain reaction occurs, in which case quantum yields higher than 1 may be observed. Quantum yields depend on the chemical properties of the species in its electronically excited states and not on the molar absorptivity.

The energy content of a mole of photons is given by

$$E = N^{\circ}hc/L = (1,20 \times 10^8)/L \quad (9-1)$$

where N° = Avogadro's number, $6.02 \times 10^{23} \text{ mol}^{-1}$,

h = Planck's constant, $6.63 \times 10^{-34} \text{ J}\cdot\text{s}$,

c = velocity of light, $2.998 \times 10^8 \text{ m}\cdot\text{s}^{-1}$,

and L = wavelength of light ($\text{\AA}$).¹ For violet light of wavelength 400 nm, equation 9-1 gives $E = 299 \text{ kJ}\cdot\text{mol}^{-1}$.

The accuracy of experimental determination of quantum yields varies from 10 to 50 pct, depending on the magnitude of the quantum yield, the molar absorptivity at the wavelength employed, and the complexity of the system being investigated. The magnitudes of quantum yields depend on the nature of the electronically excited states, which determines what photochemical reactions will occur. Different bands in the absorption spectrum correspond to excitation to different electronically excited states. Consequently, the observed photochemical reactions and quantum yields vary with the wavelength of the absorbed light. Within the wavelength range of a single absorption band, the same photochemical reactions usually occur, and the quantum yield often does not vary greatly.

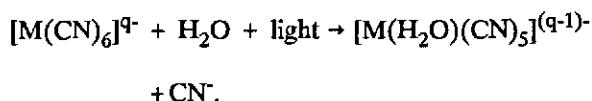
Often the product of a photochemical reaction absorbs light and may undergo further photochemical reactions. The extent to which this occurs may cause experimental difficulties in quantum yield determinations. Consequently, determination of the quantum yield for the first photochemical reaction in an irradiated system can be challenging. There are many examples, such as the hexacyanoferrates, for which there is much disagreement in published quantum yields.

Photochemical reactions also occur indirectly in the form of photosensitized reactions. In photosensitized reactions, an accessory solution species, the photosensitizer, absorbs light and is raised to an excited electronic state. The excited photosensitizer then transfers the energy of its electronic excited state to another species, the substrate, and raises it to an excited electronic state, and the excited substrate undergoes reactions. The energy of the electronic excited state of the photosensitizer must be greater than the energy of the electronic excited state of the substrate. Hence, the photosensitizer must absorb light at a shorter wavelength (higher energy) than the substrate. The excited electronic state of the substrate generated in a photosensitization may be different from the excited electronic states obtained when the substrate absorbs light directly; consequently, different photochemical reactions may occur.

¹Italic numbers in parentheses refer to items in the list of references at the end of this chapter.

Photochemical reaction products may be thermodynamically unstable with respect to the ground-state substrate or its thermal reaction products. If the requisite equilibria are not rapidly established, the photochemical reaction products can be isolated and characterized. The cyanide complexes of Co, Fe, and Cr are characterized by slow thermal reactions. The cyanide complexes of these metals undergo photochemical reactions with formation of reaction products that are thermodynamically unstable with respect to the ground-state substrates. However, those products are relatively unreactive and can be isolated and characterized.

For the hexacyanometallates of Co(III), Fe(II), Fe(III), and Cr(III), the initial photochemical reaction observed in near-ultraviolet irradiation is substitution of one CN^- by H_2O :



The aquopentacyanometallate product is thermodynamically unstable with respect to reacting with CN^- to reform the hexacyanometallate, but the rate of this reaction is relatively slow. If the photochemical decomposition is conducted at pH below 9, the liberated CN^- is converted to HCN and can be easily removed to prevent the reverse of this photochemical reaction. The aquopentacyanometallate product then undergoes other reactions.

Most of the remainder of this chapter reviews the photochemistry of the cyanide complexes of these four metal ions. Sharpe's monograph (2) is the major source of data, but a number of more recent or otherwise important references were also consulted (3-36). Table 5-2 may be consulted to correlate the absorption spectral data with the photochemical data.

COBALT

Near-ultraviolet irradiation of hexacyanocobaltate(III) $[\text{Co}(\text{CN})_6]^{3-}$ results initially in aquation with loss of 1 mol CN^- per mole cobalt and formation of $[\text{Co}(\text{H}_2\text{O})(\text{CN})_5]^{2-}$. The latter is a weak acid and forms $[\text{Co}(\text{OH})(\text{CN})_5]^{2-}$ at pH above about 10. The quantum efficiency of this photochemical reaction at pH 2 to 7 is 0.31, independent of wavelength from 254 to 365 nm (3). Further ultraviolet irradiation results in loss of more CN^- , with formation of $[\text{Co}(\text{H}_2\text{O})_2(\text{CN})_4]^-$ and $[\text{Co}(\text{H}_2\text{O})_3(\text{CN})_3]$ or the hydroxo species formed by dissociation of H^+ from them (4-6). Continued irradiation is said to result in conversion to cobalt oxides, but no data are given (5-6).

Regarding photosensitized aquation of $[\text{Co}(\text{CN})_6]^{3-}$, only one publication on photosensitization by biacetyl, $\text{H}_3\text{C}-\text{CO}-\text{CO}-\text{CH}_3$, was located (7).

Photochemically assisted destructive oxidation of $[\text{Co}(\text{CN})_6]^{3-}$ by O_3 has been reported; no details were given (8).

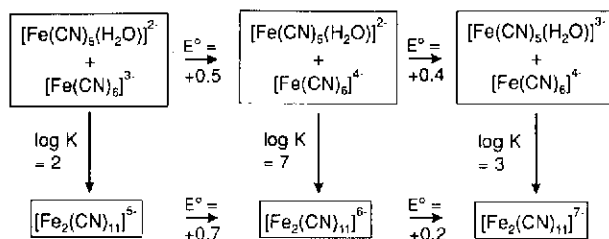
IRON

Near-ultraviolet irradiation of $[\text{Fe}(\text{CN})_6]^{4-}$ results initially in loss of 1 mol CN^- per mole iron and formation of $[\text{Fe}(\text{CN})_5(\text{H}_2\text{O})]^{3-}$. Reported values of the quantum efficiency vary widely. This was attributed to inadequate experimental techniques and the complexity of the system, which was not realized by many earlier investigators (9). The quantum yield is the same at 313 and 365 nm and is constant at pH 4 to 10 (10). The quantum yield was redetermined at 365 nm and is 0.9 at pH 5 to 11, but drops steadily to 0.5 at pH 1 (9). The lower values in acid solution were attributed to formation of $[\text{HFe}(\text{CN})_6]^{3-}$ and $[\text{H}_2\text{Fe}(\text{CN})_6]^{3-}$. The initial product $[\text{Fe}(\text{CN})_5(\text{H}_2\text{O})]^{3-}$ is also photosensitive, but no quantum yield data were located. Intermediates such as $[\text{Fe}(\text{CN})_4(\text{H}_2\text{O})_2]^{2-}$ have not been characterized in aqueous solution at any pH. Continued near-ultraviolet irradiation leads to complete decomposition to Fe^{2+} and HCN in acid solution in the absence of O_2 . In alkaline solution in the presence of O_2 , $[\text{Fe}(\text{CN})_5(\text{H}_2\text{O})]^{3-}$ is oxidized to $[\text{Fe}(\text{CN})_5(\text{OH})]^{3-}$, and continued irradiation results in conversion to Fe(III) oxide products with liberation of free CN^-/HCN , which may be oxidized to an unknown extent.

Irradiation of $[\text{Fe}(\text{CN})_6]^{3-}$ with blue to near-ultraviolet light results initially in loss of 1 mol CN^- per mole iron and formation of $[\text{Fe}(\text{CN})_5(\text{H}_2\text{O})]^{2-}$. The latter species is a weak acid and forms $[\text{Fe}(\text{CN})_5(\text{OH})]^{2-}$ at pH above about 8. As is the case for the Fe(II) system, reported values of the quantum efficiency vary widely, and this may be attributed to inadequate experimental techniques in view of the complexity of the system (11). The quantum efficiency of the reaction is low and independent of pH. The quantum efficiency was redetermined at pH 11 to be 0.04 at 254 nm and 0.016 at 366 nm (11). The initial product $[\text{Fe}(\text{CN})_5(\text{H}_2\text{O})]^{2-}$ or $[\text{Fe}(\text{CN})_5(\text{OH})]^{2-}$ is also photosensitive. The quantum yield for loss of 1 mol CN^- per mole iron from $[\text{Fe}(\text{CN})_5(\text{H}_2\text{O})]^{2-}$ at pH 7 is about 0.015 at 365 nm (12). Intermediates such as $[\text{Fe}(\text{H}_2\text{O})_2(\text{CN})_4]^-$ have not been characterized in aqueous solution at any pH. Continued irradiation results in formation of prussian blue in acid solution or Fe(III) oxides in alkaline solution, with liberation of free CN^-/HCN , which may be oxidized to an unknown extent.

The information in the preceding two paragraphs is summarized in figure 9-1. Figure 9-1 also shows pertinent thermal reactions, such as oxidation by O_2 which are described in chapter 8. With both $[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{Fe}(\text{CN})_6]^{3-}$ in the presence of air, the ultimate product is

Figure 9-1



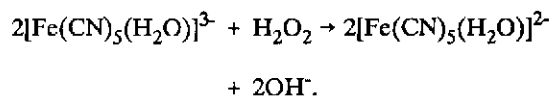
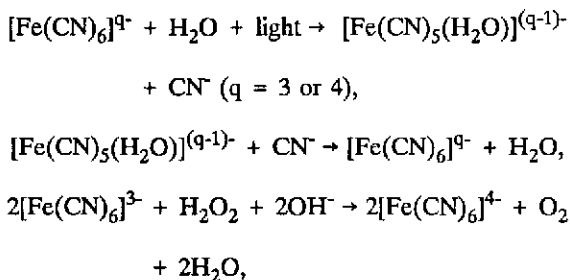
Photochemical decomposition of hexacyanoferrates.

prussian blue in acid solutions and $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ in alkaline solutions.

As noted above, many photochemical studies of iron cyanide species seriously disagree, e.g., in regard to published quantum yields. The disagreements have been attributed to use of nonmonochromatic light, spectrophotometric observations at only one wavelength, failure to prevent oxidation of Fe(II) species by O_2 , competing photochemical reactions of initial products, interfering reactions of analytical reagents, failure to recognize condensation reactions that form dinuclear species (see chapter 8), and the instability of $\text{Na}_3[\text{Fe}(\text{CN})_5(\text{H}_2\text{O})]$ used as a reagent (9, 13).

Broderius (14) published extensive calculations of the photochemical decomposition rates of $[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{Fe}(\text{CN})_6]^{3-}$ as a function of solar illumination versus latitude and time of year. His values of molar absorptivity for both complexes are about 5 pct higher than the values given in table 5-2. He determined the respective quantum yields in sunlight as 0.14 and 0.0023, which are based on liberated CN^-/HCN in the presence of air. These values are much lower than the values given above for the photochemical elimination of 1 mol CN^- per mole iron from $[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{Fe}(\text{CN})_6]^{3-}$, which shows that further photochemical degradation of the initially produced aquopentacyanoferrates is relatively less efficient.

The near-ultraviolet irradiation of $[\text{Fe}(\text{CN})_6]^{4-}$ or $[\text{Fe}(\text{CN})_6]^{3-}$ in alkaline solution in the presence of H_2O_2 results in photocatalytic decomposition of the H_2O_2 (15-16):



The initial photochemical reaction products $[\text{Fe}(\text{CN})_5(\text{H}_2\text{O})]^{(q-1)-}$ undergo thermal condensation reactions with water elimination, with themselves or with $[\text{Fe}(\text{CN})_6]^{q-}$, to form $[\text{Fe}(\text{CN})_{102}(\text{H}_2\text{O})]^{q-}$, $[\text{Fe}_2(\text{CN})_{10}]^{q-}$, and $[\text{Fe}_2(\text{CN})_{11}]^{q-}$, as described in chapter 8. All of these species and their redox and photochemical reactions make the environmental chemistry of iron cyanide species quite complex. As also stated in chapters 5 and 8, many of these iron cyanide species require improved characterization with regard to their visible and ultraviolet absorption spectra and their thermal chemical and photochemical reactions.

The fate of CN^- liberated during photochemical decomposition of $[\text{Fe}(\text{CN})_6]^{q-}$ is unknown. In alkaline photodecomposition of $[\text{Fe}(\text{CN})_6]^{3-}$, CN^- was reported to be oxidized to NCO^- (17-18), but detailed data were not available. It is possible that the presence of Fe(III) species or O_2 leads to oxidation of CN^- to NCO^- in alkaline solutions or to C_2N_2 or HNCO in acid solution. The $[\text{Fe}(\text{CN})_6]^{3-}$ and other Fe(III) species oxidize CN^{3-} to NCO^- in alkaline solution in the presence of catalytically active copper species (see chapter 8). The role of light and the possibility of catalysis by iron oxides, other iron species, other copper species, or other agents such as clays or carbonaceous materials are unknown.

No literature was located regarding photosensitized decomposition of iron cyanide complexes.

Ultraviolet irradiation in the presence of oxidants has been reported to destroy iron cyanide complexes (9, 19-20). With O_3 as the oxidant, total CN^- , 7.6 $\text{mg} \cdot \text{L}^{-1}$ as $[\text{Fe}(\text{CN})_6]^{4-}$ or $[\text{Fe}(\text{CN})_6]^{3-}$, decreased to 0.3 $\text{mg} \cdot \text{L}^{-1}$ in 1 h (19). Another study with ClO_2 as the oxidant was reported (20); the ClO_2 is photodecomposed to reactive radicals that oxidize CN^- . Electrochemical oxidation of liberated CN^- has also been utilized (21). Another Japanese study with no oxidant specified was also reported (22-23).

Photocatalytic degradation of 0.001M $[\text{Fe}(\text{CN})_6]^{3-}$ in sunlight-irradiated 0.01M $\text{TiO}_2 \cdot x\text{H}_2\text{O}$ at pH 10 was recently claimed (24). The $\text{TiO}_2 \cdot x\text{H}_2\text{O}$ suspension was prepared by addition of TiCl_4 to water, and stabilized after alkali addition to pH 10 with polyvinyl alcohol. The disappearance of $[\text{Fe}(\text{CN})_6]^{3-}$ was monitored by absorbance measurements at its 420-nm absorption maximum. The reaction products were assumed, not demonstrated, to be oxidation products of CN^- . The evidence does not necessarily support the claim that $[\text{Fe}(\text{CN})_6]^{3-}$ was degraded. The molar absorptivity of $[\text{Fe}(\text{CN})_6]^{4-}$ at 420 nm is lower than that of $[\text{Fe}(\text{CN})_6]^{3-}$ by a factor of 10^3 (see chapter 5). Titanium(IV) and $[\text{Fe}(\text{CN})_6]^{4-}$ react at pH 2 to form an

orange-colored precipitate (25-26), but at pH 10, $\text{Ti(IV)-[Fe(CN)}_6\text{]}^{4-}$ species would be expected to convert to $\text{TiO}_2 \cdot x\text{H}_2\text{O}$ and dissolved $[\text{Fe(CN)}_6]^{4-}$. If absorbance was monitored at 420 nm alone, $[\text{Fe(CN)}_6]^{4-}$ or the orange $\text{Ti(IV)-[Fe(CN)}_6\text{]}^{4-}$ species would not have been detected. Consequently, the observed disappearance of $[\text{Fe(CN)}_6]^{3-}$ may have been caused simply by photocatalyzed reduction to $[\text{Fe(CN)}_6]^{4-}$ and not by photocatalyzed oxidative degradation of $[\text{Fe(CN)}_6]^{3-}$.

CHROMIUM

Near-ultraviolet irradiation of $[\text{Cr(CN)}_6]^{3-}$ results initially in loss of 1 mol CN^- per mole chromium and formation of $[\text{Cr(H}_2\text{O)(CN)}_5]^{2-}$. The latter species is a weak acid and forms $[\text{Cr(OH)(CN)}_5]^{2-}$ at pH above about 9. Marchaj and Stasicka (27) have reviewed the literature and reported their own observations; the quantum yield is 0.10 to 0.12 at pH 3 to 9 over the wavelength range 265 to 405 nm. Continued near-ultraviolet irradiation results in progressive elimination of more CN^- (27-28), and most of the intermediate species have been characterized as described in chapter 8. The final products are Cr(III) oxides in alkaline or neutral solutions and Cr^{3+} in acid solution. The quantum yield for loss of 1 mol CN^- per mole chromium from $[\text{Cr(H}_2\text{O)(CN)}_5]^{2-}$ at pH 6 is 0.04 at 436 nm; the quantum yield for loss of 1 mol CN^- per mole chromium from $[\text{Cr(OH)(CN)}_5]^{2-}$ at pH 14 is 0.06 at 313 nm and 0.09 at 436 nm (27).

Photosensitized decomposition of hexacyanochromate(III) by acridine, naphthalene, pyrazine, and xanthone has been reported (29).

No publications concerning photochemically assisted oxidative destruction of Cr(III) cyanide complexes were located except for the reported formation of CrO_4^{2-} during irradiation in the presence of O_2 (28). A systematic investigation of this reaction was not conducted.

SUMMARY OF PHOTOCHEMISTRY OF METAL CYANIDE COMPLEXES

The cyanide complexes of Co, Fe, and Cr undergo photochemical reactions in blue to ultraviolet light, i.e., wavelengths below 500 nm. Solar ultraviolet radiation down to 300 nm penetrates to the Earth's surface. The Co, Fe, and Cr cyanide complexes all absorb light in the 300- to 500-nm region, and they are subject to photochemical degradation by solar radiation. The ultimate metal-containing decomposition products in aerated alkaline solutions are metal oxides. The extent to which liberated CN^- is oxidized during environmental photochemical degradation of Co, Fe, and Cr cyanide complexes is not known.

The extent to which photosensitization influences the decomposition of metal cyanide complexes by accessory environmental chemical species such as humic and fulvic acid components has not been adequately investigated.

PHOTOCATALYTIC OXYGEN OXIDATION OF FREE CYANIDE

In 1977, the oxidation of free CN^- by O_2 , catalyzed by both the anatase and rutile forms of TiO_2 and sunlight or artificial ultraviolet light, was reported (30-32). A solution of KCN initially 0.001M was 99 pct oxidized in 2 days of sunlight exposure in the presence of anatase. Cyanate was qualitatively identified as an oxidation product. Tests for other oxidation products apparently were not performed. Photocatalyzed oxidation of CN^- on ZnO and CdS was also reported (31), but ZnO and CdS were reported to degrade after extended use (32).

Other groups of investigators have subsequently investigated the photocatalyzed oxidation of CN^- on TiO_2 (33-37). With anatase, the reaction was 6 times faster at pH 11 than at pH 14; if the anatase was platinized, the rate was 20 times faster than with untreated anatase at pH 11 (34).

Recently it was found that roasted ilmenite photocatalyzed the oxidation of CN^- by O_2 with efficiency comparable to that of anatase (36). Anatase was observed to be more effective than rutile, but this difference was attributed to different specific surface areas (36).

The formation of NCO^- as an oxidation product in the photocatalyzed oxygen oxidation of CN^- was demonstrated (36). Further investigation showed that NCO^- was further photocatalytically oxidized on anatase to NO_2^- and NO_3^- .

REFERENCES

1. Balzani, V., and V. Carassiti. *Photochemistry of Coordination Compounds*. Academic, 1970, 432 pp.
2. Sharpe, A. G. *The Chemistry of Cyano Complexes of the Transition Metals*. Academic, 1976, 302 pp.
3. Adamson, A. W., A. Chiang, and E. Zinato. *Photochemistry of Aqueous Cobalt(III) Cyano Complexes*. *J. Am. Chem. Soc.*, v. 91, 1969, pp. 5467-5475.
4. Wrighton, M., and D. Bredesen. *Photochemistry of Aquo- and Hydroxopentacyanocobaltate(III)*. *Inorg. Chem.*, v. 12, 1973, pp. 1707-1709.
5. Viaene, L., J. D'Olieslager, and S. de Jaegere. *Synthesis and Properties of Cyanoaquo and Cyanohydroxo Complexes of Cobalt(III)*. *J. Inorg. Nucl. Chem.*, v. 37, 1975, pp. 2435-2438.
6. Viaene, L., J. D'Olieslager, and S. de Jaegere. *Isomerization reactions of Tetracyanodiaquocobaltate(III)*. *Inorg. Chem.*, v. 14, 1975, pp. 2736-2739.
7. Scandola, M. A., and F. Scandola. *Photosensitized Reactions of Cobalt(III) Complexes. III. Photoaquation Mechanism of the Hexacyanocobaltate(III) Ion*. *J. Am. Chem. Soc.*, v. 94, 1972, pp. 1805-1810.

8. Fabjan, Ch., and R. Davies. Entgiftung Cyanidhaltiger Abwaesser mit Ozon (Detoxification of Cyanide-Containing Wastewater With Ozone). *Wasser, Luft Bctr.*, v. 30, 1976, No. 4, pp. 175-178.
9. Gaspar, V., and M. T. Beck. Kinetics of the Photoaquation of Hexacyanoferrate(II) Ion. *Polyhedron*, v. 2, 1983, pp. 387-391.
10. Shirom, M., and G. Stein. Excited State Chemistry of the Ferrocyanide Ion in Aqueous Solution. II. Photoaquation. *J. Chem. Phys.*, v. 55, 1971, pp. 3379-3382.
11. Fuller, M. W., K. M. F. Le Brocq, E. Leslie, and I. R. Wilson. The Photolysis of Aqueous Solutions of Potassium Hexacyanoferrate(III). *Aust. J. Chem.*, v. 39, 1986, pp. 1411-1419.
12. Ronco, S. E., and P. J. Aymonino. Kinetics of the Thermal and Photochemical Decomposition of Aquopentacyanoferrate(III) in Aqueous Solution. *Transition Met. Chem. (London)*, v. 12, 1987, pp. 174-178.
13. Bell, S., G. Foster, M. W. Fuller, D. Hughes, K. M. F. Le Brocq, E. Leslie, and I. R. Wilson. Spectrophotometric Measurement of Rates of Hexacyanoferrate(III) Reactions. *Int. J. Chem. Kinet.*, v. 18, 1986, pp. 651-653.
14. Broderius, S. J., and L. L. Smith, Jr. Direct Photolysis of Hexacyanoferrate Complexes. Proposed Applications to the Aquatic Environment. U.S. EPA Rep. EPA-600/3-80-003, Jan. 1980, 49 pp.
15. Eaton, D. R., and M. Pankratz. The Reaction of the Hexacyanoferrate(III) Ion With Hydrogen Peroxide. *Can. J. Chem.*, v. 63, 1985, pp. 793-797.
16. Rabai, G., K. Kustin, and I. R. Epstein. Light-Sensitive Oscillations in the Hydrogen Peroxide Oxidation of Ferrocyanide. *J. Am. Chem. Soc.*, v. 111, 1989, pp. 8271-8273.
17. Ohura, H., Y. Kisaki, and S. Yamasaki. (Photodecomposition of Hexacyanoferrate(III) in Alkaline Solution.) *Kyushu Sangyo Daigaku Kogakubu Kenkyu Hokoku*, v. 24, 1987, pp. 19-24; *Chem. Abstr.*, v. 111, 1989, No. 47918f.
18. Ohura, H., Y. Koide, A. Ohmura, and S. Yamasaki. (Effect of Hydroxide on the Photodecomposition of Hexacyanoferrate(III).) *Kyushu Sangyo Daigaku Kogakubu Kenkyu Hokoku*, v. 25, 1988, pp. 27-30; *Chem. Abstr.*, v. 111, 1989, No. 47909d.
19. Mauk, C. E., H. W. Prengle, Jr., and R. W. Legan. Chemical Oxidation of Cyanide Species by Ozone With Irradiation from Ultraviolet Light. *Trans. SME AIME*, v. 260, 1976, pp. 297-300.
20. Shabunin, I. I., N. I. Plotnikov, and N. N. Nosova. (Removal of Hexacyanoferrates From Waste Waters Using Ultraviolet Light.) *Nauchn. Tr.-Tsentr. Nauchno-Issled. Inst. Olovyannoi Prom-sti.*, 1977, No. 6, pp. 44-48; *Chem. Abstr.*, v. 89, 1978, No. 79708f.
21. Honma, H., H. Mitsu, and H. Abe. (Electrochemical Oxidation of Hexacyanoferrate(II and III) Ions Under Ultraviolet Radiation.) *Nippon Kagaku Kaishi*, 1977, pp. 1400-1404; *Chem. Abstr.*, v. 87, 1977, No. 159011x.
22. Otake, T., S. Tone, I. Komasaawa, and M. Kawashima. (Kinetic Study of Photochemical Decomposition of Alkaline Solution of Iron Complex Cyanides.) *Kagaku Kogaku Ronbunshu*, v. 8, 1982, pp. 59-64; *Chem. Abstr.*, v. 96, 1982, No. 172039t.
23. Otake, T., S. Tone, I. Komasaawa, and M. Kawashima. (Effect of Incident Light Absorbed on the Photochemical Decomposition of Iron Complex Cyanides in Alkaline Solution.) *Kagaku Kogaku Ronbunshu*, v. 8, 1982, pp. 598-603; *Chem. Abstr.*, v. 98, 1983, No. 44030n.
24. Bhakta, D., S. S. Shukla, M. S. Chandrasekharaiah, and J. L. Margrave. A Novel Photocatalytic Method for Detoxification of Cyanide Wastes. *Environ. Sci. Technol.*, v. 26, 1992, pp. 625-626.
25. Vrachnou, E., N. Vlachopoulos, and M. Graetzel. Efficient Visible Light Sensitization of Titanium Dioxide by Surface Complexation With $\text{Fe}(\text{CN})_6^{4-}$. *J. Chem. Soc., Chem. Commun.*, 1987, pp. 868-870.
26. DeSilvestro, J., S. Pons, E. Vrachnou, and M. Graetzel. Electrochemical and FTIR Spectroscopic Characterization of Ferrocyanide-Modified Titanium Dioxide Electrodes Designed for Efficient Photosensitization. *J. Electroanal. Chem. Interfacial Electrochem.*, v. 246, 1988, pp. 411-422.
27. Marchaj, A., and Z. Stasicka. Photosubstitution in Some Cyanide Complexes of Chromium(III). *Polyhedron*, v. 2, 1983, pp. 485-487.
28. Marchaj, A., Z. Stasicka, and D. Rehorek. Photochemical Production of Chromate(VI) Ions From Some Chromium(III) Complexes. *Polyhedron*, v. 2, 1983, pp. 1281-1286.
29. Sabbatini, N., M. A. Scandola, and V. Carassiti. Role of the Excited States in the Photoreaction of the Hexacyanochromate(III) Ion. Sensitization Study. *J. Phys. Chem.*, v. 77, 1973, pp. 1307-1311.
30. Frank, S. N., and A. J. Bard. Heterogeneous Photocatalytic Oxidation of Cyanide Ion in Aqueous Solutions at TiO_2 Powder. *J. Am. Chem. Soc.*, v. 99, 1977, pp. 303-304.
31. Frank, S. N., and A. J. Bard. Heterogeneous Photocatalytic Oxidation of Cyanide and Sulfite in Aqueous Solutions at Semiconductor Powders. *J. Phys. Chem.*, v. 81, 1977, pp. 1484-1488.
32. Frank, S. N., and A. J. Bard. Semiconductor Electrodes. 12. Photoassisted Oxidations and Photoelectrosynthesis at Polycrystalline TiO_2 Electrodes. *J. Am. Chem. Soc.*, v. 99, 1977, pp. 4667-4675.
33. Kogo, K., H. Yoneyama, and H. Tamura. Photocatalytic Oxidation of Cyanide on Platinized TiO_2 . *J. Phys. Chem.*, v. 84, 1980, pp. 1705-1710.
34. Rose, T. L., and C. Nanjundiah. Rate Enhancement of Photooxidation of CN^- With TiO_2 Particles. *J. Phys. Chem.*, v. 89, 1985, pp. 3766-3771.
35. Peral, J., J. Munoz, and X. Domenech. Photosensitized CN^- Oxidation Over TiO_2 . *J. Photochem. Photobiol., A: Chem.*, v. 55, 1990, pp. 251-257.
36. Zhang, J., J. L. Hendrix, and M. E. Wadsworth. Photocatalytic Oxidation of Cyanide. Ch. in *EPD Congress 1991*, ed. by D. R. Gaskell. TMS-AIME, 1991, pp. 665-677.
37. Milosavljevic, E. B., L. Solujic, J. L. Hendrix, C. H. Pollema, and J. H. Nelson. Photochemically Induced Reactions of Cyanide Ion. Ch. in *EPD Congress 1992*, ed. by J. P. Hager. TMS-AIME, 1992, pp. 205-221.

CHAPTER 10.—MIXTURES OF METAL CYANIDE SPECIES

INTRODUCTION

Cyanide process and waste solutions usually contain mixtures of cyanide species of different metals. This chapter addresses reactions between metal cyanide species and the cations and oxide species of different metals. These reactions are important under the following circumstances:

1. Insufficient CN^- is present to convert all cyanide-reactive metal species to anionic cyanide complexes. This situation occurs when oxidative removal of CN^- or natural degradation of cyanide species is incomplete.

2. Metal salts, such as Fe(II) salts, are intentionally added to precipitate cyanides. Iron(II) reacts with free CN^- and the CN^- in most weak-acid dissociable (WAD) cyanide species to form hexacyanoferrate (II) $[\text{Fe}(\text{CN})_6]^{4-}$, which is precipitated by excess Fe(II), Fe(III), or other metal cations. This practice has been employed by some processors to rapidly and inexpensively mitigate the toxicity of cyanides. However, as discussed in this chapter, the reaction of cyanide complexes of Hg, Cu, Ag, and Ni with Fe(II) salts is incomplete. This behavior correlates with the partially WAD classification of the cyanide complexes of Hg, Cu, and Ag discussed in chapter 8.

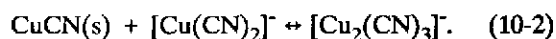
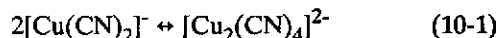
Sharpe's monograph (1)¹ is the major source of data on this subject. Other pertinent or more recent references are cited where appropriate.

REACTIONS BETWEEN DISSOLVED METAL CYANIDE SPECIES

Existence of Polynuclear Metal Cyanide Complexes of Individual Metals

The published equilibrium data for cyanide species of Zn(II), Cd(II), Hg(II), Cu(I), Ag(I), and Ni(II) (appendix D) were obtained at metal concentrations below 0.01M and show no evidence of formation of polynuclear species. Formation of polynuclear species would be favored by high metal concentrations, >0.01M, and low CN^- -metal mole ratios, CN^- -metal <3. In the Zn(II), Cu(I), Ag(I), and Ni(II) systems, the low solubility of $\text{Zn}(\text{CN})_2$, CuCN, AgCN, and $\text{Ni}(\text{CN})_2$, respectively, opposes the formation of polynuclear species, except possibly in concentrated solutions of the anionic complexes. In the case of Cu(I),

salts such as $\text{KCu}_2(\text{CN})_3$ are known; in concentrated solutions, with $\text{Cu(I)} > 0.1M$, equilibria involving polynuclear species may exist:



Reaction 10-2 implies a higher solubility of CuCN in concentrated Cu(I)- CN^- solutions than indicated by known equilibrium data.

In the Hg(II)- CN^- system, $\text{Hg}(\text{CN})_2$ is soluble, and there is evidence for polynuclear cyanide species in solutions of $\text{Hg}(\text{CN})_2$ and Hg(II) salts such as $\text{Hg}(\text{ClO}_4)_2$, e.g., $[\text{Hg}_2(\text{CN})_2]^{2+}$ (see table D-5). The soluble $\text{Cd}(\text{CN})_2$ may also form polynuclear complexes, but investigations of solutions of sufficiently high concentration have not been published.

Dinuclear iron cyanide complexes are formed by condensation reactions involving the photochemically generated pentacyanoferrates, as described in chapters 8 and 9. They are all unstable with respect to decomposition to hexacyanoferrates and insoluble iron cyanides. Dinuclear cyanide complexes are known for Co(II) and Mn(III), and are likely for Co(III) and Cr(III), as discussed in chapter 8.

In summary, polynuclear metal cyanide complexes are not expected to exist to a significant extent in mineral-processing solutions, where metal concentrations rarely exceed $10^{-2}M$. A possible exception may be iron cyanide complexes formed via photochemical reactions.

Existence of Polynuclear Cyanide Complexes in Mixtures of Different Metals

The considerations raised in connection with polynuclear cyanide complexes in solutions containing a single metal apply also to solutions containing more than one metal. In metallurgical solutions, soluble mixed-metal polynuclear cyanide complexes such as $[\text{CuAg}(\text{CN})_4]^{2-}$ are thus not expected to exist to a significant extent.

Complexes of the soluble $\text{Hg}(\text{CN})_2$ with other metal species are known. The $\text{Hg}(\text{CN})_2$ forms weak complexes (log K about 2) with the hexacyanoferrates, e.g. $[\text{Hg}(\text{CN})_2\text{Fe}(\text{CN})_6]^{4-}$, and other cyanometallate anions. Some metal cations, e.g., Ag^+ , also form weak complexes with $\text{Hg}(\text{CN})_2$. In these complexes, $\text{Hg}(\text{CN})_2$, which has a linear molecular structure NC-Hg-CN , functions like an organic nitrile R-CN , where R is an alkyl or aryl group. It is possible that $\text{Cd}(\text{CN})_2$ behaves similarly.

¹Italic numbers in parentheses refer to items in the list of references at the end of this chapter.

REACTIONS BETWEEN ANIONIC METAL CYANIDE SPECIES AND METAL CATIONS

Cyanide Species of Zinc, Cadmium, Mercury, Copper, Silver, and Nickel

The anionic cyanide complexes of Zn(II), Cd(II), Hg(II), Cu(I), Ag(I), and Ni(II) give precipitates with many heavy-metal cations. Little is known about the details of those reactions.

In some cases, there is evidence that the precipitates contain the same species as the solutions from which they were formed, e.g., $\text{Zn}[\text{Ni}(\text{CN})_4] \cdot x\text{H}_2\text{O}$. If the cation forms a stronger cyanide complex than the metal in the anionic cyanide complex initially present, the solid compound is subject to decomposition or rearrangement. For example, the yellow $[\text{Ni}(\text{CN})_2]^{2-}$ is about 10 log K units stronger than the colorless $[\text{Zn}(\text{CN})_4]^{2-}$. Addition of a solution of a Ni^{2+} salt to a solution of $[\text{Zn}(\text{CN})_4]^{2-}$ gives a light-green precipitate of $\text{Ni}[\text{Zn}(\text{CN})_4] \cdot x\text{H}_2\text{O}$, which rearranges to yellow $\text{Zn}[\text{Ni}(\text{CN})_4] \cdot x\text{H}_2\text{O}$.

In other cases, the obtained precipitates may be merely mixtures of the binary neutral cyanides of the component metals. With $\text{Hg}(\text{CN})_4^{2-}$, decomposition to soluble $\text{Hg}(\text{CN})_2$, free CN^- , and the cyanide of the other metal may occur.

No equilibrium data are available for any of the reactions just described. However, equilibrium data for cyanide species and other species of the individual metal ions can be used to indicate possible reactions between metal cyanide species and other species of different metals such as cations and oxides. This subject is treated subsequently in this chapter.

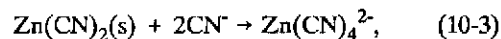
Hexacyanometallates

The hexacyanometallates of Co(III), Fe(II), Fe(III), Mn(III), and Cr(III) all give precipitates with heavy metal cations (1-2). Of these, the heavy-metal hexacyanoferrates are the best known. These compounds nearly always form as colloids or gelatinous precipitates that are not stoichiometric. They contain variable quantities of the alkali ion from the hexacyanometallate salt and variable quantities of water of hydration. Alkali metal ions can be excluded from the precipitates by using an excess of heavy-metal cation. Because of these compositional variations, there are few quantitative studies of their solubility equilibria, and the available data are of uncertain reliability. Solubility-product data for hexacyanoferrate precipitates (3-12) are compiled in table 10-1.

REACTIONS BETWEEN METAL CYANIDE SPECIES AND METAL CATIONS OR OXIDE SPECIES

General

In cyanide solutions in which there is insufficient CN^- to form soluble species of all cyanide-reactive metals, it is important to know the speciation of different metals and the reactions that may occur between these species. In such cyanide-deficient systems, metals may precipitate as cyanides, oxide species, or compounds with accessory anions such as CO_3^{2-} . The equilibrium data for metal cyanide and oxide species (appendix D) can be used to predict the reactions of individual metal species and the reactions between cyanide species and cations and oxide species of different metals. In considering these reactions, a convenient quantity to use is the ratio of log K for the reaction to the number of moles, n , of CN^- transferred. For example, for the reaction



log K from table D-2 = +4.0, and $n = 2$, so $(\log K)/n = +2.0$. Values of $(\log K)/n$ for several reactions are compiled in table 10-2. In table 10-2, the reactions are arranged in order of decreasing $(\log K)/n$, constituting a replacement series, which is analogous to the "electromotive force" series used in connection with metal cementation. Metal cations will displace CN^- from metal cyanide species with lower values of $(\log K)/n$.

In table 10-2, the reactions for the metal species could be rewritten with HCN instead of CN^- on the left sides of the equations. The $(\log K)/n$ values for the rewritten reactions would all be more negative by 9.2 log units than the tabulated values.

Note in table 10-2 that the values of $(\log K)/n$ for the hexacyanoferrates are intermediate. The hexacyanoferrates are often thought of as being stable complexes. Thermodynamically, the hexacyanoferrates are of intermediate stability; kinetic factors are responsible for their inertness. The iron cyanide complexes are discussed further below as well as in chapters 8 and 9.

Table 10-2 portrays an oversimplified picture of reactions between different metals in cyanide systems, because cyanide solutions are alkaline, and metal oxide species are present. Table 10-3 lists $(\log K)/n$ values for reactions of metal oxide compounds with CN^- , in the same format as table 10-2.

Table 10-1.-Solubility products of some heavy-metal hexacyanoferrates at 25° C

Cation	-Log K_{so}		$^1\Delta_f G^\circ$
	Reported	Selected	
$M_4Fe(CN)_6$:			
Cu	N	² 42	696.9
Ag	38-44	38	832.5
Hg ³	N	⁴ 26	899.8
$M_2Fe(CN)_6$:			
Pb	16-18	17	596.0
Zn	14-17	16	355.7
Cd	15-17	16	494.5
Hg	N	⁵ 20	956.0
Cu	14-17	16	780.1
Ni	13-15	16	560.9
Co	15-16	16	538.1
Mn	N	⁶ 15	193.4
$M_3Fe(CN)_6$:			
Cu	N	⁷ 35	722.9
Ag	28	28	847.5
Hg ³	⁸ 18	18	903.7
$M_3[Fe(CN)_6]_2$:			
Pb	N	⁹ 18	1,377.3
Zn	N	⁹ 18	1,008.3
Cd	18	18	1,216.5
Hg	N	⁵ 22	1,920.2
Cu	24	⁹ 20	1,633.4
Ni	N	⁹ 20	1,304.6
Co	N	⁹ 20	1,270.4
Mn	14-18	18	756.3

N No data.

¹Calculated from selected value of log K_{so} and $\Delta_f G^\circ$ data in tables in appendix D.

²Estimated from data for Ag(I) compound and for Cu(I) and Ag(I) complexes with CH_3CN in references 5 and 6.

³ $(1/2)Hg_2^{2+}$.

⁴Taken as 10 units higher than mean value for Zn, Cd, etc. analogs, by proportion to data for corresponding $[Fe(CN)_6]^{3-}$ compounds.

⁵Estimated as less soluble than Zn, Cd, etc. analogs.

⁶Estimated as 1 unit lower than mean value of Zn, Cd, etc. analogs, by proportion to data for corresponding $[Fe(CN)_6]^{3-}$ compounds.

⁷Estimated by same consideration as for $[Fe(CN)_6]^{4-}$ compound, with increase for interaction due to mixed Cu oxidation states.

⁸Estimated as approximately equal to value for $[Co(CN)_6]^{3-}$ analog in reference 5.

⁹Estimated as comparable to values for Cd and Mn compounds, as is the case for corresponding $[Fe(CN)_6]^{4-}$ compounds.

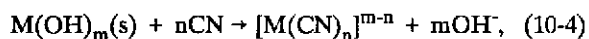
Note: Reported data (3-12) vary as indicated by ranges in values, owing to variations in composition.

Table 10-2.-Relative stabilities of some metal cyanide complexes

Reaction (X = CN)			(log K)/n ¹
Cu ⁺	+ X ⁻	→ CuX(s)	19.5
Hg ²⁺	+ 2X ⁻	→ HgX ₂	16.4
Ag ⁺	+ X ⁻	→ AgX(s)	15.7
Tl ³⁺	+ 2X ⁻	→ TlX ₂ ⁺	13.0
Co ³⁺	+ 6X ⁻	→ CoX ₆ ³⁻	(12.17)
Ni ²⁺	+ 2X ⁻	→ NiX ₂ (s)	9.75
H ¹⁺	+ X ⁻	→ HX	9.2
Fe ²⁺	+ 2X ⁻	→ (1/3)Fe ₂ Fe(CN) ₆ (s)	(8.55)
Zn ²⁺	+ 2X ⁻	→ ZnX ₂ (s)	7.8
Fe ³⁺	+ 6X ⁻	→ FeX ₆ ³⁻	7.05
TlX ₂ ⁺	+ 2X ⁻	→ TlX ₄ ⁻	7.0
Fe ²⁺	+ 6X ⁻	→ FeX ₆ ⁴⁻	5.9
Mn ³⁺	+ 6X ⁻	→ MnX ₆ ³⁻	(5.83)
Cd ²⁺	+ 2X ⁻	→ CdX ₂	5.55
Cr ³⁺	+ 6X ⁻	→ CrX ₆ ³⁻	(5.5)
NiX ₂ (s)	+ 2X ⁻	→ NiX ₄ ²⁻	5.35
(1/3)Fe ₂ Fe(CN) ₆	+ 4X ⁻	→ FeX ₆ ⁴⁻	(4.58)
AgX(s)	+ X ⁻	→ AgX ₂ ⁻	4.8
CuX(s)	+ 2X ⁻	→ CuX ₃ ²⁻	3.75
CdX ₂	+ 2X ⁻	→ CdX ₄ ²⁻	3.4
HgX ₂	+ 2X ⁻	→ HgX ₄ ²⁻	3.1
ZnX ₂ (s)	+ 2X ⁻	→ ZnX ₄ ²⁻	2.0
Mn ²⁺	+ 6X ⁻	→ MnX ₆ ⁴⁻	(1.67)

¹n is the number of free CN⁻ (= X) on left side of reaction equation. Values in parentheses are estimated. Data are from tables in appendix D.

To compare different metal-cyanide reactions as a function of pH, it is necessary to write equations to express the pH dependence. For a reaction



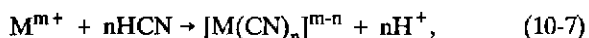
define

$$(\log K^*)/n = (\log K)/n = (m/n) \log [OH^-] \quad (10-5)$$

or

$$(\log K^*)/n = (\log K)/n + (m/n) (14 - pH). \quad (10-6)$$

Similarly, for a reaction in acid solution



write

$$(\log K^*)/n = (\log K)/n + (1/n) (pH). \quad (10-8)$$

Plots of (log K^{*})/n versus pH in accordance with equations 10-6 and 10-8 for different metal-cyanide reactions are shown in figure 10-1. At pH below 9.2, HCN is the predominant free cyanide species, and all reactions are written with HCN instead of CN⁻, and their (log K^{*})/n values are computed and plotted accordingly. Figure 10-1 may be used as a replacement series in the same way as mentioned for table 10-2. At a given pH value, metal cations or oxide species displace CN⁻ from metal cyanide species with lower values of (log K^{*})/n.

Examples of the use of tables 10-2 and 10-3 and figure 10-1 are given in chapter 11, in which examples of practical equilibrium problems are provided.

Reactions Involving Iron

The toxicity of cyanide species may be rapidly and inexpensively mitigated by addition of Fe(II) salts, which react with free CN⁻ and the CN⁻ in WAD cyanide species to form [Fe(CN)₆]⁴⁻. The [Fe(CN)₆]⁴⁻ may undergo oxidation to [Fe(CN)₆]³⁻. Photochemical decomposition of

Table 10-3.-Some reactions of metal oxide compounds with cyanide

Reaction (X = CN)				(log K)/n ¹
Ag ₂ O(s)	+	H ₂ O + 2X ⁻	→ 2AgX(s) + 2OH ⁻	+8.0
Ag ₂ O(s)	+	H ₂ O + 4X ⁻	→ 2AgX ₂ ⁻ + 2OH ⁻	+6.4
Hg(OH) ₂		+ 2X ⁻	→ HgX ₂ + 2OH ⁻	+5.5
Cu ₂ O(s)	+	H ₂ O + 2X ⁻	→ 2CuX(s) + 2OH ⁻	+4.8
Hg(OH) ₂		+ 4X ⁻	→ HgX ₄ ²⁻ + 2OH ⁻	+4.3
Cu ₂ O(s)	+	H ₂ O + 6X ⁻	→ 2CuX ₃ ²⁻ + 2OH ⁻	+4.1
HgO(s)	+	H ₂ O + 2X ⁻	→ HgX ₂ + 2OH ⁻	+3.7
HgO(s)	+	H ₂ O + 4X ⁻	→ HgX ₄ ²⁻ + 2OH ⁻	+3.4
Fe(OH) ₂ (s)		+ 6X ⁻	→ FeX ₆ ⁴⁻ + 2OH ⁻	+3.37
Ni(OH) ₂ (s)		+ 4X ⁻	→ NiX ₄ ²⁻ + 2OH ⁻	+3.25
Ni(OH) ₂ (s)		+ 2X ⁻	→ NiX ₂ (s) + 2OH ⁻	+1.15
Fe(OH) ₂ (s)		+ 2X ⁻	→ (1/3)Fe ₂ FeX ₆ (s) + 2OH ⁻	(+0.95)
Cd(OH) ₂ (s)		+ 4X ⁻	→ CdX ₄ ²⁻ + 2OH ⁻	+0.88
ZnO(s)	+	H ₂ O + 4X ⁻	→ ZnX ₄ ²⁻ + 2OH ⁻	+0.72
Cr(OH) ₃ (s)		+ 6X ⁻	→ CrX ₆ ³⁻ + 3OH ⁻	(+0.17)
FeO(OH)(s)	+	H ₂ O + 6X ⁻	→ FeX ₆ ³⁻ + 3OH ⁻	+0.1
Mn(OH) ₂ (s)		+ 6X ⁻	→ MnX ₆ ⁴⁻ + 2OH ⁻	(-0.47)
ZnO(s)	+	H ₂ O + 2X ⁻	→ ZnX ₂ (s) + 2OH ⁻	-0.55
Tl ₂ O ₃ (s)	+	3H ₂ O + 8X ⁻	→ 2TlX ₄ ⁻ + 6OH ⁻	-1.18
MnO(OH)(s)	+	H ₂ O + 6X ⁻	→ MnX ₆ ³⁻ + 3OH ⁻	(-1.2)
Cd(OH) ₂ (s)		+ 2X ⁻	→ CdX ₂ + 2OH ⁻	-1.65

¹n is the number of free CN⁻ (= X) on left side of reaction equation. Values in parentheses are estimated. Data are from tables in appendix D.

[Fe(CN)₆]⁴⁻ and [Fe(CN)₆]³⁻ liberates CN⁻, so the practice of adding Fe(II) salts to lower cyanide toxicity may be counterproductive. However, if [Fe(CN)₆]⁴⁻ and [Fe(CN)₆]³⁻ are precipitated by metal cations such as excess Fe²⁺, the precipitates may resist photochemical decomposition. Complete precipitation of [Fe(CN)₆]⁴⁻ and [Fe(CN)₆]³⁻ generally requires that the pH be near 7. The reactions of some metal cations and oxide species in the presence of [Fe(CN)₆]⁴⁻ are illustrated in equilibrium predominance area diagrams (EPAD) in figures E-17, E-39, E-148, E-97, E-165, E-167, and E-168.

Tables 10-2 and 10-3 and figure 10-1 can be used for predicting reactions in which [Fe(CN)₆]⁴⁻ is formed, but not reactions in which [Fe(CN)₆]⁴⁻ would be decomposed, owing to its kinetic inertness. They are useful for predicting the reactions of added Fe²⁺, e.g., FeSO₄, with different metal cyanide species. Figure 10-1 shows that Fe(OH)₂(s) reacts with different metal cyanide species at pH near 11 to form [Fe(CN)₆]⁴⁻ and the reaction product of the other metal as follows:

Zn: Converted to oxide species
 Cd: Converted to oxide species
 Hg: Converted to Hg(CN)₂ or Hg(OH)(CN)
 Cu: Converted to CuCN(s)

Ag: Converted to AgCN(s)
 Ni: No reaction
 Mn: Converted to oxide species

At pH near 7, the metal oxide species may react to precipitate Fe(CN)₆⁴⁻ or Fe(CN)₆³⁻. The kinetically inert Co(CN)₆³⁻ and Cr(CN)₆³⁻ are also precipitated by Fe²⁺ and other heavy-metal cations at pH near 7.

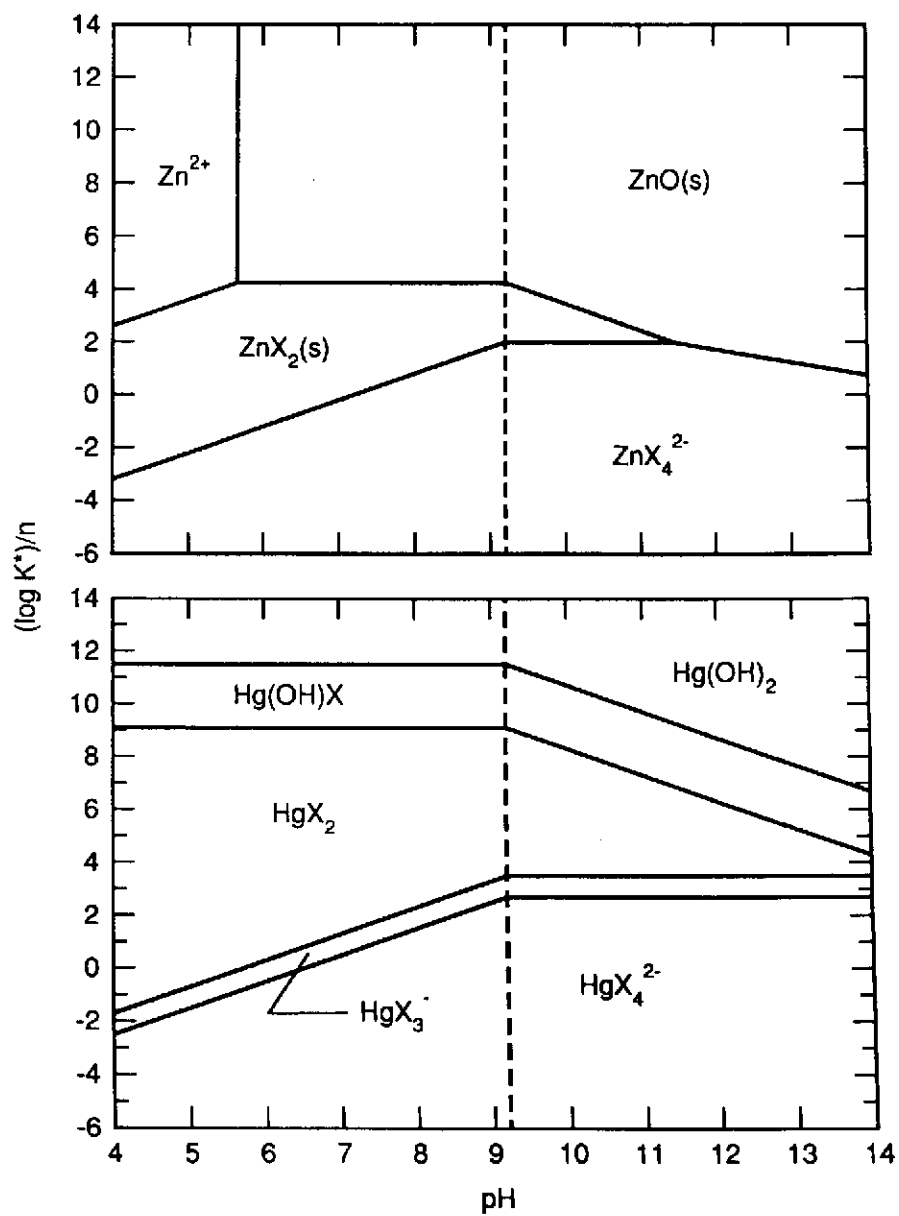
Reactions Involving Copper(II)

As noted in chapter 8, Cu(II) oxidizes CN⁻ and is reduced to Cu(I). The reaction



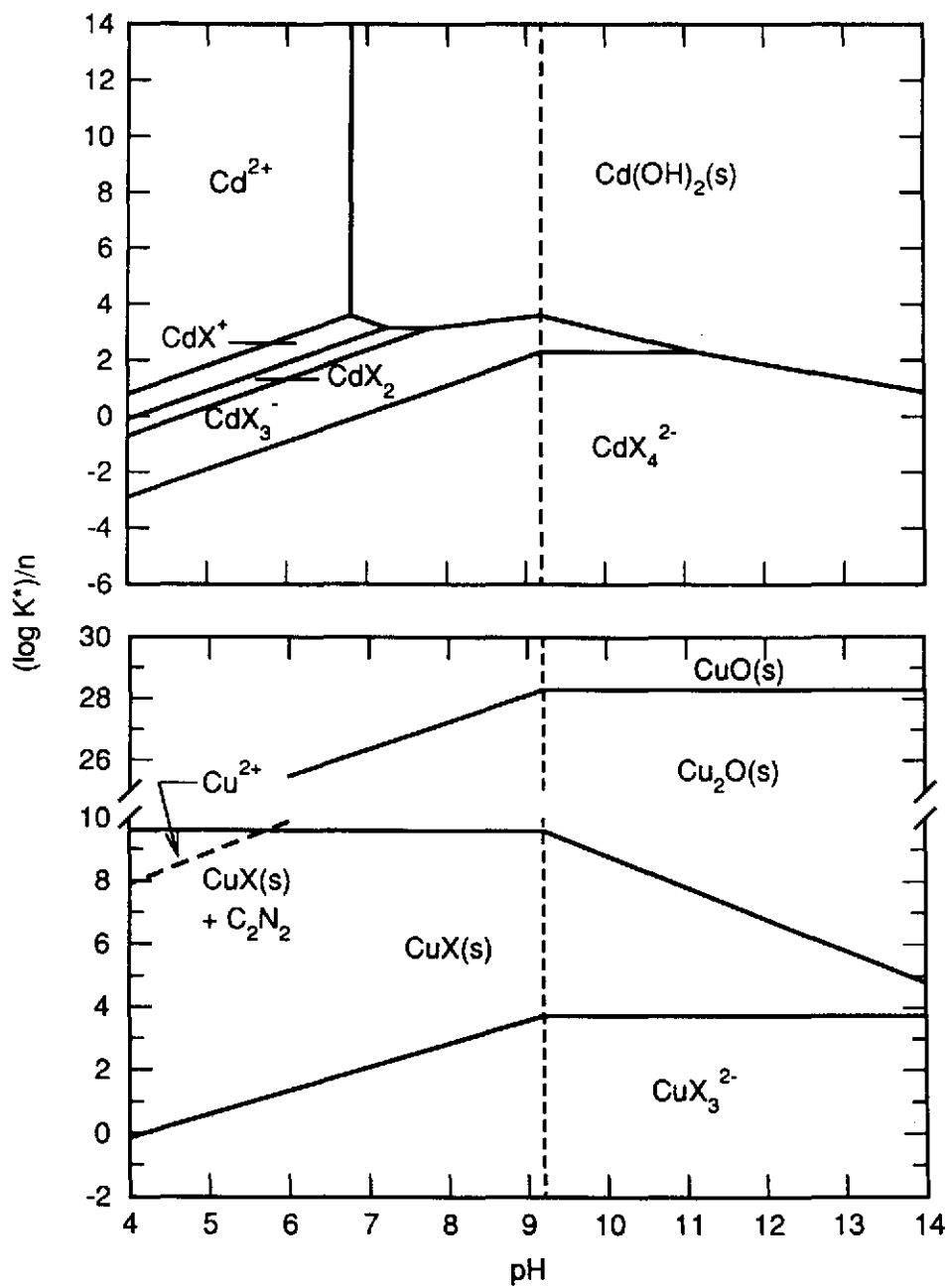
with uncomplexed Cu(I) as product, has a log K value of +39.4. In reality, the product Cu(I) is always precipitated or complexed by CN⁻ or other ligands, and the value of log K is larger. Data for the reactions are compiled in table 10-4. In table 10-4, values of (log K)/n, where n is the number of moles of CN⁻ reacting, are also listed, as in table 10-3. The values of log K are so large that Cu(II) in any form, such as CuO, ammonia complexes, or EDTA complex, oxidizes CN⁻. Values of (log K*)/n, defined as

Figure 10-1



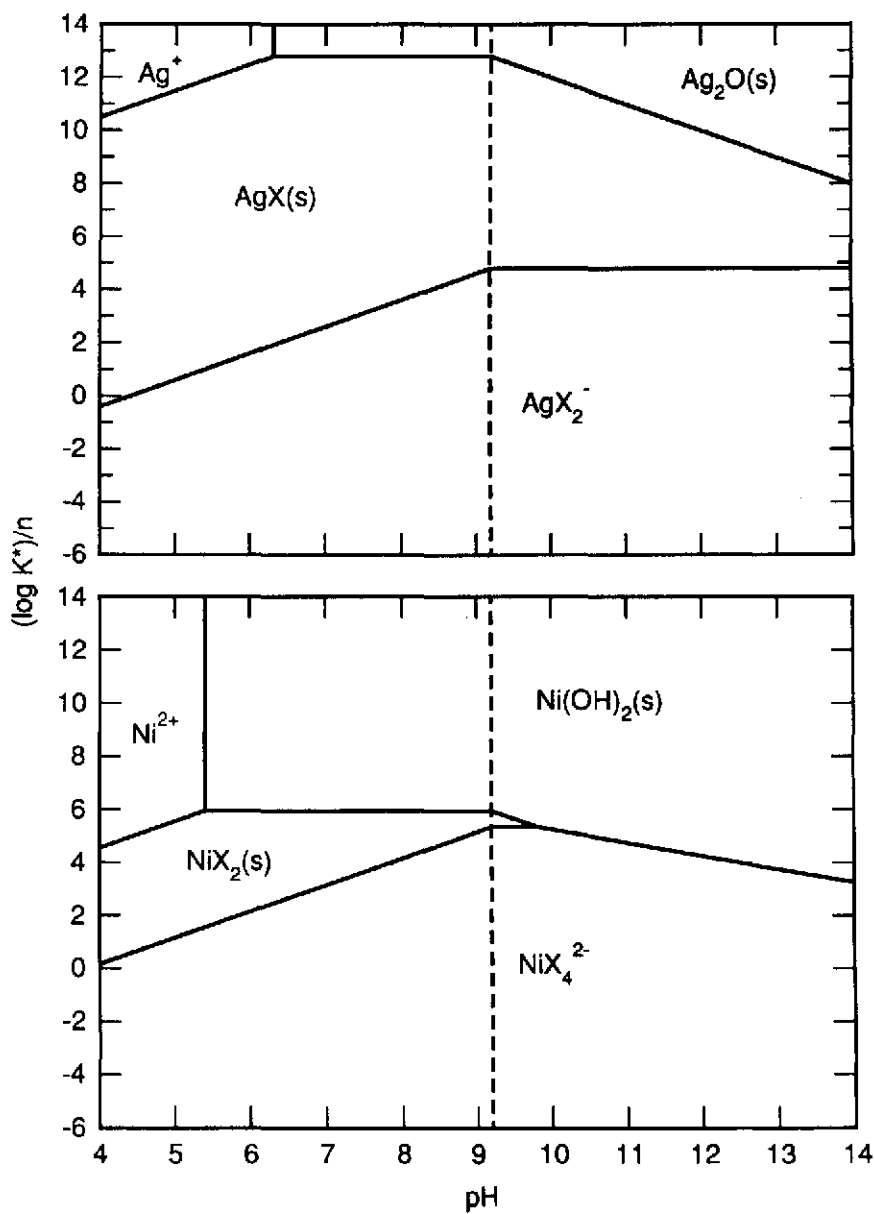
Plots of $(\log K^*)/n$ for metal cyanide species. Superposition of plots for different metal ions provides a replacement series for metal cyanide species. In each diagram, X in formulas denotes CN⁻; the plots all show breaks at $pH = 9.2 = pK_a$ of HCN.

Figure 10-1-Continued



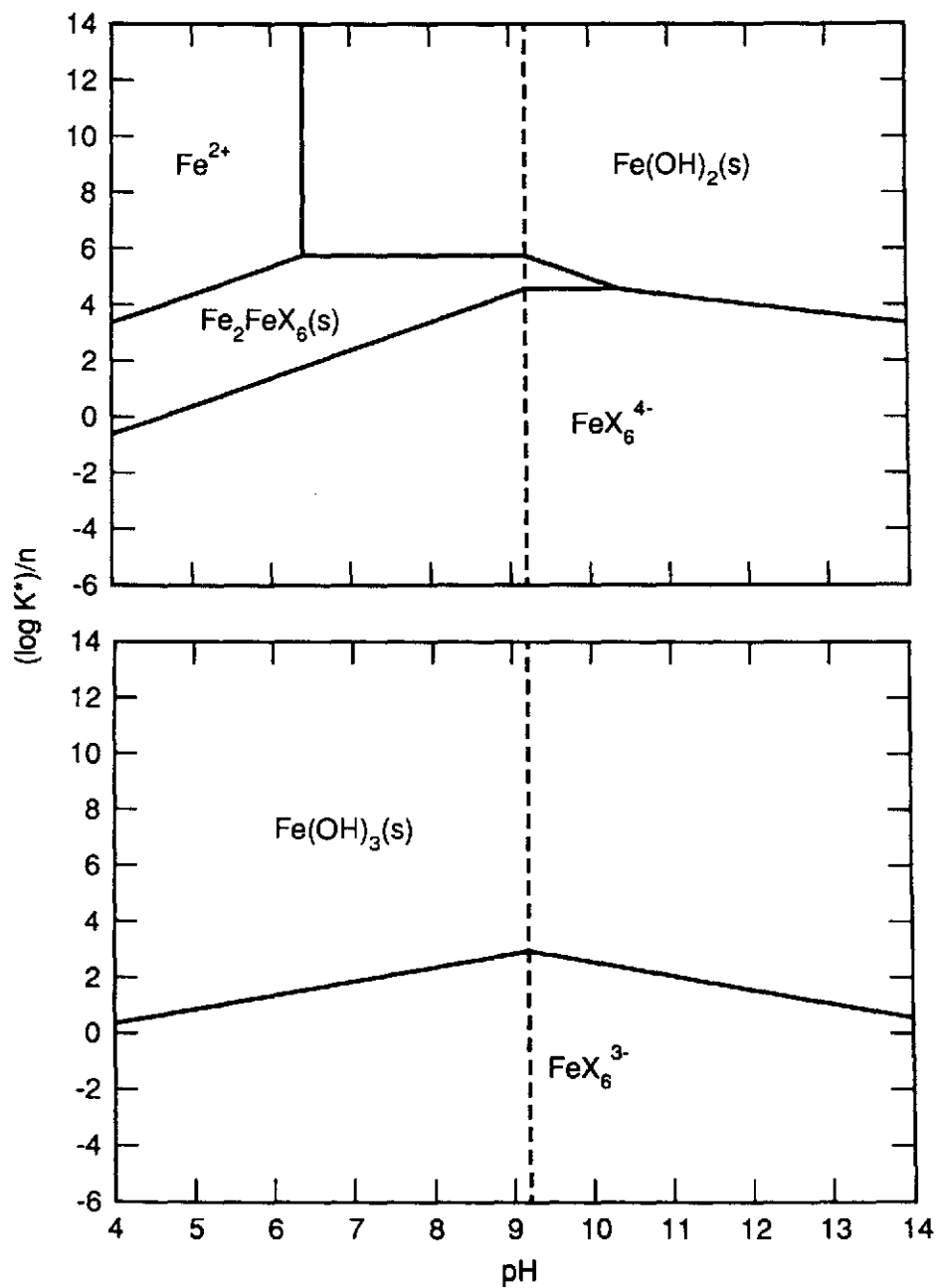
Plots of $(\log K^*)/n$ for metal cyanide species. Superposition of plots for different metal ions provides a replacement series for metal cyanide species. In each diagram, X in formulas denotes CN ; the plots all show breaks at $\text{pH} = 9.2 = \text{pK}_a$ of HCN .

Figure 10-1-Continued



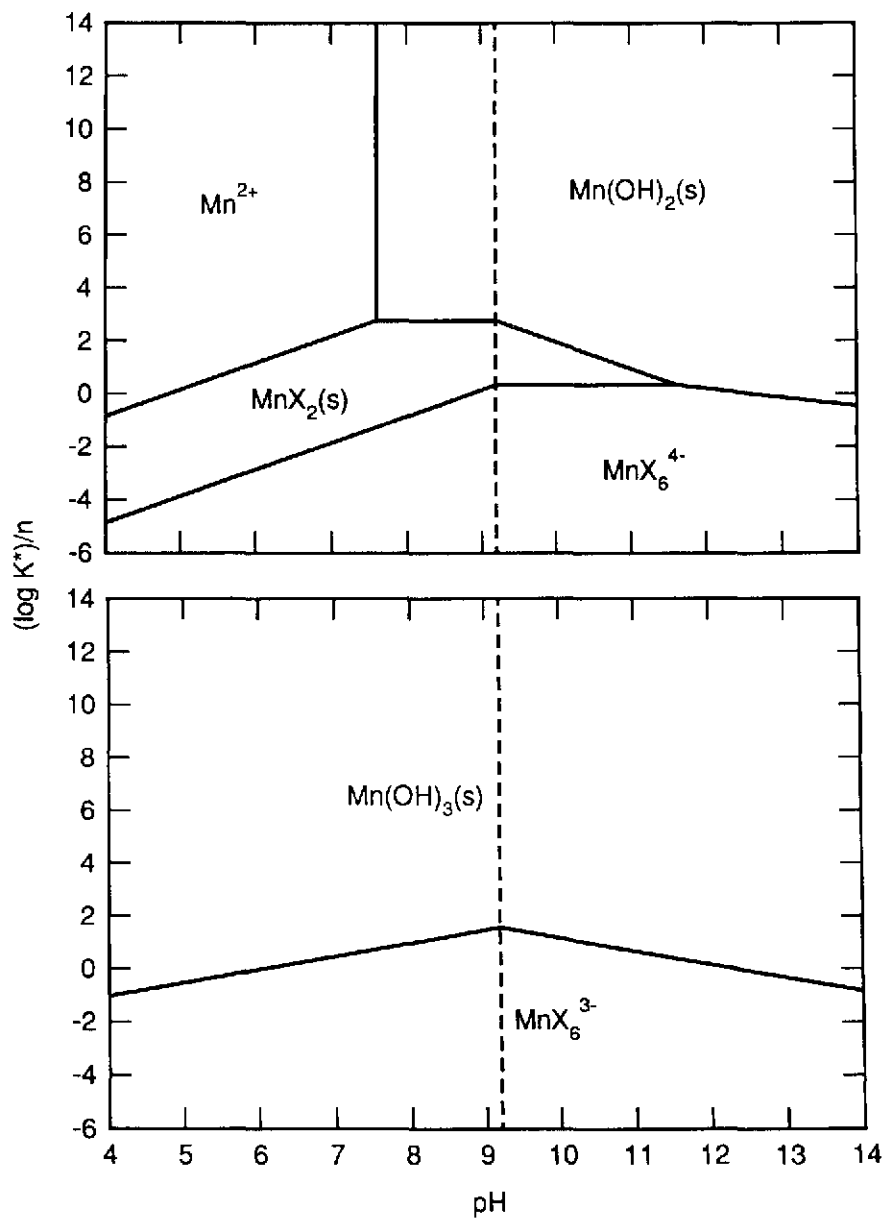
Plots of $(\log K^*)/n$ for metal cyanide species. Superposition of plots for different metal ions provides a replacement series for metal cyanide species. In each diagram, X in formulas denotes CN; the plots all show breaks at $\text{pH} = 9.2 = \text{pK}_a$ of HCN.

Figure 10-1-Continued



Plots of $(\log K^*)/n$ for metal cyanide species. Superposition of plots for different metal ions provides a replacement series for metal cyanide species. In each diagram, X in formulas denotes CN; the plots all show breaks at $\text{pH} = 9.2 = \text{p}K_a$ of HCN.

Figure 10-1-Continued



Plots of $(\log K^*)/n$ for metal cyanide species. Superposition of plots for different metal ions provides a replacement series for metal cyanide species. In each diagram, X in formulas denotes CN⁻; the plots all show breaks at $pH = 9.2 = pK_a$ of HCN.

Table 10-4.-Reactions of copper(II) with cyanide species

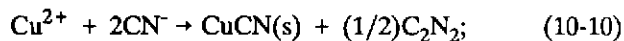
Reaction (X = CN)	log K	(log K)/n ¹
$2\text{Cu}^{2+} + 7\text{X}^- + 2\text{OH}^- \rightarrow 2\text{CuX}_3^{2-} + \text{NCO}^- + \text{H}_2\text{O}$	93.4	13.34
$2\text{Cu}^{2+} + 5\text{X}^- + 2\text{OH}^- \rightarrow 2\text{CuX}_2^- + \text{NCO}^- + \text{H}_2\text{O}$	82.8	16.56
$2\text{Cu}^{2+} + 3\text{X}^- + 2\text{OH}^- \rightarrow 2\text{CuX(s)} + \text{NCO}^- + \text{H}_2\text{O}$	78.4	26.13
$2\text{Cu}^{2+} + \text{X}^- + 4\text{OH}^- \rightarrow \text{Cu}_2\text{O} + \text{NCO}^- + 2\text{H}_2\text{O}$	68.9	68.9
$2\text{CuO} + 7\text{X}^- + \text{H}_2\text{O} \rightarrow 2\text{CuX}_3^{2-} + \text{NCO}^- + 2\text{OH}^-$	52.8	7.54
$2\text{CuO} + 5\text{X}^- + \text{H}_2\text{O} \rightarrow 2\text{CuX}_2^- + \text{NCO}^- + 2\text{OH}^-$	42.2	8.44
$2\text{CuO} + 3\text{X}^- + \text{H}_2\text{O} \rightarrow 2\text{CuX(s)} + \text{NCO}^- + 2\text{OH}^-$	37.8	12.6
$2\text{CuO} + \text{X}^- + \text{H}_2\text{O} \rightarrow 2\text{Cu}_2\text{O} + \text{NCO}^- + 2\text{OH}^-$	28.3	28.3
$2\text{CuO} + 5\text{CuX}_3^{2-} + \text{H}_2\text{O} \rightarrow 7\text{CuX}_2^- + \text{NCO}^- + 2\text{OH}^-$	15.7	NAP
$2\text{CuO} + 3\text{CuX}_2^- + \text{H}_2\text{O} \rightarrow 5\text{CuX(s)} + \text{NCO}^- + 2\text{OH}^-$	31.2	NAP
$2\text{CuO} + \text{CuX(s)} + \text{OH}^- \rightarrow (3/2)\text{Cu}_2\text{O} + \text{NCO}^- + (1/2)\text{H}_2\text{O}$	23.55	NAP

NAP Not applicable.

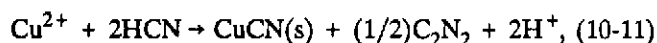
¹n is the number of free CN⁻ (= X) on left side of reaction equation. Values in parentheses are estimated. Data are from tables in appendix D.

in equation 10-6, are incorporated in figure 10-1 over the pH range 6 to 14. Figure 10-1 shows that in alkaline solution, Cu(II) is expected to oxidize the CN⁻ in all WAD metal cyanide species. This is true also for cyanocuprate(I) species; when the reactant cyanide species is CuCN, the Cu(I) product is Cu₂O. However, the rates of some of these reactions are slow, as shown by the isolation of solids that contain cationic Cu(II) complexed with an amine, and anionic Cu(I) cyanide complexes (see chapter 8). The log K values for reactions of Cu(II) with cyanocuprate(I) species are also listed in table 10-4.

In acid solution, Cu(II) oxidizes CN⁻ to C₂N₂:



log K = +26.2, n = 2, and (log K)/n = +13.1, which may be compared with the other data in table 10-2. For the reaction



log K = +7.8 and (log K)/n = +3.9. Values of (log K^{*})/n, defined as in equation 10-8, are incorporated in figure 10-1 over the pH range 0 to 6. Table 10-2 and

figure 10-1 show that in acid solution, Cu²⁺ is expected to oxidize CN⁻ in all WAD cyanide species except the partially WAD species CuCN(s), AgCN(s), [Hg(CN)]⁺, Hg(OH)(CN), and Hg(CN)₂.

REFERENCES

1. Sharpe, A. G. The Chemistry of Cyano Complexes of the Transition Metals. Academic, 1976, 302 pp.
2. Ayers, J. B., and W. H. Waggoner. Synthesis and Properties of Two Series of Hexacyanoferrates. J. Inorg. Nucl. Chem., v. 33, 1971, pp. 721-733.
3. Sillen, L. G., and A. E. Martell. Stability Constants of Metal-Ion Complexes, Supplement No. 1. Spec. Publ. No. 25, Chemical Society (London), 1971, pp. 49-51.
4. Sillen, L. G., and A. E. Martell. Stability Constants of Metal-ion Complexes. Spec. Publ. No. 17, Chemical Society (London), 1964, pp. 101-104.
5. Smith, R. M., and A. E. Martell. Critical Stability Constants, v. 4. Inorganic Complexes. Plenum, 1976, p. 21.
6. Martell, A. E., and R. M. Smith. Critical Stability Constants, v. 5. First Supplement. Plenum, 1982, p. 400.
7. Smith, R. M., and A. E. Martell. Critical Stability Constants, v. 6. Second Supplement. Plenum, 1989, p. 433.
8. Bellomo, A. Formation of Copper(II), Zinc(II), Silver(I), and Lead(II) Ferrocyanides. Talanta, v. 17, 1970, pp. 1109-1114.
9. Bellomo, A., D. DeMarco, and A. Casale. Formation of Nickel, Cobalt, Manganese, and Cadmium Ferrocyanides. Talanta, v. 19, 1972, pp. 1236-1240.

10. Bellomo, A., A. Casale, and D. DeMarco. Formation of Ferri-cyanides — I. Silver(I), Copper(II), and Cadmium(II). *Talanta*, v. 20, 1973, pp. 335-338.

11. DeRobertis, A., A. Bellomo, and D. DeMarco. Formation of Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Ag(I), and Cd(II) Ferrocyanides. *Talanta*, v. 23, 1976, pp. 732-734.

12. Chao, E. E., and K. L. Cheng. Stepwise Titration of Some Anion Mixtures and Determination of K_{sp} of Silver Precipitates with Silver Ion Selective Electrode. *Anal. Chem.*, v. 48, 1976, pp. 267-271.

CHAPTER 11.—SOLUTION OF CHEMICAL EQUILIBRIUM PROBLEMS

INTRODUCTION

In mineral processing and mine decommissioning activities, it is important to know what chemical reactions can occur in connection with the disposal or fate of cyanides. The first question to be answered is, "What chemical reactions may be expected to occur, and to what extent?" In other words, what chemical reactions are thermodynamically possible, and what are the important chemical equilibria? The second question is, "What are the reaction rates?"; this subject is addressed in chapter 12.

The answer to the question of equilibria requires thermodynamic data for the pertinent species and reactions. This publication contains many data on pertinent species and reactions in appendixes B, C, D, and E. The objective of this chapter is to show how the data in this publication may be used to obtain semiquantitative or qualitative yes/no solutions to practical chemical equilibrium problems. This chapter will show (1) the use of equilibrium predominance area diagrams (EPAD) and (2) the calculation of reaction equilibrium constants to obtain semiquantitative solutions to chemical equilibrium problems.

This chapter does not provide procedures for obtaining detailed quantitative information on solubilities and species concentrations. The required detailed calculations are best done by computer. Readers interested in such details should consult pertinent literature and published computer programs (1-7).¹

EXAMPLES OF THE USE OF EQUILIBRIUM PREDOMINANCE AREA DIAGRAMS

A collection of EPAD is useful for qualitative or semiquantitative examination of a chemical system. It shows what chemical species prevail under specified conditions and ranges of composition, and what reactions may be expected if the composition of the system is changed, e.g., by altering the pH or destroying excess CN^- with an oxidant. This section contains several examples that illustrate the use of EPAD in solving practical chemical equilibrium problems.

EPAD by definition show the predominant species in a system as a function of composition variables, often at constant temperature and pressure. Two of the composition variables are assigned to the coordinate axes of the diagram, and the others are held constant. The thermodynamic basis of EPAD, definitions of the composition

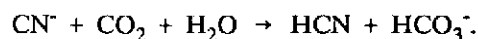
variables, and the varieties of EPAD are outlined in chapter 4. A collection of EPAD is presented in appendix E. The EPAD in appendix E are drawn for selected values of the composition variables that are held constant. For intermediate values of those composition variables, the desired results may be obtained by interpolation from the two diagrams that bracket the value of that composition variable.

Example 1: Cyanide Safety

EPAD can be used to verify whether cyanide mixture compositions may pose a safety hazard. At what free cyanide concentrations and pH values do cyanide solutions have safe HCN partial pressures? To answer this, the pL-pH diagram for free cyanide, figure E-1, is used. Figure E-1 shows the isobars for specified HCN partial pressures, $p(\text{HCN})$, overlaid on the solution-species predominance areas for HCN and CN^- . Note that the maximum allowable concentration = 10 ppm (1×10^{-5} bar line) for $p(\text{HCN})$. All solution compositions below and to the right of that line have safe $p(\text{HCN})$ values. A leach solution with 0.5 kg NaCN per metric ton ($0.5 \text{ g} \cdot \text{L}^{-1}$) solution is 0.010M in NaCN, so $p\text{L} = p\text{CN} = 2.0$. Figure E-1 shows that at $p\text{CN} = 2.0$, the pH must be at least 11.35 to maintain $p(\text{HCN})$ below 10 ppm. If the pH were 11.0, $p(\text{HCN})$ would be about 20 ppm.

Example 2: Cyanide and Carbonates

It is necessary to maintain cyanide solutions at pH 10 to 11 to avoid loss of HCN. Atmospheric CO_2 is sufficiently acidic to liberate HCN from solutions containing free CN^- or weak-acid dissociable (WAD) cyanide complexes:



The compatibility of cyanide and carbonate solutions is of interest in view of this fact. What happens when cyanide and carbonate solutions of different speciation are mixed? To answer this question, the pL-pH diagram for carbonate, figure E-2, is required in addition to that for cyanide, figure E-1. Superposition of the two diagrams shows what species coexist and what species would react. Mixing carbonated water with NaCN solution would result in liberation of HCN. The carbonated water, with CO_2 predominant, has pH below 6.3, while the NaCN solution, with CN^- predominant, has pH above 9.2. The predominance areas for CO_2 and CN^- do not overlap, so those species cannot

¹Italic numbers in parentheses refer to items in the list of references at the end of this chapter.

coexist as predominant species in the same solution. Further, HCN and HCO_3^- can coexist as predominant species at pH 6.3 to 9.2. The EPAD thus show that CO_2 and CN^- react to give HCN and HCO_3^- .

Example 3: Cyanide and Carbon Dioxide

Cyanide solutions can react with CO_2 from the air and liberate HCN, as discussed in the preceding example. The extent to which this reaction occurs bears on safety considerations and cyanide losses. The partial pressure of CO_2 is roughly a hundred times higher in exhaled air than in fresh air, which is a major reason for supplying efficient ventilation to personnel working with cyanide solutions. At what compositions do cyanide solutions absorb CO_2 from the air? Figure E-2 shows isobars for CO_2 partial pressures for fresh air and for exhaled air, $\log p(\text{CO}_2) = -3.4$ and -1.4 , respectively. Carbonate solutions with compositions below and to the right of the $\log p(\text{CO}_2) = -3.4$ isobar will absorb CO_2 from fresh air; solutions with compositions on the other side of that isobar will not absorb CO_2 from fresh air. Superposition of figures E-1 and E-2 shows that NaCN leach solutions with pH around 11 will absorb CO_2 from fresh air, because all pH 11 solution compositions lie below or to the right of the fresh-air CO_2 isobar. This fact confirms the importance of monitoring and maintaining sufficient alkalinity in cyanide leach solutions.

Example 4: Zinc Species in Cyanide Solutions

When metallic zinc is used to cement precious metals from cyanide solutions, it is converted to undissolved solids or dissolved species. The zinc concentration in the barren solutions and the zinc-containing solids may affect procedures for recycle or disposal of these solutions. The identity of zinc-containing solids is important because $\text{Zn}(\text{CN})_2$ has a low solubility. The extent to which zinc in cyanide solutions may interfere with leaching also deserves attention. This and several succeeding examples bear on this problem and show the versatility of EPAD for solving these problems. The approaches used to solve problems here can be adapted to deal with other metals in cyanide solutions.

What is the speciation of zinc in cyanide solutions? The extent to which zinc is complexed in cyanide solutions may affect the effectiveness of the solutions for leaching more ore. An effective picture is presented by a pL-pH EPAD, $L = \text{CN}^-$, for dissolved zinc species, figure E-19. The predominance areas of dissolved species are independent of zinc concentration or the presence of any zinc oxide or cyanide solid phases; they depend only on pH and

pCN. In a zinc-containing leach solution with pCN = 2.0, i.e., free $\text{CN}^- = 1 \times 10^{-2}M$ (260 ppm), and pH 11.0, the predominant zinc species is $[\text{Zn}(\text{CN})_4]^{2-}$. It is important to remember that pL refers to free, not total ligand concentration. In this example, free CN^- is $1 \times 10^{-2}M$. Total CN^- is free CN^- plus the CN^- complexed with zinc. If total zinc is $1 \times 10^{-3}M$, total $\text{CN}^- = 0.010 + 4(0.001) = 0.014M$. A calculation such as this one is approximate to the extent that the predominant species constitutes less than 100 pct of the total, and should be regarded as semiquantitative.

Suppose a solution contains $1 \times 10^{-3}M$ total CN^- (26 ppm), $2 \times 10^{-4}M$ Zn (13 ppm), and has pH 10.0. This composition may be similar to that of a diluted barren solution. What is the predominant zinc species? To the extent that CN^- is complexed with zinc, free CN^- is less than total CN^- . If the zinc were 100 pct $[\text{Zn}(\text{CN})_4]^{2-}$, free CN^- would be $0.001 - 4(0.0001) = 0.0006M$. This means that free CN^- is between 6×10^{-4} and $1 \times 10^{-3}M$, i.e., pCN is between 3.2 and 3.0. For pCN = 3.0 to 3.2 and pH = 10.0, figure E-19 shows that the predominant zinc species is $[\text{Zn}(\text{CN})_4]^{2-}$. This region on the diagram is close to the boundary with the predominance area for $[\text{Zn}(\text{CN})_3]^-$, so the latter species will contribute a significant fraction of the total zinc species.

It should be noted that on a boundary line separating the areas for two predominant solution species, those species coexist at equal concentrations. At a point where the areas of three predominant solution species meet, the three species coexist at equal concentrations. Near such a point, the predominant species will constitute less than 50 pct of the total species. Predominance of species has the same sense as plurality, not majority, as in an election with more than two candidates. The further a point in a solution-species predominance area is from any boundary of that area, the more nearly that predominant species constitutes 100 pct of the total species in the solution. For example, in figure E-19, the point at pH 11.0 and pCN 1.0 in the $[\text{Zn}(\text{CN})_4]^{2-}$ predominance area is at least 2 pH and 2 pCN units away from any boundary of the area, so nearly all zinc exists as $[\text{Zn}(\text{CN})_4]^{2-}$.

In a solution with free $\text{CN}^- = 0.1 \text{ ppm} = 4 \times 10^{-6}M$, i.e., pCN = 5.4, figure E-19 shows that the predominant dissolved zinc species contain no CN^- , regardless of pH.

Example 5: Precipitation of Zinc Cyanide in Cyanide Systems

Under some conditions, it may be advisable to remove zinc from cyanide solutions before reuse. To minimize cyanide losses in separated solids, it is of interest to avoid precipitation of solids that contain CN^- . Under what conditions can precipitation of $\text{Zn}(\text{CN})_2(s)$ be avoided? To

answer this, we need EPAD that show the solid phases in zinc cyanide systems. Figures E-20 through E-23 are pL-pH EPAD like figure E-19, but they show the predominance areas for solid phases at the $pM = pZn$ values specified in each EPAD. Figures E-20 through E-23 show that $Zn(CN)_2(s)$ does not form (1) at any pH if pCN exceeds 4.1, i.e., free CN^- concentration below $8 \times 10^{-5}M$ (2.1 ppm), or (2) if the pH exceeds 9.8, provided pZn is greater than 3.0, i.e., zinc concentration below $1 \times 10^{-3}M$ (65 ppm).

Another look at the system is provided by figures E-11 through E-14, which show pM-pH EPAD for $M = Zn(II)$ and specified values of $pL = pCN$. Figures E-11 through E-14 show that $Zn(CN)_2(s)$ does not form at any pH or pCN value if pZn is above 4.5, i.e., zinc concentration below $3 \times 10^{-5}M$ (2 ppm).

Can $Zn(CN)_2(s)$ precipitation be avoided at pH 11? Problems involving constant pH are efficiently handled with pM-pL EPAD. The zinc cyanide system at pH 11 is diagrammed in figure E-26. Figure E-26 shows that $Zn(CN)_2(s)$ forms only at pZn below 0.4, i.e., zinc concentration above $0.4M$ (about $25 g \cdot L^{-1}$). At zinc concentrations usually encountered in practice, up to $0.5 g \cdot L^{-1}$, $Zn(CN)_2(s)$ will not precipitate. However, $Zn(CN)_2(s)$ might precipitate from leach solutions allowed to evaporate or absorb CO_2 with a resultant decrease of pH.

Example 6: Recovery of Zinc as Zinc Cyanide

Recovery of cyanide values from barren Merrill-Crowe cementation solutions may be of interest in connection with cyanide recycle. One way to recover CN^- or remove zinc is by precipitation as $Zn(CN)_2(s)$. Given a solution with total $Zn = 0.002M = 130$ ppm ($pZn = 2.7$), total $CN^- = 0.009M = 230$ ppm ($pCN = 2.05$), and pH 11.3, how much Zn^{2+} is required to recover Zn or CN^- as $Zn(CN)_2(s)$? We require Zn^{2+} to precipitate the CN^- and to lower the pH by reacting with OH^- and precipitating $ZnO(s)$ or $Zn(OH)_2(s)$. Total $CN^- = 0.009M$ requires $Zn^{2+} = (1/2) \times 0.009M = 0.0045M$ to convert all CN^- to $Zn(CN)_2(s)$. The pL-pH EPAD for $pZn = 3.0$ and 2.0, figures E-22 and E-23, show that precipitation of $Zn(CN)_2(s)$ requires pH below about 10. At pH = 11.3, $[H^+] = 5 \times 10^{-12}M$ and $[OH^-] = K_w/[H^+] = (1 \times 10^{-14})M^2/[H^+] = 0.002M$. So additional $Zn^{2+} = (1/2) \times 0.002M = 0.001M$ is required to precipitate $ZnO(s)$ or $Zn(OH)_2(s)$ and lower the pH. Hence, the total zinc concentration needed is $0.0045M + 0.001M = 0.0055M$. With $0.002M$ Zn already present, the Zn^{2+} needed is $0.0055M - 0.002M = 0.0035M$. After the calculated amount of Zn^{2+} is added, the system will contain a mixture of $ZnO(s)$ and $Zn(CN)_2(s)$. Note that from the EPAD the predominance areas of Zn^{2+} and $[Zn(CN)_4]^{2-}$ are separated

from each other by the predominance areas of other species, so mixing Zn^{2+} and $[Zn(CN)_4]^{2-}$ will result in reaction as exemplified; see figures E-13 and E-14.

The EPAD can be used to estimate the composition of the supernatant solution to decide on its disposal. Figures E-21 through E-23 show that solutions with coexisting $ZnO(s)$ and $Zn(CN)_2(s)$ have $pCN = 4.1$, i.e., free $CN^- = 8 \times 10^{-5}M$, if pH is below 9.2. Figures E-11 and E-12, the pZn-pH diagrams for $pCN = 5.0$ and 4.0, show that the solubility of $Zn(CN)_2(s)$ is $pZn = 4.5$, i.e., $Zn = 3 \times 10^{-5}M$ (2 ppm), if the pH is adjusted to about 8. The predominant solution species is $Zn(CN)_2(aq)$. Total CN^- is roughly $8 \times 10^{-5} + 2(3 \times 10^{-5}) = 1.4 \times 10^{-4}M$ (3.6 ppm). This value of total CN^- may be high for immediate disposal, so treatment to remove CN^- may be required.

The recovered $Zn(CN)_2(s)$ may be converted to HCN and ZnS by treatment with H_2S , for example.

Example 7: Decomposition of Zinc Cyanide Species

If recycle of cyanide is under consideration, the possibility of recovering cyanide as HCN may be of interest. From barren Merrill-Crowe solutions, what conditions are required to totally decompose zinc cyanide species to Zn^{2+} and recover HCN? The answer depends on the zinc concentration. Figures E-11 through E-14 and E-20 through E-23 confirm that Zn^{2+} predominates in sufficiently acidic solutions, so it is possible to totally decompose all zinc cyanide species. As acid is added, decomposition occurs and HCN is liberated, which raises pCN . Thus, the total cyanide concentration of the solution will be converted to free CN^- . Suppose the solution contains $8 \times 10^{-3}M$ (210 ppm) total CN^- and $1 \times 10^{-3}M$ (65 ppm) Zn, i.e., $pZn = 3.0$. Figure E-22 shows that at $pZn = 3.0$ and $8 \times 10^{-3}M$ free CN^- ($pCN = 2.1$), acidification to pH below 5.0 will decompose all zinc cyanide species, including $Zn(CN)_2(s)$.

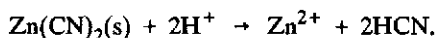
Example 8: Mixed Metals in Cyanide Systems—Zinc and Iron

A disposal alternative for barren Merrill-Crowe solutions is addition of $FeSO_4$ to complex cyanide as $[Fe(CN)_6]^{4-}$ and precipitate it as $Zn_2Fe(CN)_6$. What happens when Fe^{2+} is added to a zinc-containing cyanide solution? To answer this question, figure 10-1 is useful. Consider a waste cyanide solution containing $1 \times 10^{-4}M$ Zn (6.5 ppm, $pZn = 4.0$) and $4.8 \times 10^{-3}M$ total CN^- , made $1 \times 10^{-3}M$ in Fe^{2+} ($pFe(II) = 3.0$) to complex the CN^- . What reaction products are expected? Figure 10-1 shows that the $(\log K^*)/n$ lines for Fe(II) cyanide species are above the $(\log K^*)/n$ lines for all zinc cyanide species, so thermodynamically Fe^{2+} is expected to remove CN^- from

all zinc cyanide species. Therefore, all CN^- is expected to be converted to $(4.8 \times 10^{-3})/6 = 8 \times 10^{-4}M$ total dissolved and precipitated $[\text{Fe}(\text{CN})_6]^{4-}$. That leaves $0.001 - 0.0008 = 0.0002M$ Fe^{2+} , which will be precipitated by OH^- or $[\text{Fe}(\text{CN})_6]^{4-}$, depending on pH. The predominant species are determined by the solution pH and pCN. Given those values, the predominant zinc species are given by the zinc solution-species pCN-pH EPAD (figure E-19) and the corresponding EPAD for pZn = 4.0 (figure E-21). A pCN-pH EPAD for pZn = 4.0 with added $[\text{Fe}(\text{CN})_6]^{4-}$ is also required; the EPAD for $1 \times 10^{-4}M$ $[\text{Fe}(\text{CN})_6]^{4-}$ is shown in figure E-24. Figure E-24 shows that zinc is precipitated as $\text{Zn}_2\text{Fe}(\text{CN})_6(\text{s})$ at pH below 8.8, and $\text{ZnO}(\text{s})$ at pH above 8.8. At pH near 8 and pCN near 6, figure E-19 shows the predominant zinc solution species to be Zn^{2+} . Because $[\text{Fe}(\text{CN})_6]^{4-}$ is kinetically inert (see chapter 8), it does not dissociate if the solution is diluted or acidified. If insufficient Zn^{2+} or Fe^{2+} is present to precipitate all of the $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Fe}(\text{CN})_6]^{4-}$ will be the predominant iron solution species.

Example 9: pZn-pH Diagrams

Sometimes there are problems for which the available EPAD may not give a quick solution because the solution composition data comprise values for which EPAD are not provided. This example and the next one show how this problem can be managed. Consider figures E-12 through E-14 and the $\text{Zn}(\text{CN})_2(\text{s})$ - Zn^{2+} equilibrium. That equilibrium is represented by the boundary between the $\text{Zn}(\text{CN})_2(\text{s})$ and Zn^{2+} predominance areas. To generate the reaction equation, put the two zinc species on opposite sides. Insert successively the ligand species, HCN in this case, then H^+ or OH^- to balance charges, then H_2O to balance H and O atoms. The result in this example is



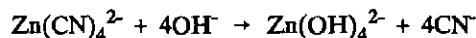
Log K for this reaction is given by

$$\log K = \log a(\text{Zn}^{2+}) + 2 \log a(\text{HCN}) - 2 \log a(\text{H}^+)$$

in accordance with equation 4-10. This equation shows that for every unit change of $\log a(\text{HCN})$, $\log a(\text{H}^+)$ = -pH changes by 1 unit. For example, the $\text{Zn}(\text{CN})_2(\text{s})$ - Zn^{2+} boundary shifts 2 pH units lower on going from figure E-12 with pCN = 4.0 to figure E-14 with pCN = 2.0. At pCN = 2.5 ($[\text{CN}^-] = 0.003M$), the boundary occurs 0.5 pH unit higher than in figure E-14.

For another example, consider the equilibrium of $\text{Zn}(\text{CN})_4^{2-}$ with $\text{Zn}(\text{OH})_4^{2-}$, which is represented by the boundary between the predominance areas for these

species in figure E-14. Proceeding as in the preceding paragraph, the reaction equation is



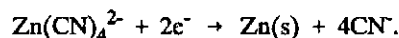
and the equilibrium expression is

$$\begin{aligned} \log K &= \log a(\text{Zn}(\text{OH})_4^{2-}) + 4 \log a(\text{CN}^-) \\ &\quad - \log a(\text{Zn}(\text{CN})_4^{2-}) - 4 \log a(\text{OH}^-). \end{aligned}$$

On the boundary, the activities of $\text{Zn}(\text{CN})_4^{2-}$ and $\text{Zn}(\text{OH})_4^{2-}$ are equal, and the log K equation shows that for every unit change of $\log a(\text{OH}^-)$, i.e., every unit change in pH, $\log a(\text{CN}^-)$ changes by 1 unit. In figure E-14, drawn for pCN = 2.0, the boundary occurs at pH 13.0. At pCN = 1.5, the boundary would be at pH = 13.5, and at pCN = 3.0 it would be at pH = 12.0. The last instance corresponds to figure E-13, which however shows that $\text{Zn}(\text{OH})_3$, not $\text{Zn}(\text{OH})_4^{2-}$, predominates at pH = 12.0. This last illustration shows that this approach fails if the predominant species changes in the composition region of interest. If the user is operating with compositions bracketed by EPAD both above and below the values of interest, changes in predominant species can be easily noted. In cases such as this, the data in table D-2 also could be used to analyze the problem.

Example 10: Reduction of Zinc in Cyanide Solutions

Conceivably one might consider electrolytic recovery of zinc from barren Merrill-Crowe solutions. Consider figure E-31, which is an Eh-pH diagram for pZn = 2.0 and pCN = 2.0, with regard to the reduction of $\text{Zn}(\text{CN})_4^{2-}$ to zinc metal. Proceeding similarly to the preceding example, the reaction equation is



For redox half-reactions, the Nernst equation, equation 4-16, is used instead of equation 4-10:

$$E = E^\circ - (2.303RT/nF) \log Q,$$

where in this example

$$\log Q = 4 \log a(\text{CN}^-) - \log a(\text{Zn}(\text{CN})_4^{2-}).$$

The factor $2.303RT/F$ is 0.05916 or approximately 0.06 V at 25° C; in this example $n = 2$, so $(2.303RT/nF) = 0.03$ V. For every negative unit change in $\log a(\text{Zn}(\text{CN})_4^{2-})$, i.e., every tenfold decrease in $a(\text{Zn}(\text{CN})_4^{2-})$, E is lower

(more negative) by 0.03 V. Similarly, for every tenfold decrease in $a(\text{CN}^-)$, E is higher (more positive) by $4 \times 0.03 = 0.12$ V.

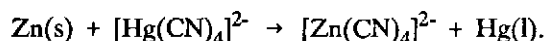
EXAMPLES OF EQUILIBRIUM CONSTANT CALCULATIONS

Often calculation of an equilibrium constant is an effective way to get an answer to a practical mineral processing problem. In complex systems, several EPAD may be required to solve a problem, and a sufficient number of EPAD may not be available. Redox reactions for example, may require complex EPAD if more than one metal or ligand is present. The choice of whether to attack a problem with EPAD or by equilibrium-constant calculations may not be clear cut; it depends on the complexity of the chemical system and the needs and objectives at hand. For complex problems, the reader may prefer to employ some of the computerized procedures cited at the beginning of this chapter.

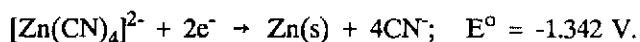
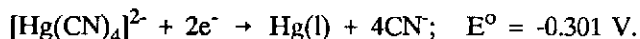
Equilibrium constants K for reactions of interest can be calculated from the thermodynamic data in appendixes B, C, and D. Tables 8-5 and 10-2, and figure 10-1, may also be used. The equations for these calculations are outlined in chapter 4. The value of K indicates the extent to which the reaction can go. It should be noted that whether the reaction will go is a matter of reaction rate. Information about rates of pertinent reactions is compiled in chapters 7 and 8. Solution of reaction rate problems is described in chapter 12.

Example 1: Cementation

Accessory metals may exist in precious metals leach solutions, and it is of interest to determine their behavior in a process. These accessory metals commonly exist in associated minerals, and they may be leached along with the precious metals. One such accessory metal is mercury. Can zinc cement mercury from cyanide solution? The answer is determined by $\log K$ for the cementation reaction



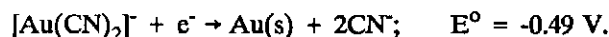
It is convenient to use the reduction half-reactions and their standard potentials in table 8-5:



These data give $E^\circ = +1.041$ V, hence $\log K = +35.2$, for the cementation reaction. Accordingly, zinc is expected to quantitatively cement mercury from cyanide solution.

Example 2: Gold Leaching

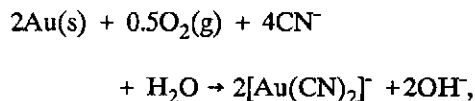
The reuse of barren cementation solutions for leaching would conserve reagents and might lower disposal costs. Barren Merrill-Crowe solutions contain zinc, but it may still be possible to recycle such solutions to leaching. Could a $\text{Zn}(\text{CN})_4^{2-}$ solution be used to leach gold? From table 8-5:



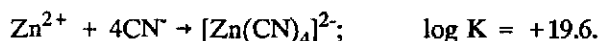
From $\Delta_r G^\circ$ data in table C-1:



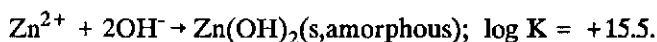
The net reaction is



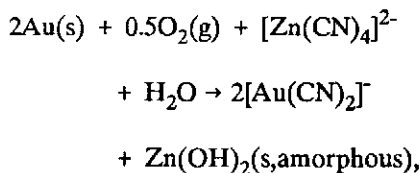
for which $E^\circ = +0.89$ V, hence $\log K = +30.1$. For $[\text{Zn}(\text{CN})_4]^{2-}$ as the cyanide source, we need its $\log K$ data from table D-2:



The zinc-containing product is expected to be $\text{Zn}(\text{OH})_2$ (s,amorphous) or $[\text{Zn}(\text{OH})_4]^{2-}$. At pH 11, the EPAD for zinc in cyanide systems, e.g., figures E-13 and E-14, show precipitation of ZnO(s) [or $\text{Zn}(\text{OH})_2$ (s,amorphous)]. For its formation (table D-2),



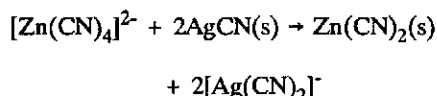
The expected leaching reaction is then



for which $\log K$ is $(+30.1) - (+19.6) + (+15.5) = +26.0$. This is only 4.1 $\log K$ units less positive than for the reaction with free CN^- , so leaching gold with $[\text{Zn}(\text{CN})_4]^{2-}$ solution is thermodynamically feasible. Therefore, it is appropriate to determine whether the rate of this reaction is satisfactory, and to what extent the precipitated $\text{Zn}(\text{OH})_2$ hinders it.

Example 3: Silver Versus Zinc Cyanide Species

If barren Merrill-Crowe solutions could be used to leach gold, would they be as effective for leaching silver? In the case of silver, the extent to which AgCN might precipitate and hinder recovery is of concern. Can AgCN(s) dissolve in $[\text{Zn}(\text{CN})_4]^{2-}$ solutions? For this mixed-metals problem, table 10-2 and figure 10-1 are convenient. Figure 10-1 shows that the answer is yes because the AgCN(s)-[Ag(CN)₂]⁻ line corresponds to larger values of $(\log K^*)/n$ than does the Zn(CN)₂(s)-[Zn(CN)₄]²⁻ line. Similarly, in tables 10-2 and 10-3, the reaction obtained by subtracting a reaction with a low value of $(\log K)/n$ or $(\log K^*)/n$ from a reaction with a high value of $(\log K)/n$ or $(\log K^*)/n$ is expected to proceed. The calculation of log K for the reaction



follows. The reactions for the silver and zinc species separately are first given.



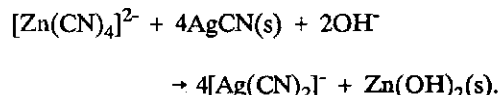
$$n = 1, (\log K)/n = +4.8.$$



$$n = 2, (\log K)/n = +2.0.$$

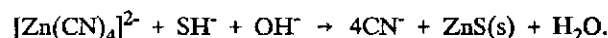
For the reaction of interest, log K is obtained by multiplying the $(\log K)/n$ values by the n's and the reaction multipliers (2 and 1, respectively) and subtracting: $\log K = (+4.8)(1)(2) - (+2.0)(2)(1) = +5.6$. Hence, stirring AgCN(s) into a solution of $[\text{Zn}(\text{CN})_4]^{2-}$ is predicted to result in dissolution of AgCN(s) and precipitation of Zn(CN)₂(s). Conversely, silver is predicted to remain dissolved in a solution containing $[\text{Zn}(\text{CN})_4]^{2-}$, and such a solution should be satisfactory for leaching silver. This calculation is applicable to solutions with pH 9 to 10, where Zn(CN)₂(s) is a stable phase. At pH 11 or higher, the stable solid phase is ZnO or Zn(OH)₂(s). A calculation similar to that above with Zn(OH)₂(s) as the product

leads to a similar conclusion; the reaction shows that high pH favors dissolution of AgCN(s):



Example 4: Regeneration of Cyanide From Zinc-Containing Solutions

If recycle of cyanide solutions is of interest, sulfide precipitation offers a means of regenerating free CN⁻ from zinc-containing solutions, via the reaction



From the thermodynamic data in tables B-1, C-1, and D-2, log K for this reaction is calculated as +5.8. For converting 0.01M total cyanide in the form of $[\text{Zn}(\text{CN})_4]^{2-}$ to free CN⁻ at pH 11, this reaction is therefore feasible.

REFERENCES

1. Nordstrom, D. K., L. N. Plummer, T. M. L. Wigley, T. J. Wolery, J. W. Ball, E. A. Jenne, R. L. Bassett, D. A. Crerar, T. M. Florence, B. Fritz, M. Hoffman, G. R. Holdren, Jr., G. M. Lafon, S. V. Mattogod, R. E. McDuff, F. Morel, M. M. Reddy, G. Sposito, and J. Thraillkill. Comparison of Computerized Chemical Models for Equilibrium Calculations in Aqueous Systems. Ch. in *Chemical Modeling in Aqueous Systems—Speciation, Sorption, Solubility, and Kinetics*, ed. by E. A. Jenne. ACS, 1979, pp. 857-894.
2. Nordstrom, D. K., and J. W. Ball. *Chemical Models, Computer Programs, and Metal Complexation in Natural Waters*, ed. by C. J. M. Kramer and J. C. Duinker. Nijlhoff, The Hague, 1984, pp. 149-164.
3. Nordstrom, D. K., and J. L. Munoz. *Geochemical Thermodynamics*. Blackwell Scientific, 1986, 477 pp.
4. Waite, T. D. *Mathematical Modeling of Trace Element Speciation*. Ch. in *Trace Element Speciation: Analytical Methods and Problems*, ed. by G. Batley. CRC Press, 1989, pp. 117-184.
5. Turnbull, A. G., and M. W. Wadsley. CHEMIX (Part of CSIRO-SGTE THERMODATA System, Version IV). CSIRO, Inst. Energy and Earth Resour., Div. Miner. Chem., Port Melbourne, Victoria, Australia, Computer program, 1985.
6. Butler, J. N. *Ionic Equilibrium: A Mathematical Approach*. Addison-Wesley, 1964, 547 pp.
7. Meites, L. *An Introduction to Chemical Equilibrium and Kinetics*. Pergamon, 1981, 549 pp.

CHAPTER 12.—SOLUTION OF REACTION RATE PROBLEMS

INTRODUCTION

Chemical reaction rate problems occur frequently in industrial processes. It is often necessary to determine the extent of a reaction during a given time, or to determine how much time is required for a desired conversion. Most chemical reactions are first or second order with respect to substrate or reagent, as outlined in chapter 7, which reviews the reactions of free CN^- and derived species such as formamide ($\text{H}-\text{CO}-\text{NH}_2$), cyanogen chloride (ClCN), and cyanate (NCO^-). As a rule, the rates of the reactions described in chapter 7 depend on pH. This chapter continues first with a discussion of the pH dependence of chemical reaction rates. The two following sections review first-order and second-order rate equations and provide the mathematical formulas useful for solving practical problems. For both kinds of rate equations, examples of their application to problems of interest in precious metals hydrometallurgy are given. Finally, the calculation of rate constants at different temperatures is discussed.

DEPENDENCE OF REACTION RATES ON pH

As a rule, the rates of chemical reactions in aqueous solution depend on pH. The nature of the pH dependence of reaction rates for a given reaction must be determined experimentally. Two major reasons that reaction rates depend on pH are the following:

- The reactants are weak acids or bases that form different species as a function of pH. These species differ in their reactivities. The species thus formed are characterized by pK_a values between 0 and 14, and appear on equilibrium predominance area diagrams (EPAD). Examples are $\text{HCN} \rightarrow \text{CN}^- + \text{H}^+$ with $\text{pK}_a = 9.2$ and $\text{HClO} \rightarrow \text{ClO}^- + \text{H}^+$ with $\text{pK}_a = 7.5$ at 25°C . There are often cases in which the most reactive species is a very strong acid with $\text{pK}_a < 0$ or is derived from a very weak acid with $\text{pK}_a > 14$, and does not appear on EPAD at pH 0 to 14.
- A reactant, even one that does not have observable acid-base equilibria, reacts with the species H_2 , H_2O , and OH^- at different rates.

The rate constants for the reactions of the different species of reactants often differ by many powers of 10; consequently, at a given pH, the reactive species is not always the predominant species that appears on EPAD.

EPAD are based solely on thermodynamic data and say nothing about reaction rates.

Example: An example of different reactivities of a substrate with H_2O and OH^- is the hydrolysis of ClCN . This reaction proceeds with a rate equation

$$-d[\text{ClCN}]/dt = k[\text{ClCN}], \quad (12-1)$$

$$\text{where } k = (k_a + k_b[\text{OH}^-]) \quad (12-2)$$

from table F-9 in appendix F. The k_a and k_b terms represent the reaction rates of ClCN with H_2O and OH^- , respectively. At 25°C , $k_a = 4.9 \times 10^{-7} \text{ s}^{-1}$ and $k_b = 12.2 (\text{mol} \cdot \text{L}^{-1})^{-1} \text{ s}^{-1}$. As shown by calculation and in figure 7-19, reaction with H_2O is faster at $\text{pH} < 6$, i.e., $k_a > k_b[\text{OH}^-]$; and reaction with OH^- is faster at $\text{pH} > 8$, i.e., $k_b[\text{OH}^-] > k_a$.

Example: An example of different reactivities of reactant species is the oxidation of CN^- by ClO^- (hypochlorite). In this reaction, CN^- and HCN (hydrocyanic acid) each react at different rates with each of the oxidant species ClO^- and HClO . The elementary reactions $\text{HCN} + \text{HClO}$, $\text{HCN} + \text{ClO}^-$, $\text{CN}^- + \text{HClO}$, and $\text{CN}^- + \text{ClO}^-$ each proceed with different rate constants. As described in chapter 7, published observations showed that at pH 12 to 14, where free cyanide and hypochlorite are nearly all CN^- and ClO^- , respectively, at ionic strength 1.00M and 25°C , the rate law is

$$-d[\text{CN}^-]/dt = (k_1 + k'_2[\text{OH}^-]^{-1})[\text{CN}^-][\text{ClO}^-], \quad (12-3)$$

$$\text{where } k_1 = 310 (\text{mol} \cdot \text{L}^{-1})^{-1} \cdot \text{s}^{-1}$$

$$\text{and } k'_2 = 583 \text{ s}^{-1}.$$

Alternatively, the k'_2 term may be expressed as a $[\text{H}^+]$ dependence:

$$-d[\text{CN}^-]/dt = (k_1 + k_2[\text{H}^+])[\text{CN}^-][\text{ClO}^-], \quad (12-4)$$

$$\text{where } k_2 = k'_2 K_w^{-1}, \quad (12-5)$$

$$\text{and } K_w = [\text{H}^+][\text{OH}^-]. \quad (12-6)$$

At ionic strength 1.00M and 25°C , $\log K_w = -13.79$ from table C-2, so equation 12-5 gives $k_2 = 3.6 \times 10^{16} (\text{mol} \cdot \text{L}^{-1})^2 \cdot \text{s}^{-1}$. The k_2 term in equation 12-4 was interpreted as an elementary reaction of CN^- with HClO , in which Cl^+ is transferred from HOCl to CN^- to form

CICN, which is the observed product. The k_1 and k_2 terms of equation 12-4 are accordingly equal at pH about 13.9. Although the pK_a of HClO is 7.5 from table C-2, so that ClO^- is the predominant oxidant species at pH 12 to 13.9, HClO is more reactive than ClO^- with CN^- in this pH range.

FIRST-ORDER REACTIONS

This section reviews first-order reactions and provides the general mathematical equations into which the user can insert pertinent data to obtain solutions to practical problems. Hydrolysis reactions of free CN^- and derived species are first-order in substrate; for these reactions, the rate constant varies with pH. At a given constant pH, hydrolysis reactions may be treated as first-order reactions and treated as described in this section.

General Solution of the Rate Equation

For a first-order reaction of substrate Z,



the rate equation is

$$d[\text{Z}]/dt = -k'[\text{Z}], \quad (12-8)$$

where $[\text{Z}]$ = concentration of Z,

and t = time.

The first-order rate constant k' has units of (time) $^{-1}$. Integration gives

$$[\text{Z}] = [\text{Z}]_0 \exp(-k't), \quad (12-9)$$

where $[\text{Z}]_0$ = concentration of Z at zero time.

The fraction of Z reacted, f_z , is

$$f_z = ([\text{Z}]_0 - [\text{Z}])/[\text{Z}]_0 = 1 - \exp(-k't). \quad (12-10)$$

The time t_f required to attain conversion f_z is

$$t_f = -(k')^{-1} \ln(1 - f_z) \quad (12-11)$$

and is independent of the concentration of Z. The times required for 50-, 90-, and 99-pct conversion are then, respectively,

$$t_{0.50} = 0.693/k', \quad (12-12)$$

$$t_{0.90} = 2.303/k', \quad (12-13)$$

$$\text{and } t_{0.99} = 4.605/k'. \quad (12-14)$$

Equations 12-10 and 12-11 are the most pertinent to solving practical problems; equations 12-12 through 12-14 are special cases of equation 12-11.

Examples

As described in chapter 7, hydrolysis reactions are first order in substrate and at a given pH may be treated as first-order reactions. Consider the importance of the hydrolysis of CN^- to formate (HCO_2^-) and ammonia (NH_3) for cyanide degradation at 25° C and pH 11.0. From table F-3, the rate equation for hydrolysis of CN^- is

$$d[\text{CN}^-]/dt = -k'([\text{CN}^-] + [\text{HCN}]), \quad (12-15)$$

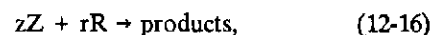
in which $k' = 1.01 \times 10^{-8} \text{ s}^{-1}$. From equations 12-12 through 12-14, the times for 50-, 90-, and 99-pct reaction of cyanide by equation 12-15 are $0.69 \times 10^8 \text{ s} = 2.2$ years; $2.3 \times 10^8 \text{ s} = 7.2$ years; and $4.6 \times 10^8 \text{ s} = 14$ years, respectively. The rate of this reaction is so slow that it may not be a major pathway for cyanide degradation. These calculations are based on the uncatalyzed reaction; no information is available concerning catalysis of this reaction.

SECOND-ORDER REACTIONS

This section reviews second-order reactions and provides the general mathematical equations into which the user can insert pertinent data to obtain solutions to practical problems. The most important practical examples of second-order reactions are the reactions of CN^- and derived species with oxidants. The rates of these reactions also depend on pH. At a given constant pH, redox reactions may be treated as second-order reactions and treated as described in this section.

General Solution of the Rate Equation

For a second-order reaction of z moles of substrate Z with r moles of reagent R,



the rate equation is

$$z^{-1}d[Z]/dt = r^{-1}d[R]/dt = -k''[Z][R]. \quad (12-17)$$

The second-order rate constant k'' has units of (concentration)⁻¹ times (time)⁻¹.

For the special case of Z and R present in stoichiometric ratio, i.e., $[Z]/z = [R]/r$, integration gives

$$[Z]/[Z]_0 = [R]/[R]_0 = (1 + r[Z]_0 k'' t)^{-1}, \quad (12-18)$$

where $[Z]_0$ and $[R]_0$ are the respective concentrations of Z and R at zero time. The conversion f_Z and the fraction of reagent consumed f_R are

$$f_Z = f_R = r[Z]_0 k'' t (1 + r[Z]_0 k'' t)^{-1}. \quad (12-19)$$

The time t_f for a given degree of conversion depends on the initial concentration of Z,

$$t_f = f_Z (1 - f_Z)^{-1} (r[Z]_0 k'')^{-1}. \quad (12-20)$$

For 50-, 90-, and 99-pct conversion of Z,

$$t_{0.50} = 1/r[Z]_0 k'', \quad (12-21)$$

$$t_{0.90} = 9/r[Z]_0 k'', \quad (12-22)$$

$$t_{0.99} = 99/r[Z]_0 k''. \quad (12-23)$$

Equations 12-19 and 12-20 are the most pertinent to solving practical problems; equations 12-21 through 12-23 are special cases of equation 12-20.

For the general case with excess reagent such as an oxidant, integration of equation 12-10 gives, with Q defined as $z[R]_0 - r[Z]_0$,

$$\begin{aligned} [Z]/[Z]_0 &= Q [\exp(-Qk''t)] \\ &\times \{z[R]_0 - r[Z]_0 \exp(-Qk''t)\}^{-1}, \end{aligned} \quad (12-24)$$

$$[R]/[R]_0 = Q / \{z[R]_0 - r[Z]_0 \exp(-Qk''t)\} \quad (12-25)$$

The fractional conversion f_Z of Z is

$$\begin{aligned} f_Z &= [1 - \exp(-Qk''t)] \\ &/ \{1 - (r/z)([Z]_0/[R]_0) \exp(-Qk''t)\}. \end{aligned} \quad (12-26)$$

The time t_f required to attain conversion f_Z is

$$\begin{aligned} t_f &= (Qk'')^{-1} \\ &\times \ln \{[1 - (r/z)([Z]_0/[R]_0)f_Z]/(1 - f_Z)\}. \end{aligned} \quad (12-27)$$

Equations 12-24 through 12-27 are the equations useful for solving practical problems.

For the case with R in very large excess over Z, equations 12-24, 12-26, and 12-27 become, approximately,

$$[Z]/[Z]_0 = \exp(-z[R]_0 k'' t), \quad (12-28)$$

$$f_Z = 1 - \exp(-z[R]_0 k'' t), \quad (12-29)$$

$$t_f = -(z[R]_0 k'')^{-1} \ln(1 - f_Z). \quad (12-30)$$

Equations 12-28 through 12-30 are equivalent to equations 12-9 through 12-11 with k' replaced by $z[R]_0 k''$. Accordingly, the kinetics of a second-order reaction with reagent in very large excess over substrate is termed "pseudo-first-order." This pseudo-first-order behavior also occurs if [R] is maintained constant, e.g., by metering it into a reactor or by a solubility equilibrium. An example of the latter is the constant concentration of dissolved O_2 during oxygen oxidations in the presence of excess air. Note that equations 12-29 and 12-30, like equations 12-10 and 12-11, are independent of the concentration of the substrate Z. Equations 12-28 through 12-30 are the equations applicable to solving practical problems.

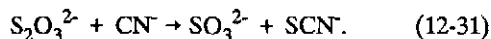
The times t_f required for a given conversion f_Z of Z decrease with the increase of the initial reagent-substrate ratio $[R]_0/[Z]_0$, the more rapidly for high f_Z . This is shown in the following tabulation, which gives relative values of t_f , namely $[R]_0 k'' t_f$, for the case of R and Z reacting in 1:1 mole ratio, namely $r = z$, calculated by means of equations 12-20 and 12-27:

$[R]_0 k'' t_f$ for $f_Z =$					
R_0/Z_0	0.5	0.9	0.99	0.999	
1.0	1.000	9.00	99.0	999.0	
1.1	.957	6.58	25.3	49.7	
1.2	.925	5.50	17.17	30.7	
1.5	.863	4.16	10.58	17.43	
2.0	.811	3.41	7.84	12.43	
5.0	.735	2.63	5.48	8.36	
10.0	.713	2.45	5.00	7.56	
Infinite	.693	2.30	4.61	6.91	

The first row of the table gives $[R]_0 k'' t_f$ for reagent and substrate in stoichiometric ratio (equation 12-20). The last row gives $[R]_0 k'' t_f$ for reagent in huge excess over substrate, i.e., pseudo-first-order conditions.

Example

In mineral process solutions, thiosulfate ($S_2O_3^{2-}$) is often present when the solutions have contacted sulfide minerals. As described in chapter 7, $S_2O_3^{2-}$ reacts with CN^- to form thiocyanate (SCN^-). Accordingly, one may ask at what rate $S_2O_3^{2-}$ converts CN^- to the less toxic SCN^- . A slow rate for this reaction would make it an impractical method for cyanide detoxification, but a rapid rate would require increased cyanide makeup for leaching. The reaction is



The reagent $S_2O_3^{2-}$ reacts with the substrate CN^- in 1:1 mole ratio, so $r = z = 1$. From table F-1, the rate equation is

$$d[CN^-]/dt = -k''[S_2O_3^{2-}][CN^-] \quad (12-32)$$

at $pH > 11$, where free cyanide is nearly all CN^- . At $25^\circ C$, $k'' = 1.2 \times 10^{-5} (\text{mol} \cdot \text{L}^{-1})^{-1} \cdot \text{s}^{-1}$ from table F-1. For initial $[Z]_0 = [CN^-]_0 = 0.010M$ and $[R]_0 = [S_2O_3^{2-}]_0 = 0.010M$, equations 12-21 through 12-23 give the times for 50-, 90-, and 99-pct reaction as $8.3 \times 10^6 \text{ s} = 96 \text{ days}$, $7.5 \times 10^7 \text{ s} = 2.4 \text{ years}$, and $8.2 \times 10^8 \text{ s} = 26 \text{ years}$, respectively. Under these conditions, the rate of this reaction is far too slow for practical detoxification of free CN^- . However, these results confirm that $S_2O_3^{2-}$ is not expected to interfere with leaching operations by robbing CN^- . Alternatively, consider the behavior if $S_2O_3^{2-}$ is held constant at $0.010M$ by metering it into the solution. In that case, pseudo-first-order behavior occurs. Then equation 12-30 gives the times for 50-, 90-, and 99-pct conversion of CN^- as $5.8 \times 10^6 \text{ s} = 67 \text{ days}$, $1.92 \times 10^7 \text{ s} = 222 \text{ days}$, and $3.8 \times 10^7 \text{ s} = 1.2 \text{ years}$, respectively. These conversion times are shorter than in the case without metered reagent and are the same for any value of the initial CN^- concentration. Again, reaction 12-31 is not practical for cyanide detoxification, but it would not rob CN^- from leaching operations. However, the $S_2O_3^{2-}$ - CN^- reaction is known to be catalyzed by copper species; in the absence of data, the effect of copper species on this reaction and on the conclusions just drawn is unknown.

EFFECT OF TEMPERATURE ON REACTION RATES

The rates of chemical reactions vary greatly with temperature. A rough rule of thumb is that reaction rates

double for a $10^\circ C$ rise in temperature. The relationship of reaction rate constant to temperature and activation parameters was discussed in chapter 7. Experimentally, data for rate constant k versus absolute temperature T usually fit an equation

$$\log k = A - BT^{-1}, \quad (12-33)$$

where A and B are empirically determined constants. The tables in appendix F present data for rate constants versus temperature for several reactions of free cyanide and derived species. For data at two temperatures, equation 12-33 is written for both temperatures T_1 and T_2 , and these two equations are combined:

$$\log (k_2/k_1) = B(T_1^{-1} - T_2^{-1}). \quad (12-34)$$

If equation 12-34 is rewritten for a data point at a third temperature, an equation for data at a third temperature can be obtained in terms of data at two other temperatures:

$$\begin{aligned} \log (k_3/k_1) &= \log (k_2/k_1) \\ &\times (T_1^{-1} - T_3^{-1}) / (T_1^{-1} - T_2^{-1}). \end{aligned} \quad (12-35)$$

Often data are available at two or more temperatures, so equation 12-35 is useful for calculating rate constants at other temperatures. If the temperature for which a rate constant is needed lies within or not far outside the temperature range of the available data, the uncertainty of the calculated rate constant is about the same as the uncertainty of the data. However, a rate constant calculated at a temperature much more than 10 pct outside the temperature range of the available data will be more uncertain than the experimental data employed.

Example

Cyanogen chloride is formed when CN^- reacts with ClO^- . The $ClCN$ hydrolyzes to NCO^- at a rate that increases with pH , as discussed above in connection with the effect of pH on reaction rate. The data are compiled in table F-9. The rate equations are equations 12-1 and 12-2. At $25^\circ C$ ($77^\circ F$), $k_a = 4.9 \times 10^{-7} \text{ s}^{-1}$ and $k_b = 12.2 (\text{mol L}^{-1})^{-1} \text{ s}^{-1}$. At $0^\circ C$ ($32^\circ F$), $k_a = 2.0 \times 10^{-8} \text{ s}^{-1}$ and $k_b = 0.47 (\text{mol L}^{-1})^{-1} \text{ s}^{-1}$. Calculate the rate constants at $15^\circ C$ ($59^\circ F$). The temperature variations of k_1 and k_2 differ, so the calculation must be done for each individually. Let $T_1 = 25^\circ C = 298 \text{ K}$, $T_2 = 0^\circ C = 273 \text{ K}$, and $T_3 = 15^\circ C = 288 \text{ K}$. Insertion of the temperatures and rate constants in equation 12-35 for k_a and k_b respectively gives at $15^\circ C$, $k_a = 1.46 \times 10^{-7} \text{ s}^{-1}$ and $k_b = 3.5 (\text{mol} \cdot \text{L}^{-1})^{-1} \cdot \text{s}^{-1}$.

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GLOSSARY

Absorbance: Amount of light absorption by a sample measured in a spectrophotometer. The absorbance A is related to the fraction of light transmitted T by $A = -\log T$. Dimensionless.

Activation parameters: The quantities activation energy, enthalpy, and entropy, which characterize the temperature dependence of the rate of a chemical reaction.

Activity: Thermodynamically effective concentration of a chemical species in a solution, related to the analytical concentration by an activity coefficient according to equation 4-24 in chapter 4. Dimensions: concentration.

Activity coefficient: Factor that relates activity to concentration. See Activity. Dimensionless.

Addition reaction: Chemical reaction in which two or more chemical species combine to form one chemical species. An example is $\text{H}_2\text{NCN} + \text{H}_2\text{O} \rightarrow \text{CO}(\text{NH}_2)_2$.

Band, absorption: Range of wavelengths of light absorbed by a chemical species.

Complexed cyanide: Cyanide bound to metal ions. Examples: $\text{Hg}(\text{CN})_2$, $[\text{Cu}(\text{CN})_3]^{2-}$.

Condensation reaction: Chemical reaction in which two reactant species combine, often with elimination of another species. An example is $2\text{Fe}(\text{CN})_5(\text{H}_2\text{O})^{3-} \rightarrow \text{Fe}_2(\text{CN})_{10}^{6-} + 2\text{H}_2\text{O}$.

Conjugate acid: Chemical species derived from another chemical species by addition of a hydrogen ion. For example, HCN is the conjugate acid of CN^- ; HCO_3^- is the conjugate acid of CO_3^{2-} .

Conjugate base: Chemical species derived from another chemical species by removal of a hydrogen ion. For example, CN^- is the conjugate base of HCN ; CO_3^{2-} is the conjugate base of HCO_3^- .

Coordination number: Number of ligands bound to a central atom, usually a metal ion.

Dinuclear: Refers to metal species that contain two metal ions per molecule or ion. An example is $\text{Fe}_2(\text{CN})_{11}^{6-}$.

Disproportionation reaction: Redox chemical reaction in which a chemical species containing an element in one oxidation state reacts with itself to form products which contain that element in two different oxidation states.

Eh: Reduction potential relative to the standard potential for the half-reaction $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$ defined as exactly zero.

Eh-pH diagram: An equilibrium predominance area diagram that shows predominant chemical species as a function of Eh and pH.

Elementary reactions or steps: Simple reactions involving usually one or two molecules or ions at a time that occur during a chemical reaction and constitute the mechanism of that reaction. See chapter 7.

Elimination reaction: Chemical reaction in which a chemical species decomposes into a related chemical species and a small molecule or ion. An example is $\text{H}_2\text{NCOS}^- \rightarrow \text{NCO}^- + \text{H}_2\text{S}$.

EPAD (equilibrium predominance area diagrams): Diagrams that show predominant chemical species in a system on the basis of equilibrium data, as a function of variables such as pH, pM, pL, or Eh. See chapter 4.

Equilibrium constant: Constant that relates the activities of chemical species in a reaction at equilibrium, defined in equation 4-10 in chapter 4.

Exchange reaction: Chemical reaction in which chemical species exchange groups of atoms. An example is $\text{CH}_3\text{COSH} + \text{NH}_3 \rightarrow \text{CH}_3\text{CONH}_2 + \text{H}_2\text{S}$.

Excitation: Elevation of a chemical species to a higher energy state.

Excited state: Energy state higher than the ground state of a chemical species. In photochemistry, electrons in a chemical species absorb light and are excited to a higher energy level, and the species is then in an electronic excited state.

Free cyanide: Cyanide not complexed with metal ions.

Ground state: State of lowest energy of a chemical species.

Induction period: Period of time elapsed from mixing of reactants to onset of reaction.

Infrared light: Light of wavelength from $700 \text{ nm} = 0.7 \mu\text{m}$ up to about $1,000 \mu\text{m}$.

Ionic strength: Half the sum of the products of the concentrations times the squared charges of all ions in a solution. See appendix A.

Kinetics: Chemical reaction rates.

Labile: Chemically reactive.

Ligand: Any chemical species that complexes with a metal ion.

Mmaximum allowable concentration: Maximum concentration of a toxic substance to which workers may be continually exposed without harm for a specified time, often 8 h.

Molar absorptivity: Measure of light absorption by a chemical species. It is related to the absorbance, the sample concentration, and the sample thickness by the Lambert-Beer law, equation 5-1. Dimensions: reciprocal concentration times reciprocal length.

Mononuclear: Refers to metal species that contain one metal ion per molecule or ion.

Non-WAD: Refers to metal cyanide species that are not decomposed by acids at pH 2 to 7 with liberation of HCN. See WAD.

Order of a chemical reaction: Dependence of a reaction rate on the concentrations of reacting species. See chapter 7.

Partially WAD: Refers to metal cyanide species that are partially decomposed by acids at pH 2 to 7 with liberation of HCN. See WAD.

pH: $-\log a(\text{H}^+)$, where $a(\text{H}^+)$ is the activity of hydrogen ion, H^+ .

Photochemical reaction: Chemical reaction caused to occur by absorption of light. See chapter 9.

Photon: Smallest unit, "particle," or quantum of light energy.

pK: $-\log K$, where K is an equilibrium constant. Often used for acid dissociation constants.

pL: $-\log a(\text{L})$, where $a(\text{L})$ is the total activity of all free ligand species.

pM: $-\log a(\text{M})$, where $a(\text{M})$ is the total activity of all metal species.

pM-pH diagram: An EPAD showing predominant chemical species as a function of pM and pH.

pM-pL diagram: An EPAD showing predominant chemical species as a function of pM and pL.

Polynuclear: Refers to metal species that contain more than one metal ion per molecule or complex ion. An example is $\text{Cr}_3(\text{OH})^{45+}$.

Polyprotic: Refers to acids or bases that can lose or gain more than one hydrogen ion, H^+ . Examples are the acid H_3PO_4 or the base $[\text{Co}(\text{NH}_3)_4(\text{OH})_2]^{1+}$.

Quantum efficiency or yield: Number of moles of photochemical reaction product per mole of absorbed photons.

Rate constant: Empirically determined numerical coefficients in a rate equation. Dimensions: $(\text{concentration})^{n+1} \text{ times } (\text{time})^{-1}$, where n is the total order of the reaction.

Rate equation or rate law: Mathematical equation that expresses how the rate of a chemical reaction depends on the concentrations of the involved chemical species.

Rate-limiting or rate-determining step: Elementary step of a chemical reaction that determines its rate.

Standard state: State of a chemical species to which its thermodynamic properties are referred. See chapter 4.

Substitution reaction: Chemical reaction in which a group of atoms in one reactant species substitutes for a group of atoms in another reactant species. An example is $\text{ClCN} + \text{I}^- \rightarrow \text{ICN} + \text{Cl}^-$.

Substrate: Reactant of primary interest, the other reactant(s) being reagent(s).

Thermal reaction: Chemical reaction that occurs only by thermodynamic driving force, as opposed to a photochemical reaction.

Ultraviolet light: Light of wavelength from 400 nm to about 10 nm. The atmospheric ozone layer cuts off solar ultraviolet light of wavelength shorter than 300 nm. Water and oxygen absorb at wavelengths below 200 nm.

Visible light: Light of wavelength 800 nm (red) to 400 nm (violet).

WAD (weak-acid dissociable): Refers to metal cyanide species that are completely decomposed by acids at pH 2 to 7 with liberation of HCN.

APPENDIX A.—IONIC STRENGTH

Ionic strength was mentioned in chapter 4 in connection with equilibrium constants in solutions. In this appendix, ionic strength is defined, and its effects on chemical equilibria and reaction rates are outlined.

Ionic strength I is defined as

$$I = (1/2) \sum_i^n c_i z_i^2, \quad (\text{A-1})$$

where c_i and z_i are respectively, the concentration and ion charge of the i th species in the solution. The concentrations c_i may be moles per liter solution (molarity) or moles per kilogram solvent (molality). For a solution of one binary salt, the right-hand side of equation A-1 contains only two terms, i.e., $n = 2$, and I is an integer multiple of the salt concentration c . Some examples are tabulated:

<i>Electrolyte type</i>	<i>Example</i>	<i>I/c</i>
1:1	NaCl	1
2:1 or 1:2	Na ₂ SO ₄ or CaCl ₂	3
3:1 or 1:3	Na ₃ [Fe(CN) ₆] or AlCl ₃	6
4:1 or 1:4	Na ₄ [Fe(CN) ₆] or ThCl ₄	10
2:2	MgSO ₄	4
3:2 or 2:3	Ca ₃ [Fe(CN) ₆] ₂ or Al ₂ (SO ₄) ₃	15
4:2 or 2:4	Mg ₂ [Fe(CN) ₆] or Th(SO ₄) ₂	12

Activity and activity coefficients were discussed in chapter 4. Activity a , activity coefficient γ , and concentration c are related by

$$a = \gamma c. \quad (\text{A-2})$$

The activity coefficient of an electrolyte varies strongly with concentration. By convention, γ is equal to 1 at infinite dilution, i.e., $c \rightarrow 0$. With increasing concentration, hence ionic strength, γ decreases to a minimum, then increases rapidly. In very dilute solutions, the variation of γ with I is given approximately by

$$\log \gamma = -Az_+z_-I^{1/2} / (1 + I^{1/2}). \quad (\text{A-3})$$

Equation A-3 is the Debye-Hueckel limiting law for electrolyte activity coefficients. The quantity A is a solvent- and temperature-dependent constant. For water at 25° C, A is 0.511. The z 's are the ion charges. For further details, the reader is referred to textbooks on thermodynamics.

The effect of ionic strength on equilibrium constants depends primarily on the numbers and charges of ionic species in the reactions. Increasing ionic strength favors the side of the reaction with the larger sum of squared ion charges, Δz^2 :

$$\Delta z^2 = \sum_i s_{i,p} z_{i,p}^2 - \sum_i s_{i,r} z_{i,r}^2, \quad (\text{A-4})$$

$$\sum_i s_{i,r} (\text{species})_{i,r} \rightarrow \sum_i s_{i,p} (\text{species})_{i,p}. \quad (\text{A-5})$$

In equation A-4, the $s_{i,p}$ and $s_{i,r}$ are the stoichiometric coefficients of the products and reactants in the reaction, represented by equation A-5; and the $z_{i,r}$ and $z_{i,p}$ are the corresponding charges of the species. Some examples follow:

<i>Reaction</i>	Δz^2	<i>Side favored</i>
$\text{Zn}^{2+} + 4\text{CN}^{-1} \rightarrow \text{Zn}(\text{CN})_4^{2-}$	-4	Left
$\text{HgCl}_2 + \text{Cl}^{-1} \rightarrow \text{HgCl}_3^{-1}$	0	Either
$\text{HgCl}_3^{-1} + \text{Cl}^{-1} \rightarrow \text{HgCl}_4^{2-}$	+2	Right
$2\text{AgCN(s)} \rightarrow \text{Ag}^{1+} + \text{Ag}(\text{CN})_2^{-1}$	+2	Right
$\text{Fe}^{3+} + \text{SO}_4^{2-} \rightarrow \text{FeSO}_4^{1+}$	-12	Left

Ionic strength affects reaction rates through the charges of the species that react in the rate-limiting step of the reaction. If the reacting species in the rate-limiting step are all neutral or involve only one ionic species, the effect of ionic strength on the rate is relatively insignificant. If two ionic species react in the rate-limiting step, the rate constant increases with increasing ionic strength if the charges of the two reacting ions have the same sign, and decreases with increasing ionic strength if their charges have opposite signs. This effect of ionic strength on reaction rates is termed the "salt effect" in the older literature.

APPENDIX B.—THERMODYNAMIC DATA FOR FREE CYANIDE AND DERIVED SPECIES

This appendix contains tables of standard enthalpies of formation $\Delta_f H^\circ$ and standard Gibbs energies of formation $\Delta_f G^\circ$ (table B-1), equilibrium data at different temperatures and ionic strengths (table B-2), and solids solubility data (table B-3) for free cyanide and derived species. Some of the $\Delta_f G^\circ$ data were calculated or estimated from the solubility data in table B-3 or other data; the details for other data are given in the footnotes of table B-1. The major data sources are the NBS tables (1),¹ the JANAF tables (2), a CODATA report (3), and the compilations by Christensen and others (4) and Martell and Smith (5-7). Other references are cited in the tables in the column "Additional references": cyanide (8-16), C(II) species (17-22), C(III) derivatives (23-35), C(IV) derivatives (36-69), and fulminate and derivatives (70-73). The oxide species, namely formate, oxalate, and carbonate, are also included in tables B-1 and B-2. Except for placing fulminate and its derivatives at the ends of the tables, we have used the same arrangement as that used in chapter 2.

REFERENCES

1. Wagman, D. D., W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney, and R. L. Nuttall. The NBS Tables of Chemical Thermodynamic Properties. Selected Values of Inorganic and C₁ and C₂ Organic Substances in SI Units. *J. Phys. Chem. Ref. Data*, suppl. 2, v. 11, 1982, 392 pp.
2. Chase, M. W., Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, and A. N. Syverud. JANAF Thermochemical Tables. *Am. Chem. Soc. and Am. Inst. Phys.*, 3rd ed., 1986, 2 vols., 1856 pp.
3. International Council of Scientific Unions. Recommended Key Values for Thermodynamics. Report of the CODATA Task Group on Key Values for Thermodynamics, 1977. *J. Chem. Thermodyn.*, v. 10, 1978, pp. 903-906.
4. Christensen, J. J., L. D. Hansen, and R. M. Izatt. Handbook of Proton Ionization Heats and Related Thermodynamic Quantities. Wiley-Interscience, 1976, 269 pp.
5. Martell, A. E., and R. M. Smith. Critical Stability Constants. V. 3, Other Organic Ligands. Plenum, 1977, 495 pp.
6. Martell, A. E., and R. M. Smith. Critical Stability Constants. V. 5, First Supplement. Plenum, 1982, 604 pp.
7. Smith, R. M., and A. E. Martell. Critical Stability Constants. V. 6, Second Supplement. Plenum, 1989, 643 pp.
8. Linke, W. F. Solubilities of Inorganic and Metal-Organic Compounds, v. 1. *Am. Chem. Soc.*, 1958, p. 1106.
9. Wilhelm, E., R. Battino, and R. J. Wilcock. Low-Pressure Solubility of Gases in Liquid Water. *Chem. Rev.*, v. 77, 1977, pp. 219-262.
10. Kotlik, S. B., and G. N. Lebedeva. (Equilibrium Pressure of Hydrocyanic Acid and Ammonia Over Aqueous Solutions.) *Russ. J. Appl. Chem. (Engl. Transl.)*, v. 47, 1974, pp. 1974-1976; *Chem. Abstr.*, v. 81, 1974, No. 69074s.
11. Tsonopoulos, C., D. M. Coulson, and L. B. Inman. Ionization Constants of Water Pollutants. *J. Chem. Eng. Data*, v. 21, 1976, pp. 190-193.
12. Broderius, S. J. Determination of Hydrocyanic Acid and Free Cyanide in Aqueous Solution. *Anal. Chem.*, v. 53, 1981, pp. 1472-1477.
13. Gaspar, V., and M. T. Beck. The Influence of the Ionic Strength on the Dissociation Constant of Hydrogen Cyanide. *Acta. Chim. Acad. Sci. Hung.*, v. 110, 1982, pp. 425-427; *Chem. Abstr.*, v. 98, 1983, No. 114688j.
14. Beck, M. T. Critical Survey of Stability Constants of Cyano Complexes. *Pure Appl. Chem.*, v. 59, 1987, pp. 1703-1720.
15. Verhoeven, P., G. Hefter, and P. M. May. Dissociation Constant of Hydrogen Cyanide in Saline Solutions. *Miner. Metall. Proc.*, v. 7, 1990, pp. 185-188.
16. Banyai, I., J. Blixt, J. Glaser, and I. Toth. On the Dissociation of Hydrogen Cyanide in Aqueous Solutions Containing Different Ionic Media. A Combined Potentiometric and Carbon-13 NMR Study. *Acta Chem. Scand.*, v. 46, 1992, pp. 138-141.
17. Engler, R., and G. Gattow. Untersuchungen Ueber Thioameisen-sauren. 4. Verhalten von HCO₂⁻, HCOS⁻, und HCS₂⁻ in Waessriger Loesung (Investigation of Thioformic Acids. 4. Behavior of HCO₂⁻, HCOS⁻, and HCS₂⁻ in Aqueous Solution). *Z. Anorg. Allg. Chem.*, v. 389, 1972, pp. 151-156.
18. Bauder, A., and H. S. Guenthard. Thermodynamische Eigenschaften von Formamid (Thermodynamic Properties of Formamide). *Helv. Chim. Acta*, v. 41, 1958, pp. 670-673.
19. Fersht, A. R., and Y. Requena. Free Energies of Hydrolysis of Amides and Peptides in Aqueous Solution at 25°. *J. Am. Chem. Soc.*, v. 93, 1971, pp. 3499-3504.
20. Wada, G., and T. Takenaka. Basicities of Formamide, Acetamide, and Their Alkyl Derivatives in Aqueous Solution. *Bull. Chem. Soc. Jpn.*, v. 44, 1971, p. 2877.
21. Mittal, S., K. S. Gupta, and Y. K. Gupta. Kinetics and Mechanism of Acid Hydrolysis of Formamide, Acetamide, Propanamide, and Butanamide Over an Extended Concentration Range: Kinetic Evidence for Fast Protonation Pre-Equilibrium. *Indian J. Chem.*, v. 21A, 1982, pp. 357-360.
22. Khan, M. N., R. Ahmad, and A. A. Khan. Kinetics and Mechanism of Base-Catalyzed Hydrolysis of Formamide—Effect of Alkalinity on the Reactive Tetrahedral Addition Intermediates. *Indian J. Chem.*, v. 14A, 1975, pp. 961-963.
23. Wang, Y. L., H. D. Lee, M. W. Beach, and D. W. Margerum. Kinetics of Base Hydrolysis of Cyanogen and 1-Cyanoformamide. *Inorg. Chem.*, v. 26, 1987, pp. 2444-2449.
24. Nunez, L., L. Barbal, and G. Pilcher. Enthalpies of Combustion of Oxamic Acid, Oxamide, and Dithiooxamide. *J. Chem. Thermodyn.*, v. 20, 1988, pp. 1211-1216.
25. Yaffe, R. P., and A. F. Voigt. The Acidity Constant, Solubility Product, and Solubility of Dithiooxamide. *J. Am. Chem. Soc.*, v. 74, 1952, p. 2941.
26. Aarts, A. J., and M. A. Herman. (Acid Dissociation Constants of Some Thiooxamides and Dithiooxamides.) *Bull. Soc. Chim. Belg.*, v. 86, 1977, pp. 757-766; *Chem. Abstr.*, v. 88, 1978, No. 37075w.
27. Van de Cappelle, G. L., M. A. Herman, and Z. Eeckhaut. (Determination of the Dissociation Constant of Monothiooxamide and Some of its Derivatives.) *Bull. Soc. Chim. Belg.*, v. 79, 1970, pp. 421-426; *Chem. Abstr.*, v. 73, 1970, No. 102586v.
28. Egan, E. P., Jr., Z. T. Wakefield, and T. D. Farr. Low Temperature Heat Capacity and Entropy of Oxamide, 10 to 310° K. *J. Chem. Eng. Data*, v. 10, 1965, pp. 138-140.

¹Italic numbers in parentheses refer to items in the list of references at the end of this appendix.

29. Prager, B., and P. Jacobson (eds.). *Beilsteins Handbuch der Organischen Chemie*, Springer, 4th ed. 1920, v. 2, p. 546.
30. Pilipenko, A. T., and N. N. Maslei. (The Acid Properties of Dithiooxalic Acid and the Stability in Time of Potassium Dithiooxalate Solutions.) *Ukr. Khim. Zh.*, v. 33, 1967, pp. 831-833; *Chem. Abstr.*, v. 68, 1968, No. 6920a.
31. Luff, B. B., and R. B. Reed. Low Temperature Heat Capacity and Entropy of Oxalic Acid and of Biuret. *J. Chem. Eng. Data*, v. 27, 1982, pp. 290-292.
32. Washburn, E. W. (ed.). *International Critical Tables*. McGraw-Hill, 1929, v. 6, p. 262.
33. Braibanti, A., E. Leporati, and F. Dallavalle. The Protonation Constant of Oxamic Acid in Aqueous Solution and in Water-Tetrahydrofuran Mixture, at Different Temperatures and Ionic Strengths. *Inorg. Chim. Acta*, v. 4, 1970, pp. 529-532.
34. Kurz, J. L., and J. M. Farrar. The Entropies of Dissociation of Some Moderately Strong Acids. *J. Am. Chem. Soc.*, v. 91, 1969, pp. 6057-6062.
35. Kettler, R. M., D. A. Palmer, and D. J. Wesolowski. Dissociation Quotients of Oxalic Acid in Aqueous Sodium Chloride Media to 175° C. *J. Solution Chem.*, v. 20, 1991, pp. 905-927.
36. De Wit, H. G. M., J. L. van Miltenburg, and C. G. de Kruij. Thermodynamic Properties of Molecular Organic Crystals Containing Nitrogen, Oxygen, and Sulphur. 1. Vapor Pressures and Enthalpies of Sublimation. *J. Chem. Thermodyn.*, v. 15, 1983, pp. 651-663.
37. May, D. R. Cyanamides. Ch. in *Kirk-Othmer Encyclopedia of Chemical Technology*. Wiley, 3rd ed., 1983, v. 7, p. 292.
38. Golov, V. G., and L. V. Kuznetsova. Vapor Pressure of Cyanamide Over its Aqueous Solutions. *Russ. J. Appl. Chem. (Engl. Transl.)*, v. 43, 1970, pp. 1987-1992.
39. Soloway, S., and A. Lipschitz. Basicity of Some Nitrilated Amines. *J. Org. Chem.*, v. 23, 1958, pp. 613-615.
40. Beck, M. T., and I. Banyai. (Acid-Base Properties and Dimerization of Cyanamide.) *Magy. Kem. Foly.*, v. 88, 1982, pp. 126-130; *Chem. Abstr.*, v. 96, 1982, No. 224114k.
41. Morgan, T. D. B., G. Stedman, and P. A. E. Whincup. The Ionization Constant of Thiocyanic Acid. *J. Chem. Soc.*, 1965, pp. 4813-4822.
42. Hamada, S. (Decomposition Equilibrium of Selenocyanate Ion.) *Nippon Kagaku Zasshi*, v. 82, 1961, pp. 1327-1330; *Chem. Abstr.*, v. 57, 1962, p. 146c.
43. Franz, P., H. Gobrecht, M. Schciba, D. Wobig, and W. Kunze. On the Thermodynamic Stability of Monoclinic Selenium. *Z. Phys. Chem. (Wiesbaden)*, v. 111, 1978, pp. 162-176.
44. Chrzasczewski, J., M. Wronski, and A. Leszczynska. (Solubility of Carbon Disulfide in Aqueous Electrolyte Solutions.) *Zesz. Nauk. Uniw. Lodz. Ser. 2, Nauki Mat.-Przyrod.*, 1957, No. 3, pp. 133-137; *Chem. Abstr.*, v. 52, 1958, p. 17903f.
45. Caramazza, R. (Measurement of Dissociation Constants of Unstable Weak Acids. II. Cyanic Acid.) *Gazz. Chim. Ital.*, v. 88, 1958, pp. 308-319; *Chem. Abstr.*, v. 53, 1959, p. 16659d.
46. Lister, M. W. Some Observations on Cyanic Acid and Cyanates. *Can. J. Chem.*, v. 33, 1955, pp. 426-440.
47. Elliott, S., E. Lu, and F. S. Rowland. Rates and Mechanisms for the Hydrolysis of Carbonyl Sulfide in Natural Waters. *Environ. Sci. Technol.*, v. 23, 1989, pp. 458-461.
48. Berg, R. L., and C. E. Vanderzee. Thermodynamics of Carbon Dioxide and Carbonic Acid. *J. Chem. Thermodyn.*, v. 10, 1978, pp. 1113-1136.
49. Harned, H. S., and R. Davis, Jr. The Ionization Constant of Carbonic Acid in Water and the Solubility of Carbon Dioxide in Water and Aqueous Salt Solutions. *J. Am. Chem. Soc.*, v. 65, 1943, pp. 2030-2037.
50. Malinin, S. D., and N. I. Savelyeva. The Solubility of CO₂ in NaCl and CaCl₂ Solutions at 25, 50, and 75° C Under Elevated CO₂ Pressures. *Geochem. Int. (Engl. Transl.)*, v. 9, 1972, pp. 410-418.
51. Plummer, L. N., and E. Busenberg. The Solubilities of Calcite, Aragonite, and Vaterite in CO₂-H₂O Solutions Between 0 and 90° C, and an Evaluation of the Aqueous Model for the System CaCO₃-CO₂-H₂O. *Geochim. Cosmochim. Acta*, v. 46, 1982, pp. 1011-1040.
52. Matyushin, Yu. N., T. S. Konkova, K. V. Titova, V. Ya. Rosolovskii, and Yu. A. Lebedev. (Enthalpies of Formation of Guanidinium Nitrate, Perchlorate, and Chloride.) *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, pp. 787-790; *Chem. Abstr.*, v. 103, 1985, No. 104474u.
53. Newman, D. J. Nitric Acid. Ch. in *Kirk-Othmer Encyclopedia of Chemical Technology*. Wiley, 3rd ed., 1981, v. 15, p. 855.
54. Titova, K. V., and V. Ya. Rosolovskii. Some Physicochemical Properties of Guanidine Perchlorate. *Russ. J. Inorg. Chem. (Engl. Transl.)*, v. 10, 1965, pp. 239-242.
55. Bonner, O. D. The Osmotic and Activity Coefficients of Some Guanidinium Salts at 298.15° K. *J. Chem. Thermodyn.*, v. 8, 1976, pp. 1167-1172.
56. Wirth, T. H., and N. Davidson. Mercury(II) Complexes of Guanidine and Ammonia, and a General Discussion of the Complexing of Mercury(II) by Nitrogen Bases. *J. Am. Chem. Soc.*, v. 86, 1964, pp. 4325-4329.
57. Albert, A., R. Goldacre, and J. Phillips. The Strength of Heterocyclic Bases. *J. Chem. Soc.*, 1948, pp. 2240-2249.
58. Fabbri, L., M. Micheloni, P. Paoletti, and G. Schwarzenbach. Protonation Processes of Unusual Exothermicity. *J. Am. Chem. Soc.*, v. 99, 1977, pp. 5574-5575.
59. Torres-Gomez, L. A., and R. Sabbah. Thermodynamique des Substances Soufrees. IV. Etude Thermochemique de la Thiouree, de la Thiosemicarbazide, et de la Thio-carbohydrazide (Thermodynamics of Sulfur-Containing Substances. IV. Thermochemical Study of Thiourea, Thiosemicarbazide, and Thio-carbohydrazide). *Thermochim. Acta*, v. 57, 1982, pp. 67-81.
60. Mackle, H., and P. A. G. O'Hare. Thermodynamic Properties of Six Sulfur-Containing Molecules. *Trans. Faraday Soc.*, v. 59, 1963, pp. 309-315.
61. Taniewska-Osinska, S., and B. Palecz. Enthalpies of Solution of Thiourea in Water From 293.15 to 333.15° K. *J. Chem. Thermodyn.*, v. 12, 1980, pp. 775-778.
62. Sadetdinov, Sh. V. The Influence of Acetamide, Urea, and Thiourea on the Solubility of Sodium Tetraborate. *Russ. J. Inorg. Chem. (Engl. Transl.)*, v. 30, 1985, pp. 1911-1913.
63. Stokes, R. H. Thermodynamics of Aqueous Urea Solutions. *Aust. J. Chem.*, v. 20, 1967, pp. 2087-2100.
64. Gattow, G., and V. Hahnkamm. Untersuchungen Ueber Dithiocarbamidsaeure. 2. Verhalten der Dithiocarbamidsaeure in waessriger Loesung (Investigation of Dithiocarbamic Acid. 2. Behavior of Dithiocarbamic Acid in Aqueous Solution). *Z. Anorg. Allg. Chem.*, v. 365, 1969, pp. 70-78.
65. Mavrovic, I., and A. A. Shirley. Urea. Ch. in *Kirk-Othmer Encyclopedia of Chemical Technology*. Wiley, 3rd ed., 1983, v. 23, p. 549.
66. Claude, B. Hydrolyse et Thermochemique de Quelques Carbamates (Hydrolysis and Thermochemistry of Some Carbamates). *Rev. Chim. Miner.*, v. 2, 1965, pp. 327-338; *Chem. Abstr.*, v. 63, 1965, No. 16196g.
67. Christensson, F., H. C. S. Koefoed, A. C. Petersen, and K. Rasmussen. Equilibrium Constants in the Ammonium Carbonate-Carbamate System. The Acid Dissociation Constant of Carbamic Acid. *Acta Chem. Scand.*, v. 32A, 1978, pp. 15-17.

68. Patterson, C. S., G. H. Slocum, R. H. Busey, and R. E. Mesmer. Carbonate Equilibria in Hydrothermal Systems. First Ionization of Carbonic Acid in NaCl Medium to 300° C. *Geochim. Cosmochim. Acta*, v. 46, 1982, pp. 1653-1663.
69. Patterson, C. S., R. H. Busey, and R. E. Mesmer. Second Ionization Constant of Carbonic Acid in NaCl Media to 25° C. *J. Solution Chem.*, v. 13, 1984, pp. 647-661.
70. Klatt, B., and K. Schwabe. Das Verhalten von Fulminaten an der Tropfenden Quecksilberelektrode (Fulminate Behavior at the Dropping Mercury Electrode). *J. Electroanal. Chem. Interfacial Electrochem.*, v. 24, 1970, pp. 61-78.
71. Linke, W. F. Solubilities of Inorganic and Metal-Organic Compounds, v. I. *Am. Chem. Soc.*, 1958, p. 1193.
72. Beck, W., P. Swoboda, K. Feldl, and R. S. Tobias. Eigenschaften und IR-Spektrum der Knallsäure, HCNO (Properties and Infrared Spectrum of Fulminic Acid, HCNO). *Chem. Ber.*, v. 104, 1971, pp. 533-554.
73. Abbasi, S. A., and J. Ahmed. Ionization of Hydroxamic Acids in Aqueous Solutions. *Bull. Chem. Soc. Jpn.*, v. 49, 1976, pp. 2013-2014.

Table B-1.-Thermodynamic formation data for free cyanide and derived and related species at 25° C

Species	$\Delta_f H^\circ$, kJ·mol ⁻¹	$\Delta_f G^\circ$, kJ·mol ⁻¹	Additional references
HCN (g)	+135.1	+124.9	
HCN (aq)	+107.1	+119.8	
CN ⁻ (aq)	+150.6	+172.4	
CO (g)	-110.5±.1	-137.2±0.1	
HCONH ₂ (l)	-254.0	-168.9	18
HCONH ₂ (g)	-189.0	-143.8	18
HCONH ₂ (aq)	-247.7	-180.9	19
HCO ₂ H (aq)	-425.4	-372.3	
HCO ₂ ⁻ (aq)	-425.5	-350.9	
C ₂ N ₂ (g)	+309.0	+297.4	
C ₂ N ₂ (aq)	N	+301.4	
H ₂ NCSCSNH ₂ (s)	-20.8	¹ +94.5	24
H ₂ NCSCSNH ₂ (aq)	N	+108.8	25
H ₂ NCOCNSH ₂ (s)	² -262.6	² -124.5	
H ₂ NCOCNSH ₂ (aq)	N	N	
H ₂ NCOCNH ₂ (s)	-504.4	-340.0	25, 28
H ₂ NCOCNH ₂ (aq)	N	-328.6	29
H ₂ NCOCOOH (s)	-661.2	³ -515.6	25, 31
H ₂ NCOCOOH (aq)	N	⁴ -506.6	32
H ₂ NCOCO ₂ ⁻ (aq)	N	-494.3	33
H ₂ C ₂ O ₄ (aq)	-815.1	-705.7	34-35
HC ₂ O ₄ (aq)	-818.4	-698.3	
C ₂ O ₄ ²⁻ (aq)	-825.1	-673.9	
ClCN (g)	-137.9	-131.0	
BrCN (g)	-186.2	-165.3	
NCNH ₂ (s)	+59.0	⁵ +128.9	
NCNH ₂ (g)	+134.2	⁶ +157.5	36
NCNH ₂ (aq)	+74.5	⁷ +126.1	37-38
NCNH ⁻ (aq)	N	+184.9	37, 40
HNCS (aq)	N	+98.4	41
NCS ⁻ (aq)	+76.4	+92.7	
NCSe ⁻ (aq)	+80.	+142.	42-43
CS ₂ (l)	+89.2	+65.0	
CS ₂ (g)	+116.9	+66.8	
CS ₂ (aq)	+88.6	+74.3	44
HNCO (aq) ⁸	-156.4	-117.4	45-46
NCO ⁻ (aq) ⁸	-146.0	-97.4	
COS (g)	-138.4	-165.6	
COS (aq)		-156.0	47
CO ₂ (g)	-393.5±0.1	-394.4±0.1	48
CO ₂ (aq)	-413.3±0.2	-386.0±0.2	48
C(NH ₂) ₃ ⁺ (aq)	-139.1	⁹ -12.	51-54

Table B-1.--Thermodynamic formation data for free cyanide and derived and related species at 25° C--Continued

Species	$\Delta_f H^\circ$, kJ·mol ⁻¹	$\Delta_f G^\circ$, kJ·mol ⁻¹	Additional references
HNC(NH ₂) ₂ (s)	-56.1	N	
HNC(NH ₂) ₂ (aq)	-63.1	+68.	56-58
CS(NH ₂) ₂ (s)	-89.1	¹⁰ +19.8	36, 59-60
CS(NH ₂) ₂ (aq)	-66.5	¹¹ +18.3	61-63
CO(NH ₂) ₂ (s)	-333.5	-197.3	
CO(NH ₂) ₂ (aq)	-318.4	-203.3	61-63, 65
H ₂ NCOOH (aq)	N	-418.6	66-67
H ₂ NCO ₂ ⁻ (aq)	-498.0	-378.1	66-67
HCO ₃ ⁻ (aq)	-689.9±0.2	-586.9±0.2	48
C ₃ ²⁻ (aq)	-675.2±0.2	-528.0±0.2	48
HCNO (aq) ¹²	N	+152.	70-72
CNO ⁻ (aq) ¹²	N	¹³ +181.	70-71

N No data.

¹Derived from estimated S° of 141.3 J·K⁻¹ obtained by assuming $\Delta_f S^\circ$ based on S₂(g) (reference 3) equal to $\Delta_f S^\circ$ for H₂NCOCONH₂.

² $\Delta_f H^\circ$ taken as average of values for H₂NCSCSNH₂ and H₂NCOCONH₂. $\Delta_f G^\circ$ derived from estimated S° of 135.5 J·K⁻¹, which is the average of the published value for H₂NCOCONH₂ (reference 28) and the estimated value for H₂NCSCSNH₂, increased by R ln 2.

³Derived from estimated S° of 122.6 J·K⁻¹, which is the average of the published values for H₂C₂O₄ and H₂NCOCONH₂ (references 31 and 28, respectively), increased by R ln 2.

⁴Derived from solubility with correction for dissociation.

⁵Derived from vapor pressure and S° of gas.

⁶Derived from S° 250 J·K⁻¹, estimated from comparison of S° values of XCH₃(g) and XCN(g) (X = F, OH, NH₂, CH₃) tabulated in reference 1.

⁷Derived from infinite-dilution Raoultian activity coefficient of 18 estimated from data in reference 38.

⁸Cyanic acid, cyanate.

⁹Derived from published solubility and activity data and estimated S° of 235 J·K⁻¹ for CN₃H₆ClO₄; the latter was derived from estimated S° of 215 J·K⁻¹ for CN₃H₆NO₃ and comparison of S° values of nitrates and perchlorates of K, Rb, and NH₄ tabulated in reference 1. The estimated S° for CN₃H₆NO₃ was assumed equal to the estimated S° of CO(NH₂)₂HNO₃, which was taken as equal to the sum of the S° values for CO(NH₂)₂ and HNO₃ (reference 1), with subtraction of 45.2 J·K⁻¹, the entropy of melting of HNO₃ (reference 53).

¹⁰Derived from published vapor pressure and S° of gas (references 36 and 60).

¹¹Derived using estimated activity coefficient of 0.86 at saturation, taken as equal to that of CO(NH₂)₂ at the same molality (reference 63).

¹²Fulminic acid, fulminate.

¹³Derived from log K for formation of aqueous Hg(CNO)₂ in reference 70 and solubility of Hg(CNO)₂ in reference 71. This required an estimated value of +342 kJ·mol⁻¹ for the standard Gibbs energy of formation of solid Hg(CNO)₂, which was estimated from data in reference 1 for cyanates and fulminates of Hg, Ag, and Na.

Table B-2.-Equilibrium data for reactions of free cyanide and derived species

Reactant	Reaction type ¹	Temperature, °C	Log K at ionic strength (<u>M</u>)				Additional references
			0.0	0.1	1.0	3.0	
HCN	s	0	1.33	N	N	N	8-10
		10	1.16	N	N	N	
		25	.90	N	N	N	
		40	.68	N	N	N	
		60	.42	N	N	N	
		90	.12	N	N	N	
HCN	a	0	² 10.00	N	N	N	11-16
		10	9.63	N	N	N	
		25	9.21	9.05	8.88	8.81	
		³ 25	9.21	9.04	8.95	9.22	
		40	8.88	N	N	N	
		60	8.4	N	N	N	
CO	s	0	-2.81	N	N	N	9
		10	-2.91	N	N	N	
		25	-3.03	N	N	N	
		40	-3.11	N	N	N	
		60	-3.17	N	N	N	
H-CS-SH	a	25	.85	N	N	N	17
H-CO-NH ₃ ⁺	a	25	-.2	N	⁴ .1	N	20-21
H-CO-NH ₂	a	25	N	N	13.	N	22
H-CO-SH	a	25	2.06	N	N	N	17
HCO-OH	a	0	3.79	N	N	N	
		10	3.76	N	N	N	
		25	3.75	3.57	3.49	3.90	
		40	3.77	N	N	N	
		60	3.81	N	N	N	
NC-CN	s	25	-.7	N	N	N	8
NC-CO-NH ₂	a	25	N	⁵ 10.8	N	N	23
H ₂ N-CS-CS-NH ₂	a	25	11.0	10.8	10.8	N	26
H ₂ N-CS-CS-NH ⁻	a	25	N	N	13.1	N	
H ₂ N-CO-CS-NH ₂	a	25	11.5	11.3	11.2	N	27
HS-CO-CO-SH	a	25	.9	N	N	N	30
HS-CO-COS ⁻	a	25	2.7	N	N	N	30

Table B-2.-Equilibrium data for reactions of free cyanide and derived species-Continued

Reactant	Reaction type ¹	Temperature, °C	Log K at ionic strength (M)				Additional references
			0.0	0.1	1.0	3.0	
H ₂ N-CO-CO-OH	a	25	2.75	N	N	N	33
H ₂ C ₂ O ₄	a	³ 0	1.25	1.01	.80	.88	34-35
		³ 10	1.25	1.01	.80	.90	
		25	1.28	1.04	1.04	1.26	
		³ 25	1.28	1.03	.82	.93	
		³ 40	1.32	1.07	.86	.96	
		³ 60	1.42	1.14	.92	.99	
		³ 90	1.53	1.25	1.02	1.06	
HC ₂ O ₄ ⁻	a	³ 0	4.22	3.80	3.51	3.61	35
		³ 10	4.24	3.81	3.50	3.58	
		25	4.28	3.83	3.56	3.81	
		³ 25	4.28	3.83	3.50	3.55	
		³ 40	4.36	3.89	3.53	3.54	
		³ 60	4.48	3.99	3.60	3.55	
		³ 90	4.71	4.18	3.74	3.62	
NC-NH ₃ ⁺	a	25	N	1.1	⁶ -1.1	N	39
NC-NH ₂	a	25	10.3	N	⁶ 10.7	N	37, 40
NC-NH ¹⁻	a	25	11.6	N	N	N	37
HNCS	a	25	1.6	N	N	N	41
HNCO	a	0	3.77	N	N	N	45-46
		10	3.62	3.7	N	N	
		25	3.47	N	N	N	
		40	3.43	N	N	N	
CO ₂	s	³ 0	-1.11	-1.12	-1.23	-1.43	48-51
		³ 10	-1.27	-1.28	-1.38	-1.56	
		³ 25	-1.47	-1.48	-1.56	-1.73	
		25	-1.47	-1.52	-1.53	-1.56	
		³ 40	-1.62	-1.63	-1.71	-1.87	
		³ 60	-1.78	-1.79	-1.87	-2.04	
		³ 90	-1.94	-1.95	-2.04	-2.20	
C(NH ₂) ₃ ⁺	a	25	⁷ 14.	N	13.5	N	56-57
H ₂ N-CS-SH	a	25	2.95	N	N	N	64
H ₂ N-CO-OH	a	25	⁸ 7.1	N	⁴ 6.8	N	66-67
		40	N	N	⁴ 6.6	N	
		60	N	N	⁴ 6.5	N	
H ₂ CO ₃	a	³ 0	6.57	6.35	6.17	6.16	48, 51, 68
		³ 10	6.45	6.23	6.05	6.05	
		³ 25	6.35	6.12	5.94	5.96	

Table B-2.-Equilibrium data for reactions of free cyanide and derived species—Continued

Reactant	Reaction type ¹	Temperature, °C	Log K at ionic strength (M)				Additional references
			0.0	0.1	1.0	3.0	
HCO ₃ ⁻	a	25	6.35	6.14	5.99	6.44	48, 51, 69
		³ 40	6.30	6.06	5.88	5.90	
		³ 60	6.28	6.03	5.84	5.86	
		³ 90	6.35	6.08	5.86	5.85	
		³ 0	10.63	10.18	9.83	9.87	
		³ 10	10.49	10.04	9.65	9.67	
		³ 25	10.33	9.87	9.48	9.47	
		³ 25	10.33	9.93	9.57	9.63	
		³ 40	10.23	9.75	9.33	9.31	
		³ 60	10.14	9.64	9.19	9.13	
HCNO	a	³ 90	10.11	9.56	9.05	8.93	72
		25	5.	N	N	N	
H-CO-NH-OH	a	25	8.78	N	N	N	73
		40	⁹ 8.62	N	N	N	

N No data.

¹a, acid dissociation, pK_a tabulated; b, base dissociation, pK_b tabulated; s, solubility, log (molal solubility) tabulated.²Extrapolated.³NaCl solutions.⁴Ionic strength 0.5M.⁵Ionic strength 0.2M.⁶Ionic strength 2.0M.⁷Estimated.⁸Estimated by adding log K values for the reactions NH₃ + HCO₃⁻ = H₂NCO₂⁻ + H₂O, H₂NCO₂H + H₂O = NH₃ + CO₂ + H₂O, and CO₂ + H₂O = HCO₃⁻ + H⁺, assuming zero ionic-strength dependence of log K for the first two of these reactions.⁹Extrapolated from data at 25° and 35° C assuming linear relationship of log K to reciprocal absolute temperature.

Table B-3.-Solubilities of solid compounds derived
from cyanide in water at 25° C

Compound	Solubility, mol·kg water	References
$\text{H}_2\text{N-CS-CS-NH}_2$	0.0031	25
$\text{H}_2\text{N-CS-CO-NH}_2$	N	
$\text{H}_2\text{N-CO-CO-NH}_2$	.01	29
$\text{H}_2\text{N-CO-CO-OH}$	.04	32
NC-NH_2	N	
$\text{CO}(\text{NH}_2)_2$	20.2	62, 65
$\text{CS}(\text{NH}_2)_2$	2.17	62

N No data.

APPENDIX C.—THERMODYNAMIC DATA FOR AUXILIARY SPECIES

This appendix contains tables of standard enthalpies of formation $\Delta_f H^\circ$ and standard Gibbs energies of formation $\Delta_f G^\circ$ (table C-1) and equilibrium data at different temperatures and ionic strengths (table C-2) for auxiliary species. The major data sources are the NBS tables (1), a CODATA report (2), the compilations by Christensen and others, (3) and Martell and Smith (4-6). A review by Wilhelm and others (7) provided references for gas solubilities. Primary-source references for additional data are listed in the column "Additional references": species containing only oxygen or hydrogen (8-11), chlorine and bromine species (12-19), sulfur species (20-37), selenium species (38-41), nitrogen species (24, 42-48), and arsenic species (49). Carbon species data are compiled in appendix B.

REFERENCES

- Wagman, D. D., W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney, and R. L. Nuttall. The NBS Tables of Chemical Thermodynamic Properties. Selected Values of Inorganic and C_1 and C_2 Organic Substances in SI Units. *J. Phys. Chem. Ref. Data*, suppl. 2, v. 11, 1982, 392 pp.
- International Council of Scientific Unions. Recommended Key Values for Thermodynamics. Report of the CODATA Task Group on Key Values for Thermodynamics, 1977. *J. Chem. Thermodyn.*, v. 10, 1978, pp. 903-906.
- Christensen, J. J., L. D. Hansen, and R. M. Izatt. Handbook of Proton Ionization Heats and Related Thermodynamic Quantities. Wiley-Interscience, 1976, 269 pp.
- Smith, R. M., and A. E. Martell. Critical Stability Constants. V. 4, Inorganic Complexes. Plenum, 1976, 257 pp.
- Martell, A. E., and R. M. Smith. Critical Stability Constants. V. 5, First Supplement. Plenum, 1982, 604 pp.
- Smith, R. M., and A. E. Martell. Critical Stability Constants. V. 6, Second Supplement. Plenum, 1989, 643 pp.
- Wilhelm, E., R. Battino, and R. J. Wilcock. Low-Pressure Solubility of Gases in Liquid Water. *Chem. Rev.*, v. 77, 1977, pp. 219-262.
- Khomutov, N. E., and A. Sh. Groisman. Temperature Dependence of the Solubility of Oxygen in Aqueous Solutions of Electrolytes. *Russ. J. Phys. Chem. (Engl. Transl.)*, v. 58, 1984, pp. 433-434.
- Kosak-Channing, L. F., and G. R. Helz. Solubility of Ozone in Aqueous Solutions of 0-0.6 M Ionic Strength at 5-30° C. *Environ. Sci. Technol.*, v. 17, 1983, pp. 145-149.
- Busey, R. H., and R. E. Mesmer. Thermodynamic Quantities for the Ionization of Water in Sodium Chloride Media to 300° C. *J. Chem. Eng. Data*, v. 23, 1978, pp. 175-176.
- Vasil'ev, V. P., L. A. Kochergina, and S. G. Ivenkova. The Thermodynamics of the Neutralization and Dissociation of Hydrogen Peroxide in Aqueous Solutions. *Russ. J. Inorg. Chem. (Engl. Transl.)*, v. 30, 1985, pp. 777-780.
- Caramazza, R. (Measurement of Dissociation Constants of Unstable Weak Acids. I. Hypochlorous Acid.) *Gazz. Chim. Ital.*, v. 87, 1957, pp. 1507-1521; *Chem. Abstr.*, v. 52, 1958, p. 13379c.
- Morris, J. C. The Acid Ionization Constant of HOCl From 5 to 35°. *J. Phys. Chem.*, v. 70, 1966, pp. 3798-3805.
- Schmitz, G. (Thermodynamic Values of Chlorite and Chlorine Dioxide in Solution). *J. Chim. Phys. Phys.-Chim. Biol.*, v. 76, 1979, pp. 209-211; *Chem. Abstr.*, v. 91, 1979, No. 10178g.
- Stanbury, D. N., and L. A. Lednický. Outer-Sphere Electron Transfer Reactions Involving the Chlorite/Chlorine Dioxide Couple. Activation Barriers for Bent Triatomic Species. *J. Am. Chem. Soc.*, v. 106, 1984, pp. 2847-2853.
- Fabian, I., and G. Gordon. Complex Formation Reactions of the Chlorite Ion. *Inorg. Chem.*, v. 30, 1991, pp. 3785-3787.
- Clyne, M. A. A., and R. T. Watson. Kinetic Studies of Diatomic Free Radicals Using Mass Spectrometry. Part 4. The Br + OClO and BrO + ClO Reactions. *J. Chem. Soc., Faraday Trans. 1*, v. 73, 1977, pp. 1169-1187.
- Johnson, G. K., P. N. Smith, E. H. Appelman, and W. N. Hubbard. The Thermodynamic Properties of the Perbromate and Bromate Ions. *Inorg. Chem.*, v. 9, 1970, pp. 119-125.
- Kelley, C. M., and H. V. Tartar. On the System: Bromine-Water. *J. Am. Chem. Soc.*, v. 78, 1956, pp. 5752-5756.
- Clarke, E. C. W., and D. N. Glew. Aqueous Nonelectrolyte Solutions. Part VIII. Deuterium and Hydrogen Sulfides Solubilities in Deuterium Oxide and Water. *Can. J. Chem.*, v. 49, 1971, pp. 691-698.
- Carroll, J. J., and A. E. Mather. The Solubility of Hydrogen Sulphide in Water From 0 to 90° C and Pressures to 1 MPa. *Geochim. Cosmochim. Acta*, v. 53, 1989, pp. 1163-1170.
- Gamsjaeger, H., W. Rainer, and P. Schindler. Löslichkeitskonstanten und Freie Bildungsenthalpien von Metallsulfiden, 4. Mitt.: Die Löslichkeit von H_2S in $HClO_4$ - $NaClO_4$ - H_2O Mischungen (Solubility Constants and Gibbs Energies of Metal Sulfides, Part 4: Solubility of H_2S in $HClO_4$ - $NaClO_4$ - H_2O Mixtures). *Monatsh. Chem.*, v. 98, 1967, pp. 1793-1802.
- Gamsjaeger, H., and P. Schindler. Löslichkeiten und Aktivitätskoeffizienten von H_2S in Elektrolytmischungen (Solubility and Activity Coefficient of H_2S in Electrolyte Solutions). *Helv. Chim. Acta*, v. 52, 1969, pp. 1395-1402.
- Tsonopoulos, C., D. M. Coulson, and L. B. Inman. Ionization Constants of Water Pollutants. *J. Chem. Eng. Data*, v. 21, 1976, pp. 190-193.
- Barbero, J. A., K. G. McCurdy, and P. R. Tremaine. Apparent Molal Heat Capacity and Volumes of Aqueous Hydrogen Sulfide and Sodium Hydrogen Sulfide Near 25° C: The Temperature Dependence of Hydrogen Sulfide Ionization. *Can. J. Chem.*, v. 60, 1982, pp. 1872-1880.
- Hershey, J. P., T. Plese, and F. J. Millero. The pK_1^* for the Dissociation of H_2S in Various Ionic Media. *Geochim. Cosmochim. Acta*, v. 52, 1988, pp. 2047-2051.
- Licht, S., and J. Manassen. The Second Dissociation Constant of H_2S . *J. Electrochem. Soc.*, v. 134, 1987, pp. 918-921.
- Giggenbach, W. F. Equilibria Involving Polysulfide Ions in Aqueous Sulfide Solutions up to 240°. *Inorg. Chem.*, v. 13, 1974, pp. 1724-1730.
- Boulegue, J., and G. Michard. (Formation Constants of Polysulfide Ions, S_3^{2-} , S_5^{2-} , and S_4^{2-} , in the Aqueous Phase.) *J. Fr. Hydrol.*, v. 9, 1978, pp. 27-33; *Chem. Abstr.*, v. 89, 1978, No. 153517.
- Licht, S., G. Hodes, and J. Manassen. Numerical Analysis of Aqueous Polysulfide Solutions and Its Application to Cadmium Chalcogenide/Polysulfide Photoelectrochemical Solar Cells. *Inorg. Chem.*, v. 25, 1986, pp. 2486-2489.
- Goldberg, R. N., and V. B. Parker. Thermodynamics of Solution of Sulfur Dioxide Gas in Water and of Aqueous Sulfur Dioxide Solutions. *J. Res. Natl. Bur. Stand. (U.S.)*, v. 90, 1985, pp. 341-358.

¹Italic numbers in parentheses refer to items in the list of references at the end of this appendix.

32. Krunchak, E. G., A. G. Rodichev, Ya. S. Khvorostin, B. S. Krungal'z, V. G. Krunchak, and Yu. I. Yusova. Determination of the Dissociation Constant of Hydrogen Sulfite Ion at Various Temperatures. *Russ. J. Inorg. Chem. (Engl. Transl.)*, v. 18, 1973, pp. 1519-1520.
33. Readnour, J. M., and J. W. Cobble. Thermodynamic Properties for the Dissociation of Bisulfate Ion and the Partial Molal Heat Capacities of Bisulfuric Acid and Sodium Bisulfate Over an Extended Temperature Range. *Inorg. Chem.*, v. 8, 1969, pp. 2174-2182.
34. Dickson, A. G., D. J. Wesolowski, D. A. Palmer, and R. E. Mesmer. Dissociation Constant of Bisulfate Ion in Aqueous Sodium Chloride Solutions to 250° C. *J. Phys. Chem.*, v. 94, 1990, pp. 7978-7985.
35. Spiro, M. The Standard Potential of the Peroxosulfate/Sulfate Couple. *Electrochim. Acta*, v. 24, 1979, pp. 313-314.
36. O'Hare, P. A. G., L. Basile, and E. H. Appelman. Thermochemistry of Inorganic Sulfur Compounds. V. Peroxymonosulfate Revisited: Standard Molar Enthalpies of Formation of $\text{KHSO}_5 \cdot \text{H}_2\text{O}(\text{cr})$, $\text{KHSO}_5(\text{cr})$, and $\text{HSO}_5^-(\text{aq})$. *J. Chem. Thermodyn.*, v. 17, 1985, pp. 473-480.
37. Price, J. S., I. R. Tasker, E. H. Appelman, and P. A. G. O'Hare. Thermochemistry of Inorganic Sulfur Compounds. IX. Molar Heat Capacity of $\text{KHSO}_5(\text{cr})$ from 5 to 300° K, and the Partial Molar Entropy of $\text{HSO}_5^-(\text{aq})$. *J. Chem. Thermodyn.*, v. 18, 1986, pp. 923-930.
38. Dubeau, C., J.-C. Sisi, and N. Ozanne. Solubility of Hydrogen Selenide Gas in Water. *J. Chem. Eng. Data*, v. 16, 1971, pp. 78-79.
39. Salomaa, P., R. Hakala, S. Vesala, and T. Aalto. Solvent Deuterium Isotope Effects on Acid-Base Reactions. Part III. Relative Acidity Constants of Inorganic Oxyacids in Light and Heavy Water. *Acta Chem. Scand.*, v. 23, 1969, pp. 2116-2126.
40. Nair, V. S. K. Dissociation of the Biselenate Anion. *J. Inorg. Nucl. Chem.*, v. 26, 1964, pp. 1911-1917.
41. Ghosh, R., and V. S. K. Nair. Studies on Metal Complexes in Aqueous Solution. III. The Biselenate Ion and Transition Metal Selenates. *J. Inorg. Nucl. Chem.*, v. 32, 1970, pp. 3041-3051.
42. Katan, T., and A. B. Campa. Vapor Pressure of Ammonia in Aqueous Potassium Hydroxide Solutions. *J. Chem. Eng. Data*, v. 8, 1963, pp. 574-575.
43. Kotlik, S. B., and G. Lebedeva. (Equilibrium Pressure of Hydrocyanic Acid and Ammonia over Aqueous Solutions.) *Russ. J. Appl. Chem. (Engl. Transl.)*, v. 47, 1974, pp. 1974-1976; *Chem. Abstr.*, v. 81, 1974, No. 69074s.
44. Clegg, S. L., and P. Brimblecombe. Solubility of Ammonia in Pure Aqueous and Multicomponent Solutions. *J. Phys. Chem.*, v. 93, 1989, pp. 7237-7248.
45. Olofsson, G. Thermodynamic Quantities for the Dissociation of the Ammonium Ion and for the Ionization of Aqueous Ammonia Over a Wide Temperature Range. *J. Chem. Thermodyn.*, v. 7, 1975, pp. 507-514.
46. Hitch, B. F., and R. E. Mesmer. The Ionization of Aqueous Ammonia to 300° C in KCl Media. *J. Solution Chem.*, v. 5, 1976, pp. 667-680.
47. Castro, A., M. Cid, and J. A. Santaballa. The Solvent Isotope Effect on the pK_a of Nitrous Acid. *J. Chem. Res. (Synop.)*, 1986, pp. 60-61.
48. Park, J.-Y., and J.-N. Lee. Solubility and Decomposition Kinetics of Nitrous Acid in Aqueous Solution. *J. Phys. Chem.*, v. 92, 1988, pp. 6294-6302.
49. Davis, H. J. The Thermodynamics of Arsine Evolution. *J. Electrochem. Soc.*, v. 124, 1977, pp. 722-723.

Table C-1.--Thermodynamic formation data for auxiliary species at 25° C

Species	$\Delta_f H^\circ$, $\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_f G^\circ$, $\text{kJ}\cdot\text{mol}^{-1}$	Additional references
O_2 (aq)	-11.7	+16.5	
O_3 (g)	+143.	+163.	
O_3 (aq)	+126.	+174.	9
H_2O (l)	-285.8±0.1	-237.2±0.1	
H^+ (aq)	0.0	0.0	
OH^- (aq)	-230.0±0.1	-157.3±0.1	
H_2O_2 (aq)	-191.2	-134.0	
HO_2^- (aq)	-159.4	-67.4	11
Cl^- (aq)	-167.1±0.1	-131.2±0.1	
Cl_2 (aq)	-23.4	+6.9	
HClO (aq)	-120.9	-79.8	12-13
ClO^- (aq)	-107.1	-36.8	
HClO_2 (aq)		+38	14-16
ClO_2^- (aq)		+27	14
ClO_2 (g)	+102. ±3	+120. ±3	17
ClO_2 (aq)		+117.	15
ClO_3^- (aq)	-104.1	-7.9	18
Br^- (aq)	-121.5±0.1	-104.0±0.1	
Br_2 (g)	+30.9	+3.1	
Br_2 (aq)	-2.6	+3.9	
HBrO (aq)	-113.0	-82.7	19
BrO^- (aq)	-94.1	-33.4	
BrO_3^- (aq)	-66.7	+19.1	18

Table C-1.-Thermodynamic formation data for auxiliary species at 25° C-Continued

Species	$\Delta_f H^\circ$, kJ·mol ⁻¹	$\Delta_f G^\circ$, kJ·mol ⁻¹	Additional references
HSeO ₄ ⁻ (aq)	-576.1	-450.8	40-41
SeO ₄ ²⁻ (aq)	-599.1	-441.3	
NH ₃ (g)	-45.9±0.4	-16.4±0.4	
NH ₃ (aq)	-81.4±0.3	-26.5±0.3	
NH ₄ ⁺ (aq)	-133.3±0.3	-79.3±0.3	
HNO ₂ (aq)	-119.2	-50.9	47-48
NO ₂ ⁻ (aq)	-104.6	-32.2	
NO ₃ ⁻ (aq)	-206.9±0.4	-110.9±0.4	
AsH ₃ (g)	+62.8	+65.3	49
AsH ₃ (aq)	N	+77.0	
As(OH) ₃ (aq)	-742.2	-639.8	
AsO(OH) ₂ ⁻ (aq)	-714.7	-587.1	
H ₃ AsO ₄ (aq)	-902.5	-766.0	
H ₂ AsO ₄ ⁻ (aq)	-909.6	-753.2	
HAsO ₄ ²⁻ (aq)	-906.3	-714.6	
AsO ₄ ³⁻ (aq)	-888.1	-648.8	

N No data.

Table C-2.-Equilibrium data for reactions of auxiliary species

Reactant	Reaction type ¹	Temperature, °C	Log K at ionic strength (M)				Additional references
			0.0	0.1	1.0	3.0	
O ₂	s	² 0	-2.67	N	N	N	8
		² 10	-2.77	-2.78	-2.92	N	
		² 25	-2.90	-2.91	-3.04	N	
		² 40	-2.98	-2.99	-3.10	N	
		² 60	-3.05	-3.06	-3.13	N	
O ₃	s	³ 0	⁴ -1.63	⁴ -1.63	⁴ -1.69	N	9
		³ 10	-1.78	-1.79	-1.88	N	
		³ 25	-1.95	-1.96	-2.10	N	
		³ 40	⁴ -2.10	⁴ -2.12	⁴ -2.30	N	
H ₂ O	a	² 0	14.94	14.74	14.68	14.93	10
		² 10	14.53	14.32	14.26	14.51	
		25	14.00	13.78	13.79	14.18	
		² 25	14.00	13.78	13.72	13.97	
		² 40	13.54	13.32	13.26	13.50	
		² 60	13.02	12.79	12.70	12.92	
		² 90	12.42	12.17	12.05	12.24	
H ₂ O ₂	a	10	11.98	N	N	N	11
		25	11.67	N	11.39	N	
		40	11.39	N	N	N	
Cl ₂	s	25	-1.21	N	N	N	
HClO	a	0	7.82	N	N	N	12-13
		10	7.70	N	N	N	
		25	7.53	N	N	N	
		40	7.45	N	N	N	
		60	⁴ 7.40	N	N	N	
HClO ₂	a	25	2.0	1.88	1.72	N	15-16
HBrO	a	0	⁴ 9.32	N	N	N	19
		10	⁴ 8.97	N	N	N	
		25	8.63	N	N	N	
		40	8.44	N	N	N	
		60	⁴ 8.28	N	N	N	
H ₂ S	s	0	-0.67	N	N	N	20-23
		10	-0.81	N	N	N	
		25	-0.99	-1.00	-1.05	-1.17	
		40	-1.17	N	N	N	
		60	-1.37	N	N	N	
		90	-1.89	N	N	N	
H ₂ S	a	0	7.43	N	N	N	24-26
		10	7.23	N	N	N	
		25	7.02	6.82	6.66	6.87	
		40	6.81	N	N	N	
		60	6.64	N	N	N	
		90	6.51	N	N	N	

Table C-2.-Equilibrium data for reactions of auxiliary species—Continued

Reactant	Reaction type ¹	Temperature, °C	Log K at ionic strength (M)				Additional references
			0.0	0.1	1.0	3.0	
SH ⁻	a	25	17.	N	N	N	27
HS ₂ O ₃ ⁻	a	25	1.6	N	N	N	
SO ₂	s	25	.09	N	.03	.06	31
H ₂ SO ₃	a	25	1.87	1.62	1.37	1.72	31
HSO ₃ ⁻	a	25	7.17	N	6.34	6.36	31-32
		40	7.41	N	N	N	
		60	7.49	N	N	N	
		90	7.55	N	N	N	
HSO ₄ ⁻	a	² 0	1.78	1.20	.79	.74	33-34
		² 10	1.85	1.31	.89	.82	
		25	1.99	1.55	1.10	.91	
		² 25	1.99	1.49	1.06	.97	
		² 40	2.15	1.68	1.24	1.13	
		² 60	2.40	1.96	1.49	1.35	
		² 90	2.82	2.37	1.85	1.67	
HSO ₅	a	25	10.1	N	N	N	35
H ₂ Se	s	0	⁴ -.84	N	N	N	38
		10	⁴ -.94	N	N	N	
		25	-1.08	N	N	N	
		40	-1.21	N	N	N	
		60	⁴ -1.35	N	N	N	
		90	⁴ -1.54	N	N	N	
H ₂ Se	a	25	3.9	N	3.5	N	
SeH ⁻	a	25	15.	N	N	N	
H ₂ SeO ₃	a	25	2.62	N	2.27	2.61	39
HSeO ₃ ⁻	a	25	8.25	N	7.78	8.05	92
HSeO ₄ ⁻	a	0	1.36	N	N	N	40-41
		10	1.46	N	N	N	
		25	1.66	N	N	N	
		40	1.89	N	N	N	
		60	³ 2.25	N	N	N	
		90	⁴ 2.92	N	N	N	

Table C-2.-Equilibrium data for reactions of auxiliary species—Continued

Reactant	Reaction type ¹	Temperature, °C	Log K at ionic strength (M)				Additional references
			0.0	0.1	1.0	3.0	
NH ₃	s	0	2.33	N	N	N	42-44
		10	2.10	N	N	N	
		25	1.78	N	1.60	N	
		40	1.47	N	1.31	N	
		60	1.11	N	.97	N	
		90	.66	N	N	N	
NH ₃	b	⁵ 0	4.86	4.65	4.46	4.40	24, 45-46
		⁵ 10	4.80	4.58	4.40	4.35	
		⁵ 25	4.75	4.53	4.34	4.29	
		⁵ 40	4.73	4.50	4.30	4.26	
		⁵ 60	4.74	4.50	4.29	4.24	
		⁵ 90	4.82	4.56	4.33	4.27	
HNO ₂	a	25	3.28	N	N	N	47-48
AsH ₃	s	10	-1.88	N	N	N	
		25	-2.05	N	N	N	
As(OH) ₃	a	25	9.23	N	9.07	N	
H ₃ AsO ₄ ⁻	a	25	2.25	N	N	N	
H ₂ AsO ₄	a	25	6.77	N	N	N	
HAsO ₄ ²⁻	a	25	11.53	N	N	N	

N No data.

¹a, acid dissociation, pK_a tabulated; b, base dissociation, pK_b tabulated; s, solubility, log (molal solubility) tabulated.²NaCl solutions.³Na₂SO₄ solutions.⁴Extrapolated.⁵KCl solutions.

APPENDIX D.—THERMODYNAMIC DATA FOR METAL SPECIES

This appendix contains tables of standard Gibbs free energies of formation $\Delta_f G^\circ$ and equilibrium data at 25° C and different ionic strengths for aqueous metal ions (table D-1) and other metal species (tables D-2 through D-23). The major data sources are the NBS tables (1),¹ a CODATA report (2), the compilations by Martell and Smith (3-5), Baes and Mesmer (6), the U.S. Bureau of Mines (7, 8), Mills (9), Sharpe (10), and Beck (11). Primary-source references are cited in the tables in the column "Additional references": Zn (12-17), Cd (12, 18-20), Hg (19, 21-24), Cu (25-29), Ag (30), Au (30-39), Ni (27, 40, 41), Co (27, 42-56), Fe (27, 57-68), Mn (43, 69-75), Cr (50, 53, 76-79), Tl (80, 81), and Pb (82-85).

Because Tl(III) forms strong cyanide complexes, the question arises as to whether Ga(III) and In(III) also form cyanide complexes. No equilibrium data exist for aqueous gallium or indium cyanide species. An analysis of equilibrium data for the oxide solid phases and aqueous hydroxide species of Cu(I), Ag(I), Au(I), Zn(II), Cd(II), Hg(II), Ga(III), In(III), and Tl(III), and the known cyanide species of these metals, was conducted to generate estimates of log K values for Ga(III) and In(III) cyanide species. The data for Ga(III) and In(III) are compiled in table D-24. The values obtained are relatively low, and consequently Ga(III) and In(III) cyanide species are not expected to be important.

Heavy-metal selenide minerals can be leached by cyanide solutions, probably with formation of dissolved selenium cyanide (SeCN^-). The standard Gibbs free energies of formation of some heavy-metal selenides are listed in table D-25. Some of the data are from compilations (1, 9, 86), other data are from elsewhere (87-92).

REFERENCES

1. Wagman, D. D., W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney, and R. L. Nuttall. The NBS Tables of Chemical Thermodynamic Properties. Selected Values of Inorganic and C₁ and C₂ Organic Substances in SI Units. *J. Phys. Chem. Ref. Data*, v. 11, suppl. 2, 1982, 392 pp.
2. International Council of Scientific Unions. Recommended Key Values for Thermodynamics. Report of the CODATA Task Group on Key Values for Thermodynamics, 1977. *J. Chem. Thermodyn.*, v. 10, 1978, pp. 903-906.
3. Smith, R. M., and A. E. Martell. Critical Stability Constants. V. 4, Inorganic Complexes. Plenum, 1976, 257 pp.
4. Martell, A. E., and R. M. Smith. Critical Stability Constants. V. 5, First Supplement. Plenum, 1982, 604 pp.
5. Smith, R. M., and A. E. Martell. Critical Stability Constants. V. 6, Second Supplement. Plenum, 1989, 643 pp.
6. Baes, C. F., Jr., and R. E. Mesmer. The Hydrolysis of Cations. Wiley, 1976, 489 pp.
7. Pankratz, L. B. Thermodynamic Properties of Elements and Oxides. USBM Bull. 672, 1982, 509 pp.
8. Pankratz, L. B., A. D. Mah, and S. W. Watson. Thermodynamic Properties of Sulfides. USBM Bull. 689, 1987, 427 pp.
9. Mills, K. C. Thermodynamic Data for Inorganic Sulphides, Selenides, and Tellurides. Butterworths (London), 1974, 845 pp.
10. Sharpe, A. G. The Chemistry of Cyano Complexes of the Transition Metals. Academic, 1976, 302 pp.
11. Beck, M. T. Critical Survey of Stability Constants of Cyano Complexes. *Pure Appl. Chem.*, v. 59, 1987, pp. 1703-1720.
12. Mussini, T., P. Longhi, and S. Rondinini. Standard Potentials of Amalgam Electrodes in Aqueous Solutions, Temperature Coefficients, and Activity Coefficients of Metals in Mercury. *Pure Appl. Chem.*, v. 57, 1985, pp. 169-179.
13. Bourcier, W. L., and H. L. Barnes. Ore Solution Chemistry. VII. Stabilities of Chloride and Bisulfide Complexes of Zinc to 350° C. *Econ. Geol.*, v. 82, 1987, pp. 1839-1863.
14. Schindler, P., M. Reinert, and H. Gamsjaeger. Zur Thermodynamik der Metallcarbonate. 3. Mitt. Löslichkeitskonstanten und Freie Bildungsenthalpien von ZnCO_3 und $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$ bei 25° C (Metal Carbonate Thermodynamics. Part 3. Solubility Products and Gibbs Energies of Formation of ZnCO_3 and $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$ at 25° C). *Helv. Chim. Acta*, v. 52, 1969, pp. 2327-2332.
15. Martin, R.-P., and M. Blanc. Etude Potentiometrique des Equilibres en Solution Aqueuse Entre les Ions Zn^{2+} , la L-Histidine, les Ions Cyanures et Leurs Melanges (Potentiometric Study of Aqueous Solution Equilibria of Zn^{2+} with L-Histidine, Cyanide, and Their Mixture). *Bull. Soc. Chim. Fr.*, 1969, pp. 1866-1871.
16. Konev, V. A., and A. O. Brandt. Mixed Complexes of Zinc With Cyanide and Ammonia. *Russ. J. Inorg. Chem. (Engl. Transl.)*, v. 19, 1974, pp. 173-175.
17. Linke, W. F. Solubilities of Inorganic and Metal-Organic Compounds, v. 2. *Am. Chem. Soc.*, 1965, p. 1656.
18. Gamsjaeger, H., H. V. Stuber, and P. Schindler. Zur Thermodynamik der Metallcarbonate. 1. Mitt. Löslichkeitskonstanten und Freie Bildungsenthalpie von Kadmiumcarbonat, ein Beitrag zur Thermodynamik des Ternären Systems $\text{Cd}^{2+}(\text{aq})\text{-H}_2\text{O}(\text{l})\text{-CO}_2(\text{g})$ (Metal Carbonate Thermodynamics. Part 1. Solubility Products and Gibbs Energy of Formation of Cadmium Carbonate. Contribution to the Thermodynamics of the Ternary System $\text{Cd}^{2+}(\text{aq})\text{-H}_2\text{O}(\text{l})\text{-CO}_2(\text{g})$). *Helv. Chim. Acta*, v. 48, 1965, pp. 723-729.
19. Linke, W. F. Solubilities of Inorganic and Metal-Organic Compounds, v. 1. *Am. Chem. Soc.*, 1958, pp. 707, 1196, 1201.
20. Beck, M., and L. Dosza. (Solubility of Cadmium Thiocyanate and Cyanide.) *Magy. Kem. Foly.*, v. 70, 1964, pp. 163-164; *Chem. Abstr.*, v. 61, 1964, p. 2533g.
21. Vanderzee, C. E., and J. A. Swanson. The Enthalpy of Precipitation of Mercury(I) Chloride and the Thermodynamic Properties of Aqueous Mercury(I) and Mercury(II) Ions. *J. Chem. Thermodyn.*, v. 6, 1974, pp. 827-843.
22. Bain, R. I. Multi-Nuclear NMR Studies of the System: $\text{Hg}(\text{CN})_2\text{-Hg(II) ion-D}_2\text{O}$ in Perchlorate Media. *J. Inorg. Nucl. Chem.*, v. 43, 1981, pp. 2481-2483.
23. Belevantsev, V. I., B. I. Peshchevskii, and K. A. Udachin. (Equilibria in a System of Mixed Mercury(II) Chloro-Cyano Complexes in an Aqueous Solution.) *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1979, No. 1, pp. 23-31; *Chem. Abstr.*, v. 90, 1979, No. 175508g.

¹Italic numbers in parentheses refer to items in the list of references at the end of this appendix.

24. Belevantsev, V. I., B. I. Peshchevskii, and K. A. Udachin. Consecutive Replacement of Br⁻ by CN⁻ in HgBr₄²⁻ in Aqueous Solution. *Russ. J. Inorg. Chem. (Engl. Transl.)*, v. 25, 1980, pp. 366-369.
25. Gedansky, L. M., E. M. Woolley, and L. G. Hepler. Thermochemistry of Compounds and Aqueous Ions of Copper. *J. Chem. Thermodyn.*, v. 2, 1970, pp. 561-576.
26. Ciavatta, L., D. Ferri, and R. Palombari. On the Equilibrium $\text{Cu}^{2+} + \text{Cu(s)} = 2\text{Cu}^+$. *J. Inorg. Nucl. Chem.*, v. 42, 1980, pp. 593-598.
27. Larson, J. W., P. Cerutti, H. K. Garber, and L. G. Hepler. Electrode Potentials and Thermodynamic Data for Aqueous Ions. Copper, Zinc, Cadmium, Iron, Cobalt, and Nickel. *J. Phys. Chem.*, v. 72, 1968, pp. 2902-2907.
28. Hancock, R. D., N. P. Finkelstein, and A. Evers. Some Observations on a Recent Determination of the Stability of the Dicyanocuprate(I) Ion. *J. Inorg. Nucl. Chem.*, v. 38, 1976, pp. 343-344.
29. Katagiri, A., S. Yoshimura, and S. Yoshizawa. Formation Constant of the Tetracyanocuprate(II) Ion and the Mechanism of Its Decomposition. *Inorg. Chem.*, v. 20, 1981, pp. 4143-4147; Correction, *Inorg. Chem.*, v. 25, 1986, p. 2278.
30. Webster, J. G. The Solubility of Gold and Silver in the System Au-Ag-S-O₂-H₂O at 25° C and 1 atm. *Geochim. Cosmochim. Acta.*, v. 50, 1986, pp. 1837-1845.
31. Skibsted, L. H., and J. Bjerrum. Studies on Gold Complexes. III. The Standard Electrode Potentials of Aqua Gold Ions. *Acta Chem. Scand.*, v. A31, 1977, pp. 155-156.
32. Johnson, P. R., J. M. Pratt, and R. I. Tilley. Experimental Determination of the Standard Reduction Potential of the Gold(I) Ion. *J. Chem. Soc. Chem. Commun.*, 1978, pp. 606-607.
33. Gadet, M.-C., and M. J. Pouradier. Hydrolyse des Complexes de l'Or(I). (Hydrolysis of Gold(I) Complexes.) *C. R. Hebd. Seances Acad. Sci., Ser. C*, v. 275, 1972, pp. 1061-1064.
34. De Cugnac-Pailletot, A., and M. J. Pouradier. Proprietes Thermodynamiques du Sulfure d'Or. (Thermodynamic Properties of Gold Sulfide.) *C. R. Hebd. Seances Acad. Sci., Ser. C*, v. 275, 1972, pp. 551-554.
35. Skibsted, L. H., and J. Bjerrum. Studies on Gold Complexes. II The Equilibrium Between Gold(I) and Gold(III) in the Ammonia System and the Standard Potentials of the Couples Involving Gold, Diamminegold(I), and Tetraamminegold(III). *Acta Chem. Scand.*, v. A28, 1974, pp. 764-770.
36. Silver, H. G. Chemical Behavior of the Components of the KCN/KAu(CN)₂ Electroplating System. *J. Electrochem. Soc.*, v. 116, 1968, pp. 26C-32C.
37. Hoare, J. P. A Study of the Rest Potentials in the Gold-Oxygen-Acid System. *J. Electrochem. Soc.*, v. 110, 1963, pp. 245-249.
38. Ashcroft, S. J., and E. Schwarzmann. Standard Enthalpy of Formation of Crystalline Gold(III) Oxide. *J. Chem. Soc., Faraday Trans. 1*, v. 68, 1972, pp. 1360-1361.
39. Skibsted, L. H., and J. Bjerrum. Studies on Gold Complexes. I. Robustness, Stability, and Acid Dissociation of the Tetraamminegold(III) Ion. *Acta Chem. Scand.*, v. A28, 1974, pp. 740-746.
40. Gamsjaeger, H., F. Reiterer, and R. Heindl. Solubility Constants and Free Enthalpies of Metal Sulphides and Carbonates. *Ber. Bunsenges. Phys. Chem.*, v. 86, 1982, pp. 1046-1049.
41. Hume, D. N., and I. M. Kolthoff. The Polarography of the Nickel Cyanide Complexes and the Solubility and Constitution of Nickel Cyanide. *J. Am. Chem. Soc.*, v. 72, 1950, pp. 4423-4426.
42. Biedermann, G., S. Orecchio, V. Romano, and R. Zingales. On the Formal Potential of the Co³⁺/Co²⁺ Couple at -5° C in 6.5 Molal HClO₄ Medium. *Acta Chem. Scand.*, v. A40, 1986, pp. 161-167.
43. Avsar, E., and B. Basaran. Formation of Cyanide Complexes of Cobalt(II) and Manganese(II). *Polyhedron*, v. 6, 1987, pp. 1909-1912.
44. Mooliman, M. B., and J. M. Pratt. Reaction of H₂ With [Co(CN)₅]³⁻ Ions in Aqueous Solutions; the Role of Ion Pairs. *J. Mol. Catal.*, v. 27, 1984, pp. 367-371.
45. Hem, J. D., C. E. Roberson, and C. J. Lind. Thermodynamic Stability of CoOOH and Its Coprecipitation With Manganese. *Geochim. Cosmochim. Acta*, v. 49, 1985, pp. 801-810.
46. Balt, S. Kinetics of the *cis-trans* Isomerization of the Diaquo-tetraamminecobalt(III) Cation and Conjugate Bases. *Recl. Trav. Chim. Pays-Bas*, v. 91, 1972, pp. 1026-1040.
47. Schwarzenbach, G., J. Boesch, and H. Egli. The Formation of Dinuclear *mu*-Hydroxocobalt(III) Complexes. *J. Inorg. Nucl. Chem.*, v. 33, 1971, pp. 2141-2156.
48. Skibsted, L. H., and P. C. Ford. Acid Dissociation of Aqua-amminecobalt(III) Complexes in Aqueous Solution. *Acta Chem. Scand.*, v. A34, 1980, pp. 109-113.
49. Howland, K., and L. H. Skibsted. Aqueous Solution Photochemistry of *cis*- and *trans*-Diaquabis(ethylenediamine)rhodium(III) Ions and Their Conjugate Bases. Photoisomerization and Photostationary States and Their Correlation With Spectroscopic Properties. *Acta Chem. Scand.*, v. A37, 1983, pp. 647-657.
50. Chan, S. C., and K. Y. Hui. The Acid Dissociation Constants of Aquopentaamminecobalt(III) and Aquopentaamminechromium(III) Cations in Water, Deuterium Oxide, and Aqueous Dioxan. *Aust. J. Chem.*, v. 21, 1968, pp. 3061-3063.
51. Splinter, R. C., S. J. Harris, and R. S. Tobias. The Solvent Isotope Effect on the Dissociation of the Aquopentaammine-Cobalt(III) Ion. *Inorg. Chem.*, v. 7, 1968, pp. 897-902.
52. Richens, D. T., and A. G. Sykes. Reduction Potentials for *mu*-Superoxo/*mu*-Peroxodicobalt(III) Couples. *J. Chem. Soc., Dalton Trans.*, 1982, pp. 1621-1624.
53. Nakashima, M., and A. W. Adamson. Photocalorimetry. 3. Enthalpies of Substitution Reactions of Some Cr(III) Amines and Cr(III) and Co(III) Cyano Complexes in Aqueous Solution. *J. Phys. Chem.*, v. 86, 1982, pp. 2910-2912.
54. Izatt, R. M., G. D. Watt, C. H. Bartholomew, and J. J. Christensen. Thermodynamics of Metal Cyanide Coordination. VIII. A Calorimetric Study of Co²⁺-CN⁻ Interaction. *Inorg. Chem.*, v. 7, 1968, pp. 2236-2239.
55. Wrighton, M., and D. Bredeisen. Photochemistry of Aquo- and Hydroxopentacyanocobaltate(III). *Inorg. Chem.*, v. 12, 1973, pp. 1707-1709.
56. Burnett, M. G., and W. M. Gilfillan. The Mechanism and Kinetics of the Substitution of Azide, Thiocyanate, and Cyanide Ions in Aquopentacyanocobaltate(III) and Pentacyanohydroxocobaltate(III). *J. Chem. Soc., Dalton Trans.*, 1981, pp. 1578-1582.
57. Flynn, C. M., Jr. The Hydrolysis of Inorganic Iron(III) Salts. *Chem. Rev.*, v. 84, 1984, pp. 31-41.
58. Sadiq, M., and W. L. Lindsay. Standard Free Energy of Formation of Some Chemical Species: Discrepancies and Selections. *Arabian J. Sci. Eng.*, v. 6, 1981, pp. 95-104; *Chem. Abstr.*, v. 95, 1981, No. 139739c.
59. James, A. D., and R. S. Murray. Kinetic and Equilibrium Studies on Iron(II) and Iron(III) Pentacyanoferrates. *J. Chem. Soc., Dalton Trans.*, 1975, pp. 1530-1533.
60. Gaspar, V., and M. T. Beck. Kinetics of the Photoaquation of Hexacyanoferrate(II) Ion. *Polyhedron*, v. 2, 1983, pp. 387-391.
61. Malin, J. M., and R. C. Koch. Protonation of the Pentacyanoaquaferrate(II) Ion, Fe(CN)₅(OH₂)³⁻(aq). *Inorg. Chem.*, v. 17, 1978, pp. 752-754.
62. Toma, H. E. Iron(II) Catalysis in the Oxidation of the Aquopentacyanoferrate(II) Complex by Molecular Oxygen. *Inorg. Chim. Acta*, v. 15, 1975, pp. 205-211.
63. Davies, G., and A. R. Garafalo. Stoichiometry and Kinetics of the Substitution-Controlled Oxidation of Pentacyanoaquairon(II) Species by Hydrogen Peroxide and by *tert*-Butyl Hydroperoxide in Aqueous Sodium Perchlorate Solution. *Inorg. Chem.*, v. 15, 1976, pp. 1101-1106.
64. Domingo, P. L., B. Garcia, and J. M. Leal. Acid-Base Behavior of the Ferrocyanide Ion in Perchloric Acid Media. Potentiometric and Spectrophotometric Study. *Can. J. Chem.*, v. 65, 1987, pp. 583-589.

65. Toma, H. E., and C. Creutz. Pentacyanoferrate(II) Complexes: Evaluation of Their Formal Potentials and Mechanism of Their Quenching of Tris(2,2'-bipyridine)ruthenium(II) Luminescence. *Inorg. Chem.*, v. 16, 1977, pp. 545-550.
66. Hrepic, N. V., and J. M. Malin. Electron Transfer and Ligand Substitution Reactions of the Ion Pentacyano(4-aminopyridine)ferate(II). *Inorg. Chem.*, v. 18, 1979, pp. 409-413.
67. Mentasti, E., F. Secco, and M. Venturini. Complex Formation Between Iron(III) and Highly Charged Ligands: Equilibria and Reaction Mechanisms. *Inorg. Chem.*, v. 21, 1982, pp. 2314-2320.
68. Meeussen, J. C. L., M. G. Keizer, W. H. van Riemsdijk, and F. A. M. de Haan. Dissolution Behavior of Iron Cyanide (Prussian Blue) in Contaminated Soils. *Environ. Sci. Technol.*, v. 26, 1992, pp. 1832-1838.
69. Zordan, T. A., and L. G. Hepler. Thermochemistry and Oxidation Potentials of Manganese and Its Compounds. *Chem. Rev.*, v. 68, 1968, pp. 737-745.
70. Biedermann, G., and R. Palombiari. On the Hydrolysis of the Manganese(III) Ion. *Acta Chem. Scand.*, v. A32, 1978, pp. 381-390.
71. Gamsjaeger, H., W. Kraft, and P. Schindler. Zur Thermodynamik der Metallocarbonate. 4. Mitt. Potentiometrische Untersuchungen am System Mn^{2+} - CO_2 - H_2O (Metal Carbonate Thermodynamics. Part 4. Potentiometric Investigation of the System Mn^{2+} - CO_2 - H_2O). *Helv. Chim. Acta*, v. 53, 1970, pp. 290-299.
72. Bricker, O. Some Stability Relations in the System $Mn-O_2-H_2O$ at 25° C and One Atmosphere Total Pressure. *Am. Mineral.*, v. 50, 1965, pp. 1296-1354.
73. Hamm, R. E., and J. C. Templeton. Kinetics of the Reaction of the 1,2-Diaminocyclohexanetetraacetatomanganate(III) Anion With Cyanide Ion. *Inorg. Chem.*, v. 12, 1973, pp. 755-757.
74. Trageser, G., and H. H. Eysel. Disproportionation of Hexacyanomanganate(III) into Hexacyanomanganate(IV) and Hexaquomanganese(II) in Acidic Aqueous Solution. *Inorg. Chim. Acta*, v. 26, 1978, pp. L56-L58.
75. Lopez-Cueto, G., and C. Ubide. Fast Disproportionation of Hexacyanomanganate(III) in Acidic Solution. Formation of Hexacyanomanganate(IV) and Kinetics of Its Decomposition. *Can. J. Chem.*, v. 64, 1986, pp. 2301-2304.
76. Dellien, I., F. M. Hall, and L. G. Hepler. Chromium, Molybdenum, and Tungsten. Thermodynamic Properties, Chemical Equilibria, and Standard Potentials. *Chem. Rev.*, v. 76, 1976, pp. 283-310.
77. Stuenzi, H., L. Spiccia, F. P. Rotzinger, and W. Marty. Early Stages of the Hydrolysis of Chromium(III) in Aqueous Solution. 4. Stability Constants of the Hydrolytic Dimer, Trimer, and Tetramer at 25° C and $I = 1.0M$. *Inorg. Chem.*, v. 28, 1989, pp. 66-71.
78. Andersen, P., A. Doessing, J. Glerup, and M. Rude. Triammine Complexes of Chromium(III). Synthesis and Characterization of the Two Isomeric Series. *Acta Chem. Scand.*, v. 44, 1990, pp. 346-352.
79. Sakabe, Y., and Y. Matsumoto. The Synthesis of Potassium Pentacyanohydroxochromate(III). *Bull. Chem. Soc. Jpn.*, v. 54, 1981, pp. 1253-1254.
80. Longhi, P., T. Mussini, S. Rondinini, and B. Sala. Standard Aqueous Potentials for the Thallium Amalgam and Thallium Amalgam-Thallos Chloride Electrode From 283.15 to 328.15 K and for the Thallium and Thallium-Thallos Chloride Electrode From 288.15 to 308.15° K, and Thermodynamic Solubility Product of Thallos Chloride From 283.15 to 328.15° K. *J. Chem. Thermodyn.*, v. 11, 1979, pp. 73-81.
81. Blixt, B., B. Gyoeri, and J. Glaser. Determination of Stability Constants for Thallium(III) Cyanide Complexes in Aqueous Solution by Means of ^{13}C and ^{205}Tl NMR. *J. Am. Chem. Soc.*, v. 111, 1989, pp. 7784-7791.
82. Nasanen, R., and E. Lindell. Studies on Lead(II) Hydroxide Salts. Part I. The Solubility Product of Lead(II) Hydroxide Chloride. *Finn. Chem. Lett.*, 1976, pp. 95-98; *Chem. Abstr.*, v. 86, 1977, No. 9216h.
83. Nasanen, R., and E. Lindell. Studies on Lead(II) Hydroxide Salts. Part III. The Solubility Product of Dilead(II) Trihydroxide Chloride. *Finn. Chem. Lett.*, 1978, pp. 227-230; *Chem. Abstr.*, v. 90, 1979, No. 93191j.
84. Kellogg, H. H. Critical Evaluation of the Thermochemical Properties of Lead Sulfates. *Metall. Trans.*, v. 20B, 1989, pp. 77-85.
85. Taylor, P., and V. J. Lopata. Stability and Solubility Relationships Between Some Solids in the System $PbO-CO_2-H_2O$. *Can. J. Chem.*, v. 62, 1984, pp. 395-402.
86. Pankratz, L. B., J. M. Stuve, and N. A. Gokcen. Thermodynamic Data for Mineral Technology. *USBM Bull.* 677, 1985, 355 pp.
87. Nasar, A., and M. Shamsuddin. Thermodynamic Properties of Zinc Selenide. *Z. Metallkd.*, v. 81, 1990, pp. 244-246.
88. _____. Thermodynamic Properties of Cadmium Selenide. *J. Less-Common Met.*, v. 158, 1990, pp. 131-135.
89. Hepler, L. G., and G. Olofsson. Mercury: Thermodynamic Properties, Chemical Equilibria, and Standard Potentials. *Chem. Rev.*, v. 75, 1975, pp. 585-602.
90. Gedansky, L. M., E. M. Woolley, and L. G. Hepler. Thermochemistry of Compounds and Aqueous Ions of Copper. *J. Chem. Thermodyn.*, v. 2, 1970, pp. 561-576.
91. Morozova, M. P., V. A. Vladimirova, T. A. Stolyarova, and V. I. Nepomnyashchaya. (Enthalpy of Formation of Nickel Selenides.) *Zh. Fiz. Khim.*, v. 48, 1974, pp. 769-770; *Chem. Abstr.*, v. 81, 1974, No. 82983g.
92. Boone, S., and O. J. Kleppa. Enthalpies of Formation for Group IV Selenides ($GeSe_2$, $GeSe_2$ (am), $SnSe$, $SnSe_2$, $PbSe$). *Thermochim. Acta*, v. 197, 1992, pp. 109-121.

Table D-1.--Standard Gibbs free energies of formation
of aqueous metal ions at 25° C

Ion	$\Delta_f G^\circ$, kJ·mol ⁻¹	References
Zn ²⁺	-147.0± 0.2	12
Cd ²⁺	-77.6± 0.2	12
Hg ₂ ²⁺	153.6± 0.2	21
Hg ²⁺	164.6± 0.2	21
Cu	48.9± 0.2	25, 26
Cu ²⁺	65.2± 0.4	25, 27
Ag	77.1± 0.1	
Au	164.± 3.	31, 32
Au ³⁺	¹ 434.2±30.	31
Ni ²⁺	-44.4± 0.4	27
Co ²⁺	-55.8± 0.4	27
Co ³⁺	² 125.6± 1.1	42
Fe ²⁺	-91.3± 0.6	27, 57, 58
Fe ³⁺	³ -17.0± 0.8	57, 58
Mn ²⁺	-231. ± 2.	68
Mn ³⁺	⁴ -81.4± 2.5	69
Cr ³⁺	-226. ±10.	75
Tl	-31.6±0.1	79
Tl ³⁺	+215.	
Pb ²⁺	-24.0	
Mg ²⁺	-456.0	
Ca ²⁺	-553.1	

¹Derived from the value for Au and value of +1,5±0.1 V for standard reduction potential for Au³⁺ + 2e⁻ = Au.

²Derived from value for Co²⁺ and value of +1,88±0.01 V for standard reduction potential for Co³⁺ + e⁻ = Co²⁺.

³Derived from value for Fe²⁺ and value of +0.77±0.01 V for standard reduction potential for Fe³⁺ + e⁻ = Fe²⁺.

⁴Derived from value for Mn²⁺ and value of +1.55±0.01 V for standard reduction potential for Mn³⁺ + e⁻ = Mn²⁺.

Table D-2.-Thermodynamic data for zinc(II) species at 25° C

Reaction	Log K at ionic strength (M)				-Δ _f G° of underlined species kJ·mol ⁻¹	Additional references
	0.0	0.1	1.0	3.0		
$\text{Zn}^{2+} + \text{nOH}^- = \underline{\text{Zn}(\text{OH})_n}^{2-n}$, n = 1 2 3 4	5.0 10.2 13.9 15.5	N N N N	N N N N	3.8 8.3 13.7 18.0	332.8 519.8 698.2 864.7	
$2\text{Zn}^{2+} + \text{OH}^- = \underline{\text{Zn}_2(\text{OH})}^{3+}$	5.0	N	N	5.5	479.8	
$\underline{\text{ZnO}}(\text{s}) + \text{H}_2\text{O} = \text{Zn}^{2+} + 2\text{OH}^-$	-16.7	N	N	N	320.	
$\underline{\text{Zn}(\text{OH})_2(\text{cr})} = \text{Zn}^{2+} + 2\text{OH}^-$	-16.5	N	N	N	555.8	
$\underline{\text{Zn}(\text{OH})_2(\text{am})} = \text{Zn}^{2+} + 2\text{OH}^-$	-15.5	N	N	N	550.1	
$\text{Zn}^{2+} + \text{nCl}^- = \underline{\text{ZnCl}_n}^{2-n}$, n = 1 2 3 4	.5 .6 .5 .2	N N N N	0.0 .0 -.1 N	-.2 -.4 0.0 -.7	281.1 412.8 543.5 672.9	
$\underline{\text{ZnS}}(\text{s}) + 2\text{H}^+ = \text{Zn}^{2+} + \text{H}_2\text{S}$	-4.4	N	N	N	200.	
$\text{Zn}^{2+} + \text{nSH}^- = \underline{\text{Zn}(\text{SH})_n}^{2-n}$, n = 1 2 3 4	¹ 7. ¹ 13. ¹ 14. ¹ 14.	N N N N	N N N N	N N N N	174.7 196.6 190.0 177.7	13 13 13 13
$\text{Zn}^{2+} + \text{nS}_2\text{O}_3^{2-} = \underline{\text{Zn}(\text{S}_2\text{O}_3)_n}^{2-2n}$, n = 1 2 3	2.4 ² 4.7 ² 4.9	N N N	N N N	1.0 1.9 3.3	683.2 1,218.8 1,742.5	
$2\text{Zn}^{2+} + 2\text{S}_2\text{O}_3^{2-} = \underline{\text{Zn}_2(\text{S}_2\text{O}_3)_2}$	³ 8.6	N	N	5.8	1,388.1	
$\text{Zn}^{2+} + \text{nSO}_4^{2-} = \underline{\text{Zn}(\text{SO}_4)_n}^{2-2n}$, n = 1 2	2.3 ⁴ 3.7	N N	.9 1.2	.7 .7	904.6 1,657.1	

Table D-2.-Thermodynamic data for zinc(II) species at 25° C-Continued

Reaction	Log K at ionic strength (M)				-Δ _f G° of underlined species kJ·mol ⁻¹	Additional references
	0.0	0.1	1.0	3.0		
$\text{Zn}^{2+} + n\text{NH}_3 = \underline{\text{Zn}(\text{NH}_3)_n}^{2+}$, n = 1 2 3 4	2.2 4.5 6.9 8.9	N N N N	2.3 4.8 7.1 9.3	N N N N	186.1 225.7 265.9 303.8	
$\text{Zn}^{2+} + \text{HCO}_3 = \underline{\text{Zn}(\text{HCO}_3)}$	0.7	N	N	0.3	737.9	
$\text{Zn}^{2+} + n\text{CO}_3^{2-} = \underline{\text{Zn}(\text{CO}_3)_n}^{2-2n}$, n = 1 2	5.1 58.1	N N	N N	4.2 N	704.1 1,249.2	
$\underline{\text{ZnCO}_3}(\text{s}) = \text{Zn}^{2+} + \text{CO}_3^{2-}$	-10.8	N	N	N	736.6	14
$\underline{\text{Zn}_5(\text{OH})_6}(\text{CO}_3)_2(\text{s}) = 5\text{Zn}^{2+} + 6\text{OH}^- + 2\text{CO}_3^{2-}$	-74.3	N	N	N	3,158.9	14
$\text{Zn}^{2+} + n\text{NCS}^- = \underline{\text{Zn}(\text{NCS})_n}^{2-n}$, n = 1 2 3 4	1.3 1.9 2.0 1.6	1.1 N N N	0.7 1.0 1.2 1.5	60.9 61.4 61.7 62.2	61.7 -27.6 -119.7 -214.7	
$\text{Zn}^{2+} + n\text{CN}^- = \underline{\text{Zn}(\text{CN})_n}^{2-n}$, n = 1 2 3 4	5.4 11.1 16.0 19.6	N 10.6 15.7 20.0	N N N N	5.3 11.0 16.7 21.6	5.4 -134.4 -278.9 -430.7	15 15 15, 16
$\underline{\text{Zn}(\text{CN})_2}(\text{s}) = \text{Zn}(\text{CN})_2$	-4.5	N	N	-4.5	-108.8	17

N No data.

¹Extrapolated to 25° C.²Estimated from ionic-strength dependence for reactions of corresponding Cd complexes.³Estimated by assuming zero ionic-strength dependence for $2\text{Zn}(\text{S}_2\text{O}_3) = \text{Zn}_2(\text{S}_2\text{O}_3)_2$.⁴Estimated from ionic-strength dependence for corresponding reactions of other divalent metal ions.⁵Estimated from data for corresponding complexes of other divalent metal ions.⁶Interpolated.

Table D-3.-Thermodynamic data for cadmium(II) species at 25° C

Reaction	Log K at ionic strength (M)				-Δ _f G° of underlined species kJ·mol ⁻¹	Additional references
	0.0	0.1	1.0	3.0		
$\text{Cd}^{2+} + \text{nOH}^- = \underline{\text{Cd}(\text{OH})_n}^{2-n}$, n = 1 2 3 4	3.9 7.7 7.8 8.0	N N N N	N N N N	3.0	257.2 436.2 594.0 752.5	
$2\text{Cd}^{2+} + \text{OH}^- = \underline{\text{Cd}_2(\text{OH})}^{3+}$	4.6	N	N	5.1	338.8	
$\underline{\text{CdO}}(\text{s}) + \text{H}_2\text{O} = \text{Cd}^{2+} + 2\text{OH}^-$	-13.1	N	N	N	228.	
$\underline{\text{Cd}(\text{OH})_2}(\text{cr}) = \text{Cd}^{2+} + 2\text{OH}^-$	-14.4	N	N	N	470.4	
$\underline{\text{Cd}(\text{OH})_2}(\text{am}) = \text{Cd}^{2+} + 2\text{OH}^-$	-13.7	N	N	N	470.4	
$\text{Cd}^{2+} + \text{nCl}^- = \underline{\text{CdCl}_n}^{2-n}$, n = 1 2 3 4	2.0 2.6 2.4 1.7	1.5 N N N	1.4 1.7 1.5 N	1.5 2.2 2.3 1.6	220.2 354.8 484.9 612.1	
$\underline{\text{CdS}}(\text{s}) + 2\text{H}^+ = \text{Cd}^{2+} + \text{H}_2\text{S}$	-7.1	N	N	N	146.	
$\text{Cd}^{2+} + \text{nSH}^- = \underline{\text{Cd}(\text{SH})_n}^{2-n}$, n = 1 2 3 4	¹ 8.1 ¹ 15.1 ¹ 17.0 ¹ 19.4	N N N N	7.6 14.6 16.5 18.9	N N N N	111.5 139.2 137.7 139.1	
$\text{Cd}^{2+} + \text{nS}_2\text{O}_3^{2-} = \underline{\text{Cd}(\text{S}_2\text{O}_3)_n}^{2-2n}$, n = 1 2 3	3.9 6.3 ² 7.3	3.2 N N	2.8 4.6 6.4	2.7 4.7 6.9	622.4 1,158.6 1,686.8	
$2\text{Cd}^{2+} + 2\text{S}_2\text{O}_3^{2-} = \underline{\text{Cd}_2(\text{S}_2\text{O}_3)_2}$	³ 13.6	N	N	11.2	1,277.8	
$\text{Cd}^{2+} + \text{nSO}_4^{2-} = \underline{\text{Cd}(\text{SO}_4)_n}^{2-2n}$, n = 1 2	2.5 ⁴ 3.8	N N	1.0 1.6	.7 .9	836.4 1,588.3	
$\text{Cd}^{2+} + \text{nNH}_3 = \underline{\text{Cd}(\text{NH}_3)_n}^{2+}$, n = 1 2 3 4	2.5 4.6 5.9 6.7	N N N N	2.6 4.8 6.2 7.1	N N N N	118.4 156.9 190.8 221.8	

Table D-3.-Thermodynamic data for cadmium(II) species at 25° C-Continued

Reaction	Log K at ionic strength (M)				-Δ _f G° of underlined species kJ·mol ⁻¹	Additional references
	0.0	0.1	1.0	3.0		
$\text{Cd}^{2+} + \text{HCO}_3 = \underline{\text{Cd}(\text{HCO}_3)}$	⁵ 2.1	N	N	N	676.5	
$\text{Cd}^{2+} + \text{nCO}_3^{2-} = \underline{\text{Cd}(\text{CO}_3)_n}^{2-2n}, n = 1$	⁵ 3.5	N	N	N	625.6	
$n = 2$	⁵ 6.4	N	N	N	1,170.1	
$\underline{\text{CdCO}_3(\text{s})} = \text{Cd}^{2+} + \text{CO}_3^{2-}$	-12.0	N	N	-11.2	674.1	18
$\text{Cd}^{2+} + \text{nNCS}^- = \underline{\text{Cd}(\text{NCS})_n}^{2-n}, n = 1$	1.9	1.6	1.3	1.4	-4.3	
$n = 2$	2.8	2.3	2.0	2.2	-91.8	
$n = 3$	2.9	N	2.1	2.5	-183.9	
$n = 4$	2.3	N	1.9	2.5	-280.1	
$\text{Cd}^{2+} + \text{nCN}^- = \underline{\text{Cd}(\text{CN})_n}^{2-n}, n = 1$	6.0	N	N	5.6	-60.6	
$n = 2$	11.1	N	N	10.8	-203.8	
$n = 3$	15.6	N	N	15.7	-350.6	
$n = 4$	17.9	N	N	19.2	-509.8	
$\underline{\text{Cd}(\text{CN})_2(\text{s})} = \text{Cd}(\text{CN})_2$	⁶ -1.3	N	N	N	-196.4	19, 20

N No data.

¹Estimated from ionic-strength dependence for reactions of corresponding halide and NCS⁻ complexes.²Estimated from data for corresponding Hg complexes.³Estimated by assuming zero ionic-strength dependence for $2\text{Cd}(\text{S}_2\text{O}_3) = \text{Cd}_2(\text{S}_2\text{O}_3)_2$.⁴Estimated from ionic-strength dependence for corresponding reactions of other divalent metal ions.⁵Estimated from data at ionic strength 0.05M and corresponding data for complexes of other divalent metal ions.⁶Calculated from published solubility and complex formation data.

Table D-4.-Thermodynamic data for mercury(I) species at 25° C

Reaction	Log K at ionic strength (M)				-Δ _f G° of underlined species kJ·mol ⁻¹	Additional references
	0.0	0.1	1.0	3.0		
$\text{Hg}_2^{2+} + \text{OH}^- = \underline{\text{Hg}_2(\text{OH})}$	9.3	N	N	9.3	56.8	
$2\text{Hg}_2^{2+} + \text{OH}^- = \underline{\text{Hg}_2}_2(\text{OH})^{3+}$	11.5	N	N	11.5	479.8	
$\underline{\text{Hg}_2\text{Cl}}_2 = \text{Hg}_2^{2+} + 2\text{Cl}^-$	-17.9	N	N	N	211.0	
$\text{Hg}_2^{2+} + n\text{SO}_4^{2-} = \underline{\text{Hg}_2(\text{SO}_4)_n}^{2-2n}, n = 1, 2$	12.7 15.3	N N	N N	N N	606.3 1,365.7	
$\underline{\text{Hg}_2\text{SO}}_4 = \text{Hg}_2^{2+} + \text{SO}_4^{2-}$	-6.1	N	N	N	625.7	
$\underline{\text{Hg}_2\text{CO}_3(\text{s})} = \text{Hg}_2^{2+} + \text{CO}_3^{2-}$	-14.0	N	N	-13.2	454.3	
$\underline{\text{Hg}_2(\text{NCS})}_2 = \text{Hg}_2^{2+} + 2\text{NCS}^-$	-19.5	N	N	N	-227.6	

N No data.

¹Estimated from ionic-strength dependence for corresponding reactions of other divalent metal ions (data given in reference 15 for Hg complexes at ionic strength 0.5M).

Table D-5.-Thermodynamic data for mercury(II) species at 25° C

Reaction	Log K at ionic strength (M)				-Δ _f G° of underlined species kJ·mol ⁻¹	Additional references
	0.0	0.1	1.0	3.0		
$\text{Hg}^{2+} + \text{nOH}^- = \underline{\text{Hg}(\text{OH})_n^{2-n}}$, n = 1 2 3 4	10.6 21.8 20.9 18.9	N 21.2 N N	10.1 21.3 N N	10.7 22.2 N N	53.2 274.4 426.6 572.5	
$2\text{Hg}^{2+} + \text{OH}^- = \underline{\text{Hg}_2(\text{OH})^{3+}}$	10.7	N	N	11.5	-110.8	
$\underline{\text{HgO}}(\text{s}) + \text{H}_2\text{O} = \text{Hg}^{2+} + 2\text{OH}^-$	-25.4	N	N	-25.6	58.5	
$\text{Hg}^{2+} + \text{nCl}^- = \underline{\text{HgCl}_n^{2-n}}$, n = 1 2 3 4	26.8 213.2 214.0 215.1	N N N N	6.7 13.2 14.2 15.3	7.2 14.0 15.1 16.1	5.4 173.1 308.9 446.4	
$\underline{\text{HgCl}_2}(\text{s}) = \text{HgCl}_2$	-0.9	N	N	N	178.3	
$\text{HgCl}^+ + \text{H}_2\text{O} = \underline{\text{HgCl}(\text{OH})} + \text{H}^+$	-3.0	N	-3.0	-3.0	225.5	
$\underline{\text{Hg}_3\text{O}_2\text{Cl}_2} = 2\text{HgO}(\text{s}) + \text{HgCl}_2$	-4.2	N	N	N	4314.	
$\underline{\text{Hg}_5\text{O}_4\text{Cl}_2} = 4\text{HgO}(\text{s}) + \text{HgCl}_2$	-6.6	N	N	N	4445.	
$\underline{\text{HgS}}(\text{s}) + 2\text{H}^+ = \text{Hg}^{2+} + \text{H}_2\text{S}$	-32.2	N	N	N	47.	
$\text{Hg}^{2+} + \text{nSH}^- = \underline{\text{Hg}(\text{SH})_n^{2-n}}$, n = 1 2	17. 37.	N N	N N	N N	-79.9 22.0	
$\text{Hg}(\text{SH})_2 = \underline{\text{HgS}(\text{SH})} + \text{H}^+$	-5.	N	-6.2	N	-6.5	
$\text{HgS}(\text{SH})^- = \underline{\text{HgS}_2^{2-}} + \text{H}^+$	-7.	N	-8.3	N	-46.5	
$\text{Hg}^{2+} + \text{nS}_2\text{O}_3^{2-} = \underline{\text{Hg}(\text{S}_2\text{O}_3)_n^{2-2n}}$, n = 1 2 3	14. 29.2 30.6	N N N	N N N	N N N	437.8 1,047.1 1,577.6	
$2\text{Hg}^{2+} + 2\text{S}_2\text{O}_3^{2-} = \underline{\text{Hg}_2(\text{S}_2\text{O}_3)_2}$	32.	N	N	N	898.5	
$\text{Hg}^{2+} + \text{nSO}_4^{2-} = \underline{\text{Hg}(\text{SO}_4)_n^{2-2n}}$, n = 1 2	2.7 4.2	N N	N N	N N	595.3 1,348.4	

Table D-5.-Thermodynamic data for mercury(II) species at 25° C-Continued

Reaction	Log K at ionic strength (M)				-Δ _f G° of underlined species kJ·mol ⁻¹	Additional references
	0.0	0.1	1.0	3.0		
$\text{Hg}^{2+} + n\text{NH}_3 = \underline{\text{Hg}(\text{NH}_3)_n^{2+}}$, n = 1 2 3 4	9.0 17.7 18.7 19.3	N N N N	N N N N	3.0	-86.7 -10.6 21.6 51.6	
$\text{Hg}^{2+} + \text{HCO}_3 = \underline{\text{Hg}(\text{HCO}_3)}$	¹⁰ 6.	N	N	5.4	456.5	
$\text{Hg}^{2+} + n\text{CO}_3^{2-} = \underline{\text{Hg}(\text{CO}_3)_n^{2-2n}}$, n = 1 ¹⁰ 12. ¹⁰ 15.5, n = 2	¹⁰ 12. ¹⁰ 15.5	N N	N N	11.0 N	431.9 979.9	
$\text{HgCO}_3 + \text{H}_2\text{O} = \underline{\text{Hg}(\text{CO}_3)(\text{OH})} + \text{H}^+$	¹⁰ -7.	N	N	6.6	629.2	
$\underline{\text{HgCO}_3(\text{s})} = \text{Hg}^{2+} + \text{CO}_3^{2-}$	¹¹ -14.	N	N	N	437.6	
$\underline{\text{Hg}_3\text{O}_2(\text{CO}_3)(\text{s})} + 2\text{H}_2\text{O} = 3\text{Hg}^{2+} + 4\text{OH}^- + \text{CO}_3^{2-}$	-67.2	N	N	-67.2	572.6	
$\text{Hg}^{2+} + n\text{NCS}^- = \underline{\text{Hg}(\text{NCS})_n^{2-n}}$, n = 1 2 3 4	¹² 9.2 17.3 20.0 21.8 -2.7	N 16.4 19.1 21.2 N	9.1 16.9 19.7 21.7 -2.7	N	-204.8 -251.3 -328.5 -411.0 -235.8	
$\underline{\text{Hg}(\text{NCS})_2} = \text{Hg}(\text{NCS})_2$	³ -3.4	N	-3.4	N	13.0	
$\text{Hg}(\text{NCS})^+ + \text{H}_2\text{O} = \underline{\text{Hg}(\text{NCS})(\text{OH})} + \text{H}^+$						
$\text{Hg}^{2+} + n\text{CN}^- = \underline{\text{Hg}(\text{CN})_n^{2-n}}$, n = 1 2 3 4	17.0 32.8 36.3 39.0 -0.4	17.7 34.1 37.9 40.8 N	N N N N N	N	-240.0 -322.2 -474.6 -631.6 -319.9	19
$\underline{\text{Hg}(\text{CN})_2(\text{s})} = \text{Hg}(\text{CN})_2$	¹³ 2.4	N	N	N	-17.0	
$\text{Hg}(\text{CN})_2 + \text{Hg}(\text{OH})_2 = 2\underline{\text{Hg}(\text{OH})(\text{CN})}$						
$\underline{\text{Hg}_2\text{O}(\text{CN})_2} + \text{H}_2\text{O} = 2\underline{\text{Hg}(\text{OH})(\text{CN})}$	-1.2	N	N	N	-257.5	19
$\text{Hg}(\text{CN})_2(\text{s}) + \text{OH}^- = \underline{\text{Hg}(\text{OH})(\text{CN})_2}$	0.0	N	N	N	-162.6	22

Table D-5.-Thermodynamic data for mercury(II) species at 25° C-Continued

Reaction	Log K at ionic strength (M)				-Δ _f G° of underlined species kJ·mol ⁻¹	Additional references
	0.0	0.1	1.0	3.0		
Hg ²⁺ + mCl ⁻ + nCN ⁻ = <u>HgCl_m(CN)_n</u> ^{2-m-n} , m = 1, n = 1	1423.5	N	N	N	-71.7	23
1	1433.2	N	N	N	-188.7	23
1	1436.8	N	N	N	-340.5	23
2	1423.8	N	N	N	61.2	23
2	1433.6	N	N	N	-55.2	23
3	1424.2	N	N	N	194.7	23
Hg ²⁺ + mNCS ⁻ + nCN ⁻ = <u>Hg(NCS)_m(CN)_n</u> ^{2-m-n} , m = 1, n = 1	1524.8	N	N	N	-288.1	24
1	1533.6	N	N	N	-410.3	24
1	1537.3	N	N	N	-561.6	24
2	1526.2	N	N	N	-372.8	24
2	1535.0	N	N	N	-495.0	24
3	1527.8	N	N	N	-456.4	24

N No data.

¹Estimated from data for corresponding hydrosulfide complexes.²Calculated from Gibbs energy data in reference 1.³Estimated assuming zero ionic-strength dependence.⁴Gibbs energy data estimated on basis of data for Br analogs in reference 1, by assuming equal enthalpies of formation from HgO and Hg(II) halide; log K values then calculated.⁵Estimated from data for corresponding halide and NCS⁻ complexes.⁶Estimated.⁷Estimated from data for corresponding Zn and Cd complexes, assuming slight instability to disproportionation.⁸Estimated by assuming log K = 4 for reaction 2Hg(S₂O₃) = Hg₂(S₂O₃)₂ by comparison with corresponding reactions of Zn and Cd complexes.⁹Estimated from ionic-strength dependence for corresponding reactions of other divalent metal ions (data given in reference 3 for Hg complexes at ionic strength 0.5 M).¹⁰Estimated from additional data at ionic strength 0.5 M and corresponding data for other divalent metal ions.¹¹Estimated by comparison of data for other divalent metal carbonates and lower stability toward decomposition to HgO and CO₂ than Hg₂O₂CO₃.¹²Estimated from ionic-strength dependence for reactions of corresponding halide complexes.

Table D-5.-Thermodynamic data for mercury(II) species at 25° C--Continued

¹³Log K = 2.5 at 30° C and ionic strength 2.0M, and enthalpy change estimated as +5 kcal, from data in reference 3; corrected to 25° C, zero ionic-strength dependence assumed.

¹⁴Data in reference 23 are log K values for successive replacement of Cl⁻ by CN⁻ in chloro complexes at ionic strength 2.0M. To estimate values at zero ionic strength, these replacement log K values were multiplied by constant factors for each respective x + y = 2, 3, 4, such that the sum of replacement constants for each value of x + y equaled the difference of the formation log K values of the respective chloro and cyano complexes at zero ionic strength, namely 19.6, 22.3, 23.9 for x + y = 2, 3, 4, respectively. The tabulated formation constants were then calculated from the obtained replacement log K values.

¹⁵Data in reference 24 are log K values for successive replacement of Br⁻ by CN⁻ in HgBr₄²⁻ at ionic strength 2.0M. Values at zero ionic strength were estimated in the same way as for the corresponding chloro complexes for x + y = 4. For x + y = 2, 3, values were estimated via the trends in the values for the corresponding chloro complexes. The differences of the formation log K values for bromo and cyano complexes are 15.4, 16.7, 18.1 for x + y = 2, 3, 4, respectively. Corresponding differences for thiocyanato and cyano complexes are 15.5, 16.3, 17.2. To estimate the replacement log K values for NCS⁻ by CN⁻, the replacement log K values of Br⁻ by CN⁻ were multiplied by constant factors for each respective x + y = 2, 3, 4, such that the sum of replacement log K values equaled the difference of formation log K values of the respective thiocyanate and cyanide complexes. The tabulated formation constants were then calculated from the obtained replacement log K values.

Table D-6.-Thermodynamic data for copper(I) species at 25° C

Reaction	Log K at ionic strength (M)				-Δ _f G° of underlined species kJ·mol ⁻¹	Additional references
	0.0	0.1	1.0	3.0		
$\text{Cu}^+ + \text{nOH}^- = \underline{\text{Cu}(\text{OH})_n^{1-n}}$, n = 1 2	¹ 4.5 ¹ 9.7	N N	N N	N N	134.1 321.1	
$\text{Cu}_2\text{O}(\text{s}) + \text{H}_2\text{O} = 2\text{Cu}^+ + 2\text{OH}^-$	-29.5	N	N	N	148.	
$\text{Cu}^+ + \text{nCl}^- = \underline{\text{CuCl}_n^{1-n}}$, n = 1 2 3 4	² 2.7 5.5 5.7 ² 5.7 -6.7	N N N N N	N 5.2 N N N	N 5.5 5.2 N N	97.7 244.9 377.2 508.4 120.5	
$\underline{\text{CuCl}} = \text{Cu}^+ + \text{Cl}^-$	-26.3	N	N	N	80.	
$\text{Cu}_2\text{S}(\text{s}) + 2\text{H}^+ = 2\text{Cu}^+ + \text{H}_2\text{S}$	³ 14. ³ 16.	N N	N N	N N	18.7 17.8	
$\text{Cu}^+ + \text{nSH}^- = \underline{\text{Cu}(\text{SH})_n^{1-n}}$, n = 1 2	⁴ 8.	N	N	N	-27.0	
$\text{CuSH} = \underline{\text{CuS}} + \text{H}^+$	⁴ 9.	N	N	N	-33.5	
$\text{Cu}(\text{SH})_2^- = \underline{\text{CuS}(\text{SH})_2^{2-}} + \text{H}^+$	³ 42.	N	N	N	25.1	
$2\text{Cu}^+ + 3\text{SH}^- + \text{OH}^- = \underline{\text{Cu}_2\text{S}(\text{SH})_2^{2-}} + \text{H}_2\text{O}$	⁵ 11.0 ⁵ 13.0 ⁵ 14.7	N N N	10.3 12.2 13.5	N N N	536.4 1,070.3 1,602.5	
$\text{Cu}^+ + \text{nS}_2\text{O}_3^{2-} = \underline{\text{Cu}(\text{S}_2\text{O}_3)_n^{1-2n}}$, n = 1 2 3	⁶ 1.	N	N	N	701.3	
$\text{Cu}^+ + \text{SO}_4^{2-} = \underline{\text{Cu}(\text{SO}_4)^{1-}}$	5.8 10.6	N N	N N	N N	10.7 64.6	
$\text{Cu}^+ + \text{nNH}_3 = \underline{\text{Cu}(\text{NH}_3)_n^{1+}}$, n = 1 2	⁷ 5. ⁷ 11. ⁷ 11. ⁷ 11.	N N N N	N N N N	N N N N	-113.1 -171.5 -264.2 -356.9	
$\text{Cu}^+ + \text{nNCS}^- = \underline{\text{Cu}(\text{NCS})_n^{1-n}}$, n = 1 2 3 4	⁷ 13.	N	N	N	-67.4	
$\underline{\text{CuNCS}} = \text{Cu}^+ + \text{NCS}^-$						

Table D-6.-Thermodynamic data for copper(I) species at 25° C-Continued

Reaction	Log K at ionic strength (M)				$-\Delta_f G^\circ$ of underlined species kJ·mol ⁻¹	Additional references
	0.0	0.1	1.0	3.0		
$\text{Cu}^+ + n\text{CN}^- = \underline{\text{Cu}(\text{CN})_n}^{1-n}$, n =						
1	⁸ 10.5	N	N	N	-161.4	28
2	21.7	N	N	N	-269.8	
3	27.0	N	N	N	-412.0	
4	28.5	N	N	N	-575.8	
$\underline{\text{Cu}(\text{CN})_2(\text{s})} = \text{Cu}^+ + \text{CN}^-$	-19.5	N	N	N	-110.0	
$\text{Cu}^+ + \text{CN}^- + \text{OH}^- = \underline{\text{Cu}(\text{CN})(\text{OH})}^-$	⁹ 14.7	N	N	N	19.9	

N No data.

¹Estimated via trends in corresponding Zn, Cd, Hg complexes.²Estimated via trends in corresponding Ag complexes.³Estimated via trends in corresponding Ag and Au complexes and analogous halide and SCN⁻ complexes.⁴Assumed similar to values for corresponding Ag complexes.⁵Estimated from ionic-strength dependence for reactions of corresponding Ag complexes.⁶Estimated via comparison of corresponding Ag and Tl complexes.⁷Estimated from ionic-strength dependence for reactions of corresponding Ag complexes (data given in reference 3 for ionic strength 0.5M).⁸Derived from estimate of $\log K = -9$ for $\text{CuCN}(\text{s}) = \text{CuCN}$.⁹Derived from estimate of $\log K = -2$ for $\text{Cu}(\text{CN})_2^- + \text{Cu}(\text{OH})_2^- = 2\text{Cu}(\text{CN})(\text{OH})^-$ ($\log K = +1.5$ for corresponding reaction of Ag complexes).

Table D-7.-Thermodynamic data for copper(II) species at 25° C

Reaction	Log K at ionic strength (M)				-Δ _f G° of underlined species kJ·mol ⁻¹	Additional references
	0.0	0.1	1.0	3.0		
$\text{Cu}^{2+} + n\text{OH}^- = \underline{\text{Cu}(\text{OH})_n^{2-n}}$, n = 1	6.5	6.1	N	6.8	129.2	
2	11.8	N	12.8	N	316.8	
3	15.0	N	14.5	N	492.3	
4	16.4	N	15.6	N	657.6	
$2\text{Cu}^{2+} + 2\text{OH}^- = \underline{\text{Cu}_2(\text{OH})_2^{2+}}$	17.4	16.8	17.0	17.6	283.5	
$3\text{Cu}^{2+} + 4\text{OH}^- = \underline{\text{Cu}_3(\text{OH})_4^{2+}}$	35.2	33.5	N	N	634.5	
$\underline{\text{CuO}}(\text{s}) + \text{H}_2\text{O} = \text{Cu}^{2+} + 2\text{OH}^-$	-20.3	N	N	N	128.	
$\underline{\text{Cu}(\text{OH})_2(\text{cr})} = \text{Cu}^{2+} + 2\text{OH}^-$	-19.3	N	N	N	359.6	
$\underline{\text{Cu}(\text{OH})_2(\text{am})} = \text{Cu}^{2+} + 2\text{OH}^-$	-18.8	N	N	N	356.7	
$\text{Cu}^{2+} + n\text{Cl}^- = \underline{\text{CuCl}_n^{2-n}}$, n = 1	.2	N	-2	.0	67.1	
2	.0	N	-5	-.4	197.2	
$\underline{\text{Cu}_2(\text{OH})_3\text{Cl}} = 2\text{Cu}^{2+} + 3\text{OH}^- + \text{Cl}^-$	-34.6	N	-34.3	N	670.2	
$\underline{\text{CuS}}(\text{s}) + 2\text{H}^+ = \text{Cu}^{2+} + \text{H}_2\text{S}$	-16.4	N	N	N	56.	
$\text{Cu}^{2+} + n\text{SO}_4^{2-} = \underline{\text{Cu}(\text{SO}_4)_n^{2-2n}}$, n = 1	2.3	N	.8	.5	692.4	
$\underline{\text{Cu}_4(\text{OH})_6(\text{SO}_4)_2(\text{s})} = 4\text{Cu}^{2+} + 6\text{OH}^- + \text{SO}_4^{2-}$	-68.6	N	-67.4	N	1,504.5	
$\text{Cu}^{2+} + n\text{NH}_3 = \underline{\text{Cu}(\text{NH}_3)_n^{2+}}$, n = 1	4.0	N	4.1	N	-15.9	
2	7.5	N	7.6	N	30.6	
3	10.3	N	10.5	N	73.1	
4	11.8	N	12.6	N	108.2	
$\text{Cu}^{2+} + \text{HCO}_3^- = \underline{\text{Cu}(\text{HCO}_3)_2^+}$	1.8	N	1.0	N	532.0	

Table D-7.-Thermodynamic data for copper(II) species at 25° C-Continued

Reaction	Log K at ionic strength (M)				-Δ _f G° of underlined species kJ·mol ⁻¹	Additional references
	0.0	0.1	1.0	3.0		
$\text{Cu}^{2+} + n\text{CO}_3^{2-} = \underline{\text{Cu}(\text{CO}_3)_n}^{2-2n}, n = 1$ $n = 2$	6.8 10.2	N N	5.7 9.3	N N	501.6 1,049.0	
$\underline{\text{CuCO}_3}(\text{s}) = \text{Cu}^{2+} + \text{CO}_3^{2-}$	¹ -11.0	N	N	N	525.6	
$\underline{\text{Cu}_2(\text{OH})_2(\text{CO}_3)}(\text{s}) = 2\text{Cu}^{2+} + 2\text{OH}^- + \text{CO}_3^{2-}$	-33.3	N	N	N	902.3	
$\underline{\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2}(\text{s}) = 3\text{Cu}^{2+} + 2\text{OH}^-$ $+ 2\text{CO}_3^{2-}$	-44.9	N	N	N	1,431.3	
$\text{Cu}^{2+} + n\text{NCS}^- = \underline{\text{Cu}(\text{NCS})_n}^{2-n}, n = 1$ 2	2.3 3.6	1.9 3.0	1.7 2.7	1.9 N	-144.8 -230.1	
$\text{Cu}^{2+} + n\text{CN}^- = \underline{\text{Cu}(\text{CN})_n}^{2-n}, n = 4$	² 22.2	N	N	N	-627.9	29
$2\underline{\text{Cu}(\text{CN})_2}(\text{s}) = \text{Cu}^{2+} + \text{Cu}(\text{CN})_4^{2-}$	³ -10.	N	N	N	-318.1	
$\underline{\text{Cu}_3(\text{CN})_4}(\text{s}) = \text{Cu}^{2+} + 2\underline{\text{Cu}(\text{CN})_2}^-$	⁴ -15.				-519.2	

N No data.

¹Estimated from data for carbonates of other divalent metal ions, consistent with the stability of the hydroxide carbonates.²Calculated from reduction potential of +0.54 V to $\text{Cu}(\text{CN})_4^{3-}$ in reference 29 and data for $\text{Cu}(\text{I})$ complexes.³Estimated from data for cyanides of Ni and Zn.⁴Estimated assuming a solubility of about 10^{-5}M and stability with respect to disproportionation to CuCN and $\text{Cu}(\text{CN})_2$.

Table D-8.-Thermodynamic data for silver(I) species at 25° C

Reaction	Log K at ionic strength (M)				-Δ _f G° of underlined species kJ·mol ⁻¹	Additional references
	0.0	0.1	1.0	3.0		
$\text{Ag}^+ + \text{nOH}^- = \underline{\text{Ag}(\text{OH})_n^{1-n}}$, n = 1 2	2.0 4.0	N N	N N	N 3.6	91.6 260.3	
$\underline{\text{Ag}_2\text{O}(\text{s})} + \text{H}_2\text{O} = 2\text{Ag}^+ + 2\text{OH}^-$	-15.4	-15.2	-14.4	-14.8	11.3	
$\text{Ag}^+ + \text{nCl}^- = \underline{\text{AgCl}_n^{1-n}}$, n = 1 2 3 4	3.3 5.2 5.2 5.2	3.1 5.1 N N	3.4 5.2 N N	13.3 15.6 15.5 15.6	72.9 215.0 346.2 477.4	
$\underline{\text{AgCl}} = \text{Ag}^+ + \text{Cl}^-$	-9.7	N	-9.7	-10.0	109.8	
$\underline{\text{Ag}_2\text{S}(\text{s})} + 2\text{H}^+ = 2\text{Ag}^+ + \text{H}_2\text{S}$	-29.0	N	N	N	39.	
$\text{Ag}^+ + \text{nSH}^- = \underline{\text{Ag}(\text{SH})_n^{1-n}}$, n = 1 2	16.2 18.0	13.6 17.7	13.3 17.2	N N	3.1 1.0	30 30
$\text{AgSH} = \underline{\text{AgS}^-} + \text{H}^+$	28.3	8.3	N	N	-44.3	30
$\text{Ag}(\text{SH})_2^- = \underline{\text{AgS}(\text{SH})_2^{2-}} + \text{H}^+$	29.5	9.5	N	N	-53.2	30
$2\text{Ag}^+ + 3\text{SH}^- + \text{OH}^- = \underline{\text{Ag}_2\text{S}(\text{SH})_2^{2-}} + \text{H}_2\text{O}$	346.	N	44.7	N	-8.4	30
$\text{Ag}^+ + \text{nS}_2\text{O}_3^{2-} = \underline{\text{Ag}(\text{S}_2\text{O}_3)_n^{1-2n}}$, n = 1 2 3	8.7 13.4 14.0	N N N	N 12.5 12.8	N 12.8 13.3	495.1 1,044.4 1,570.3	
$\text{Ag}^+ + \text{SO}_4^{2-} = \underline{\text{Ag}(\text{SO}_4)^-}$	1.3	N	.3	0.2	674.8	
$\text{Ag}^+ + \text{nNH}_3 = \underline{\text{Ag}(\text{NH}_3)_n^+}$, n = 1 2	3.3 7.2	N N	3.3 7.4	3.5 7.6	-31.8 17.0	
$\underline{\text{Ag}_2\text{CO}_3} = 2\text{Ag}^+ + \text{CO}_3^{2-}$	-11.1	N	N	N	437.2	
$\text{Ag}^+ + \text{nNCS}^- = \underline{\text{Ag}(\text{NCS})_n^{1-n}}$, n = 1 2 3 4	4.8 8.2 9.5 9.7	4.6 8.1 9.3 10.5	N N N N	14.6 18.2 19.5 110.5	-142.4 -215.7 -301.0 -392.5	

Table D-8.-Thermodynamic data for silver(I) species at 25° C-Continued

Reaction	Log K at ionic strength (M)				-Δ _f G° of underlined species kJ·mol ⁻¹	Additional references
	0.0	0.1	1.0	3.0		
<u>AgNCS</u> = Ag ⁺ + NCS ⁻	-12.0	-11.8	N	N	-101.3	
Ag ⁺ + nCN ⁻ = <u>Ag(CN)_n</u> ¹⁻ⁿ , n = 1 2 3 4	⁴ 9.7	N	N	N	-194.1	
	20.5	20.0	20.0	N	-304.9	
	21.4	N	20.7	N	-472.1	
	⁵ 21.4	N	21.2	N	-644.5	
<u>Ag(CN)(s)</u> = Ag ⁺ + CN ⁻	-15.7	-15.2	-15.4	N	-159.9	
Ag ⁺ + CN ⁻ + OH ⁻ = <u>Ag(CN)(OH)</u> ⁻	13.2	N	12.7	N	-16.9	

N No data.

¹ Interpolated.² Estimated.³ Derived by assuming zero ionic-strength dependence of the reaction 2Ag(SH)₂²⁻ + H₂S.⁴ Derived from estimate of log K = -6 for AgCN(s) = AgCN.⁵ Estimated via trends in corresponding halide and NCS⁻ complexes.

Table D-9.-Thermodynamic data for gold(I) species at 25° C

Reaction	Log K at ionic strength (M)				-Δ _f G° of underlined species kJ·mol ⁻¹	Additional references
	0.0	0.1	1.0	3.0		
$\text{Au}^+ + \text{NOH}^- = \underline{\text{Au}(\text{OH})_n^{1-n}}$, n = 1 2	¹ 10. ² 22. -19.5	N	N	N	50.4 276.2 3-28.	33
$\underline{\text{Au}_2\text{O}(\text{s})} + \text{H}_2\text{O} = 2\text{Au}^+ + 2\text{OH}^-$		N	N	N		
$\text{Au}^+ + \text{nCl}^- = \underline{\text{AuCl}_n^{1-n}}$, n = 1 2	¹ 4.5 ² 9.3	N	N	N	-7.1 151.5	31
$\text{AuCl}_2^- + \text{OH}^- = \underline{\text{Au}(\text{OH})\text{Cl}^{1-}} + \text{Cl}^-$	6.7	N	N	N	215.8	33
$\underline{\text{AuCl}} = \text{Au}^+ + \text{Cl}^-$	-8.9	N	N	N	418.	
$\underline{\text{Au}_2\text{S}(\text{s})} + 2\text{H}^+ = 2\text{Au}^+ + \text{H}_2\text{S}$	-47.7	N	N	N	-28.	34
$\text{Au}^+ + \text{nSH}^- = \underline{\text{Au}(\text{SH})_n^{1-n}}$, n = 1 2	20. 33. ⁵ 6.	N	N	N	-62.1 -2 -96.4	30 30 30
$\text{AuSH} = \underline{\text{AuS}} + \text{H}^+$		N	N	N		
$\text{Au}(\text{SH})_2^- = \underline{\text{AuS}(\text{SH})_2^-} + \text{H}^+$	⁵ 8.	N	N	N	-45.9	30
$2\text{Au}^+ + 3\text{SH}^- + \text{OH}^- = \underline{\text{Au}_2\text{S}(\text{SH})_2^{2-}} + \text{H}_2\text{O}$	73.	N	N	N	-28.1	30
$\text{Au}^+ + \text{nS}_2\text{O}_3^{2-} = \underline{\text{Au}(\text{S}_2\text{O}_3)_n^{1-2n}}$, n = 1 2	¹ 18. ² 26.2	N	N	N	461.2 1030.5	31
$\text{Au}^+ + \text{SO}_4^{2-} = \underline{\text{Au}(\text{SO}_4)^-}$	⁶ 1.	N	N	N	586.2	
$\text{Au}^+ + \text{nNH}_3 = \underline{\text{Au}(\text{NH}_3)_n^+}$, n = 1 2	¹ 8. ² 19.3	N	N	N	-91.8 -1.0	31, 35
$\text{Au}^+ + \text{nNCS}^- = \underline{\text{Au}(\text{NCS})_n^{1-n}}$, n = 1 2	¹ 8.5 ² 17.6	N	N	N	-208.2 -248.9	31
$\text{Au}(\text{NCS})_2^- + \text{OH}^- = \underline{\text{Au}(\text{OH})(\text{NCS})^-} + \text{NCS}^-$	2.5	N	N	N	15.3	33
$\underline{\text{AuNCS}} = \text{Au}^+ + \text{NCS}^-$	⁷ -14.				-176.8	

Table D-9.-Thermodynamic data for gold(I) species at 25° C-Continued

Reaction	Log K at ionic strength (M)			-Δ _f G° of underlined species kJ·mol ⁻¹	Additional references
	0.0	0.1	1.0	3.0	
$\text{Au}^+ + n\text{CN}^- = \underline{\text{Au}(\text{CN})_n}^{1-n}$, n = 1	⁸ 18.	N	N	N	
2	² 37.0	N	N	N	31
$\underline{\text{Au}(\text{CN})}(\text{s}) = \text{Au}^+ + \text{CN}^-$	⁹ -32.	N	N	N	36
$\text{Au}^+ + \text{CN}^- + \text{OH}^- = \underline{\text{Au}(\text{CN})(\text{OH})}^-$	⁸ 30.	N	N	N	

N No data.

¹Estimated via trends in Zn, Cd, Hg complexes versus values for Cu, Ag complexes.²Calculated from difference of reduction potentials of uncomplexed Au⁺ and the complex.³Estimated assuming slightly unstable to disproportionation to Au and Au₂O₃.⁴Estimated from standard enthalpy of formation and data for AgCl.⁵Assumed 2 log K units more acidic than corresponding Ag complexes.⁶Estimated from comparison of corresponding Ag, Tl complexes.⁷Estimated from values for Au halides and corresponding Ag compounds (values for AuBr and AuI estimated in same way as AuCl).⁸Estimated log K = +1 for Au(CN)₂⁻ + Au(OH)₂⁻ = 2Au(CN)(OH)⁻ from values for corresponding reactions for halide and NCS⁻ complexes and corresponding reactions of analogous Hg(II) complexes; estimated log K = 12 for AuCN + OH⁻ = Au(CN)(OH)⁻ in the same way; tabulated values then calculated.⁹Derived from estimate of log K = +5 for AuCN(s) + CN⁻ = Au(CN)₂⁻ suggested by information in reference 36.

Table D-10.-Thermodynamic data for gold(III) species at 25° C

Reaction	Log K at ionic strength (M)				-Δ _f G° of underlined species kJ·mol ⁻¹	Additional references
	0.0	0.1	1.0	3.0		
$\text{Au}^{3+} + \text{noH}^- = \underline{\text{Au}(\text{OH})_{n-1}^{3-n}}$, n = 1	115.	N	N	N	-191.3	
2	129.7	N	N	N	49.9	
3	43.7	N	N	N	287.4	31
4	251.7	N	N	N	490.2	37, 38
$\underline{\text{Au}_2\text{O}_3(\text{s})} + 3\text{H}_2\text{O} = 2\text{Au}(\text{OH})_3$	-11.0	N	N	N	-74.	
$\text{Au}^{3+} + \text{nCl}^- = \underline{\text{AuCl}_{n-1}^{3-n}}$, n = 3	20.3	N	N	N	75.6	
4	225.3	N	N	N	235.3	31
$\text{AuCl}_3 + \text{H}_2\text{O} = \underline{\text{AuCl}_3(\text{OH})^-} + \text{H}^+$	-1.0	N	-0.6	N	307.1	
$\text{AuCl}_{4-n}(\text{OH})_n^- + \text{OH}^- =$						
$\underline{\text{AuCl}_{3-n}(\text{OH})_{n+1}^-} + \text{Cl}^-$, n = 0	8.0	N	N	N	307.1	
1	7.0	N	N	N	373.1	
2	6.0	N	N	N	433.5	
$\text{Au}^{3+} + \text{nNH}_3 = \underline{\text{Au}(\text{NH}_3)_{n-1}^{3+}}$, n = 3	149.5	N	N	N	-71.9	39
4	259.8	N	N	N	13.4	31, 39
$\text{Au}(\text{NH}_3)_3^{3+} + \text{H}_2\text{O} = \underline{\text{Au}(\text{NH}_3)_3(\text{OH})^{2+}} + \text{H}^+$	1-1.	N	-0.7	N	171.0	39
$\text{Au}(\text{NH}_3)_4^{3+} = \underline{\text{Au}(\text{NH}_3)_3(\text{NH}_2)^{2+}} + \text{H}^+$	1-7.	N	-7.5	N	-26.6	39
$\text{Au}^{3+} + \text{nNCS}^- = \underline{\text{Au}(\text{NCS})_{n-1}^{3-n}}$, n = 3	333.1	N	N	N	-523.3	
4	243.6	N	N	N	-556.1	31
$\text{Au}(\text{NCS})_3 + \text{H}_2\text{O} = \underline{\text{Au}(\text{NCS})_3(\text{OH})^{1-}} + \text{H}^+$	3-1.	N	N	N	231.0	

Table D-10.-Thermodynamic data for gold(III) species at 25° C-Continued

Reaction	Log K at ionic strength (M)			-Δ _f G° of underlined species kJ·mol ⁻¹	Additional references
	0.0	0.1	1.0	3.0	
Au(NCS) _{4-n} (OH) _n ⁻ + OH ⁻ =					
Au(NCS) _{3-n} (OH) _{n+1} ⁻ + NCS ⁻ , n = 0	³ 2.5	N	N	-291.8	
1	³ 2.2	N	N	-29.7	
2	³ 1.8	N	N	231.0	
Au ³⁺ + nCN ⁻ = Au(CN) _n ³⁻ⁿ , n = 4	² 81.1	N	N	-660.7	31
AuX ₄ ⁻ + 2CN ⁻ = Au ₂ (CN) ₂ ⁻ + 2X ⁻ , X = Cl	⁴ 25.0	N	N	-229.4	
NCS	⁵ 21.4	N	N	-593.4	

N No data.

¹Estimated.²Calculated from difference of standard reduction potentials of uncomplexed Au³⁺ and the complex.³Assumed acidity of Au(NCS)₃ same as for the corresponding chloro complex; estimated log K values for OH⁻ substitution reactions by multiplying log K values for corresponding reactions of chloro complexes by constant factor given by differences in formation log K values of AuCl₄⁻ or Au(NCS)₄⁻ and Au(OH)₄⁻ of 26.5 and 8.2 respectively; tabulated values then obtained.⁴Derived from data for Au(CN)₂⁻ + Cl₂ = Au(CN)₂Cl₂⁻. Formation log K is 50.3.⁵Estimated formation log K = 65 by comparing values for the corresponding halide complexes obtained in the same way as for the chloro complex; tabulated value then derived.

Table D-11.--Thermodynamic data for nickel(II) species at 25° C

Reaction	Log K at ionic strength (M)				-Δ _f G° of underlined species kJ·mol ⁻¹	Additional references
	0.0	0.1	1.0	3.0		
$\text{Ni}^{2+} + \text{NOH}^- = \underline{\text{Ni}(\text{OH})_n}^{2-n}, n = 1$	4.1	3.6	3.7	N	225.1	
2	9.	N	N	N	410.4	
3	12.	N	N	N	584.8	
4	11.	N	N	N	736.4	
$\underline{\text{NiO}}(\text{s}) + \text{H}_2\text{O} = \text{Ni}^{2+} + 2\text{OH}^-$	-15.9	N	N	N	212.	
$\underline{\text{Ni}(\text{OH})_2}(\text{cr}) = \text{Ni}^{2+} + 2\text{OH}^-$	-17.2	N	N	N	457.2	
$\underline{\text{Ni}(\text{OH})_2}(\text{am}) = \text{Ni}^{2+} + 2\text{OH}^-$	-15.2	N	N	N	445.8	
$\text{Ni}^{2+} + \text{nCl}^- = \underline{\text{NiCl}_n}^{2-n}, n = 1$	1.3	N	.0	-.6	177.3	
$\underline{\text{NiS}}(\text{s}) + 2\text{H}^+ = \text{Ni}^{2+} + \text{H}_2\text{S}$	-3.1	N	N	N	90.	
$\text{Ni}^{2+} + \text{nSO}_4^{2-} = \underline{\text{Ni}(\text{SO}_4)_n}^{2-2n}, n = 1$	2.3	1.0	.7	.3	802.0	
$\text{Ni}^{2+} + \text{nNH}_3 = \underline{\text{Ni}(\text{NH}_3)_n}^{2+}, n = 1$	2.7	2.7	2.8	N	86.3	
2	4.9	4.9	5.0	N	125.4	
3	6.6	N	6.7	N	161.6	
4	7.7	N	7.8	N	194.4	
5	8.3	N	N	N	224.3	
6	8.3	N	N	N	250.8	
$\text{Ni}^{2+} + \text{HCO}_3^- = \underline{\text{Ni}(\text{HCO}_3)}^+$	2.4	N	N	N	645.0	
$\text{Ni}^{2+} + \text{nCO}_3^{2-} = \underline{\text{Ni}(\text{CO}_3)_n}^{2-2n}, n = 1$	24.5	N	N	N	598.1	
2	17.5	N	N	N	1143.2	

Table D-11.-Thermodynamic data for nickel(II) species at 25° C-Continued

Reaction	Log K at ionic strength (M)				-Δ _f G° of underlined species kJ·mol ⁻¹	Additional references
	0.0	0.1	1.0	3.0		
$\text{NiCO}_3(\text{s}) = \text{Ni}^{2+} + \text{CO}_3^{2-}$	-11.0	N	N	N	635.2	40
$\text{Ni}^{2+} + n\text{NCS}^- = \underline{\text{Ni}(\text{NCS})_n}^{2-n}, n = 1$	1.8	1.3	1.1	1.3	-38.0	
2	12.5	N	1.6	N	-126.7	
$\text{Ni}^{2+} + n\text{CN}^- = \underline{\text{Ni}(\text{CN})_n}^{2-n}, n = 4$	30.2	30.5	N	31.1	-472.8	
5	329.2	N	N	30.4	-650.9	
$\text{Ni}(\text{CN})_2(\text{s}) = \text{Ni}^{2+} + 2\text{CN}^-$	-19.5	N	N	N	-189.1	41

N No data.

¹Estimated from data for corresponding species of other divalent metal ions.²Estimated from data at ionic strength 0.7M and data for corresponding complexes of other divalent metal ions.³Estimated from data for equally charged Ag(I) complexes.

Table D-12.-Thermodynamic data for cobalt(II) species at 25° C

Reaction	Log K at ionic strength (M)				-Δ _f G° of underlined species kJ·mol ⁻¹	Additional references
	0.0	0.1	1.0	3.0		
$\text{Co}^{2+} + n\text{OH}^- = \underline{\text{Co}(\text{OH})_n}^{2-n}$, n = 1	4.3	N	4.0	4.0	237.6	
2	9.2	N	8.7	N	422.9	
3	10.5	N	9.9	N	587.6	
4	9.7	N	N	N	740.4	
$\underline{\text{CoO}}(\text{s}) + \text{H}_2\text{O} = \text{Co}^{2+} + 2\text{OH}^-$	-13.8	N	N	N	214.	
$\underline{\text{Co}(\text{OH})_2}(\text{cr}) = \text{Co}^{2+} + 2\text{OH}^-$	-15.7	N	N	N	460.0	
$\underline{\text{Co}(\text{OH})_2}(\text{am}) = \text{Co}^{2+} + 2\text{OH}^-$	-14.9	N	N	N	452.0	
$\text{Co}^{2+} + n\text{Cl}^- = \underline{\text{CoCl}_n}^{2-n}$, n = 1	1.3	N	.0	-.2	188.7	
$\underline{\text{CoS}}(\text{s}) + 2\text{H}^+ = \text{Co}^{2+} + \text{H}_2\text{S}$	-2.2	N	N	N	96.	
$\text{Co}^{2+} + n\text{SO}_4^{2-} = \underline{\text{Co}(\text{SO}_4)_n}^{2-2n}$, n = 1	2.3	N	.7	.2	813.4	
$\text{Co}^{2+} + n\text{NH}_3 = \underline{\text{Co}(\text{NH}_3)_n}^{2+}$, n = 1	22.0	2.1	N	N	93.7	
2	23.4	N	N	N	128.2	
3	24.3	N	N	N	159.8	
4	25.0	N	N	N	190.3	
5	24.9	N	N	N	216.3	
6	24.2	N	N	N	238.8	
$\text{Co}^{2+} + \text{HCO}_3^- = \underline{\text{Co}(\text{HCO}_3)}^+$	2.2	N	N	N	655.3	
$\text{Co}^{2+} + n\text{CO}_3^{2-} = \underline{\text{Co}(\text{CO}_3)_n}^{2-2n}$, n = 1	34.0	N	N	N	606.6	
n = 2	16.5	N	N	N	1,148.9	
$\underline{\text{CoCO}_3}(\text{s}) = \text{Co}^{2+} + \text{CO}_3^{2-}$	-10.0	N	N	N	640.9	

Table D-12.-Thermodynamic data for cobalt(II) species at 25° C-Continued

Reaction	Log K at ionic strength (<u>M</u>)			-Δ _f G° of underlined species kJ·mol ⁻¹	Additional references
	0.0	0.1	1.0	3.0	
Co ²⁺ + nNCS ⁻ = <u>Co(NCS)_n</u> ²⁻ⁿ , n = 1 2	1.7 12.2	1.4 2.0	1.0 1.3	-27.2 -117.0	
Co ²⁺ + nCN ⁻ = <u>Co(CN)_n</u> ²⁻ⁿ , n = 5	423.	N	23.0	-674.9	43
<u>Co(CN)₂(s)</u> = Co ²⁺ + 2CN ⁻	5-18.	N	N	-186.3	
2Co(CN) ₅ ³⁻ + H ₂ (g) = 2 <u>CoH(CN)₅</u> ³⁻	1.9	1.9	1.9	-664.1	44

N No data.

¹Estimated from data for corresponding complexes of other divalent metal ions.²Corrected to 25° C with enthalpy data estimated from data for corresponding Ni(II) and Cu(II) complexes.³Estimated from data at ionic strength 0.7M and data for corresponding complexes of other divalent metal ions.⁴Reaction of Co(II) aminopolycarbonxylate complexes with cyanide indicates log K >20 (reference 10).⁵Estimated from data for cyanides of other divalent metal ions.

Table D-13.-Thermodynamic data for cobalt(III) species at 25° C

Reaction	Log K at ionic strength (M)				-Δ _f G° of underlined species kJ·mol ⁻¹	Additional references
	0.0	0.1	1.0	3.0		
$\text{Co}^{3+} + \text{noH}^- = \underline{\text{Co}(\text{OH})_n^{3-n}}$, n = 1 2 3 4	¹ 13. ¹ 25. ¹ 34. ¹ 39.	N N N N	N N N N	13.5 N N N	105.9 331.7 540.4 726.2	
$2\text{Co}^{3+} + 2\text{OH}^- = \underline{\text{Co}_2(\text{OH})_2^{4+}}$	¹ 31.	N	N	N	240.3	
$\underline{\text{CoO}(\text{OH})}(\text{s}) + \text{H}_2\text{O} = \text{Co}^{3+} + 3\text{OH}^-$	-48.5	N	N	N	386.	45
$\underline{\text{Co}(\text{OH})_3}(\text{aged}) = \text{Co}^{3+} + 3\text{OH}^-$	¹ -46.	N	N	N	608.9	
$\underline{\text{Co}(\text{OH})_3}(\text{fresh}) = \text{Co}^{3+} + 3\text{OH}^-$	¹ -44.	N	N	N	597.5	
$\underline{\text{Co}_3\text{O}_4}(\text{s}) + 2\text{H}_2\text{O} = 2\text{CoO}(\text{OH}) (\text{s}) + \text{Co}^{2+} + 2\text{OH}^-$	-23.5	N	N	N	802.	
$\text{Co}^{3+} + \text{nCl}^- = \underline{\text{CoCl}_n^{3-n}}$, n = 1 2	¹ 2.1 ¹ 2.9	N N	N N	1.4 N	17.6 153.4	
$\text{Co}^{3+} + \text{nSO}_4^{2-} = \underline{\text{Co}(\text{SO}_4)_n^{3-2n}}$, n = 1 2	¹ 4.0 ¹ 5.4	N N	N N	N N	641.7 1,394.2	
$\text{Co}^{3+} + \text{nNH}_3 = \underline{\text{Co}(\text{NH}_3)_n^{3+}}$, n = 4cis 4tr 5 6	² 25.0 ² 23.4 ² 29.8 ² 34.	N N N N	N N N N	N N N N	123.1 114.0 177.0 227.5	46 46
$\text{Co}(\text{NH}_3)_4^{3+} + \text{H}_2\text{O} = \underline{\text{Co}(\text{NH}_3)_4(\text{OH})^{2+}} + \text{H}^+$ cis	³ -5.4	-5.7	⁴ -5.9	N	329.5	46, 47, 48, 49
trans	³ -4.3	N	⁴ -4.8	N	326.6	46, 48, 49
$\text{Co}(\text{NH}_3)_4(\text{OH})^{2+} + \text{H}_2\text{O} =$						
cis	³ -8.0	-8.0	⁴ -8.2	N	521.0	46, 47, 48, 49
trans	³ -8.1	N	⁴ -8.3	N	517.6	47, 49, 50

Table D-13.-Thermodynamic data for cobalt(III) species at 25° C-Continued

Reaction	Log K at ionic strength (M)				-Δ _f G° of underlined species kJ·mol ⁻¹	Additional references
	0.0	0.1	1.0	3.0		
$\text{Co}(\text{NH}_3)_5^{3+} + \text{H}_2\text{O} = \underline{\text{Co}(\text{NH}_3)_5(\text{OH})^{2+}} + \text{H}^+$	³ -6.0	-6.2	-6.5	N	380.0	50, 51
$\text{Co}^{3+} + n\text{CN}^- = \underline{\text{Co}(\text{CN})_n^{3-n}}, n = 5$	⁵ 62.	N	62.	N	-633.7	52
⁶ 73.		N	73.	N	-743.3	53
$\text{Co}(\text{CN})_5^{2-} + \text{H}_2\text{O} = \underline{\text{Co}(\text{CN})_5(\text{OH})^{3-}} + \text{H}^+$	⁷ -10.	N	-10.	N	-453.6	54, 55, 56
$\underline{\text{Co}_5(\text{CN})_{12}(\text{S})} = 3\text{Co}^{2+} + 2\text{Co}(\text{CN})_6^{3-}$	⁸ -20	N	N	N	-1 205.0	

N No data.

¹Estimated from data for corresponding complexes of other trivalent metal ions.²Estimated assuming near-zero ionic-strength dependence as for analogous complexes of divalent metal ions.³Estimated from ionic-strength dependence for hydrolysis reactions of metal ions with the same charges and similar sizes.⁴Estimated from data for related complexes in references 48, 49.⁵Calculated from reduction potential of -0.43 V given in reference 52, and log K for $\text{Co}(\text{CN})_5^{3-}$.⁶Estimated via enthalpies of reaction $\text{M}(\text{CN})_5^{2-} + \text{CN}^- = \text{M}(\text{CN})_6^{3-}$, M = Co, Cr, given in reference 53, and

log K for this reaction for M = Cr, assuming equal entropy changes.

⁷Estimated.⁸Estimated from data for divalent metal hexacyanoferrates(III).

Table D-14.-Thermodynamic data for iron(II) species at 25° C

Reaction	Log K at ionic strength (M)				-Δ _f G° of underlined species kJ·mol ⁻¹	Additional references
	0.0	0.1	1.0	3.0		
$\text{Fe}^{2+} + \text{nOH}^- = \underline{\text{Fe}(\text{OH})_n}^{2-n}, n = 1$	4.7	4.2	4.3	N	275.4	
2	7.4	N	N	N	448.1	
3	9.3	N	N	N	616.3	
4	8.9	N	N	N	771.3	
$\underline{\text{Fe}_{0.95}\text{O}(\text{s})} + 0.05\text{Fe}(\text{s}) + \text{H}_2\text{O} =$ $\text{Fe}^{2+} + 2\text{OH}^-$	-13.6	N	N	N	245.	
$\underline{\text{Fe}(\text{OH})_2(\text{cr})} = \text{Fe}^{2+} + 2\text{OH}^-$	-15.2	N	N	N	492.7	
$\underline{\text{Fe}(\text{OH})_2(\text{am})} = \text{Fe}^{2+} + 2\text{OH}^-$	-14.4	N	N	N	488.1	
$\text{Fe}^{2+} + \text{nCl}^- = \underline{\text{FeCl}_n}^{2-n}, n = 1$	1.2	N	-1.1	N	223.6	
$\underline{\text{FeS}(\text{s})} + 2\text{H}^+ = \text{Fe}^{2+} + \text{H}_2\text{S}$	3.3	N	N	N	100.	
$\text{Fe}^{2+} + \text{nSO}_4^{2-} = \underline{\text{Fe}(\text{SO}_4)_n}^{2-2n}, n = 1$	12.3	N	N	N	848.9	
$\text{Fe}^{2+} + \text{nNH}_3 = \underline{\text{Fe}(\text{NH}_3)_n}^{2+}, n = 1$	11.4	N	N	N	125.8	
2	12.2	N	N	N	156.9	
3	12.5	N	N	N	185.1	
4	12.5	N	N	N	211.6	
$\text{Fe}^{2+} + \text{HCO}_3^- = \underline{\text{Fe}(\text{HCO}_3)}^+$	11.7	N	N	N	687.9	
$\text{Fe}^{2+} + \text{nCO}_3^{2-} = \underline{\text{Fe}(\text{CO}_3)_n}^{2-2n}, n = 1$	13.7	N	N	N	640.4	
$n = 2$	15.7	N	N	N	1,179.8	
$\underline{\text{FeCO}_3(\text{s})} = \text{Fe}^{2+} + \text{CO}_3^{2-}$	-10.2	N	9.7	N	677.5	
$\text{Fe}^{2+} + \text{nNCS}^- = \underline{\text{Fe}(\text{NCS})_n}^{2-n}, n = 1$	1.3	N	N	0.8	6.0	

Table D-14.-Thermodynamic data for iron(II) species at 25° C-Continued

Reaction	Log K at ionic strength (M)				-Δ _f G° of underlined species kJ·mol ⁻¹	Additional references
	0.0	0.1	1.0	3.0		
$\text{Fe}^{2+} + n\text{CN}^- = \underline{\text{Fe}(\text{CN})_n^{2-n}}$, n = 5 6	² 27.4 35.4	N N	N N	N N	-614.3 -741.0	59, 60
$\underline{\text{Fe}(\text{CN})_2(\text{s})} = \text{Fe}^{2+} + 2\text{CN}^-$	³ -17.1	N	N	N	-155.9	
$\underline{\text{HFe}(\text{CN})_5^{2-}} = \text{Fe}(\text{CN})_5^{3-} + \text{H}^+$	⁴ -2.7	-2.7	N	N	-598.9	61, 62
$\text{Fe}(\text{CN})_5^{3-} + \text{H}_2\text{O} = \underline{\text{Fe}(\text{CN})_5(\text{OH})^{4-}} + \text{H}^+$	<-14.	N	N	N	N	59, 63
$\underline{\text{HFe}(\text{CN})_6^{3-}} = \text{Fe}(\text{CN})_6^{4-} + \text{H}^+$	-4.2	-3.2	N	-2.8	-717.1	64
$\underline{\text{H}_2\text{Fe}(\text{CN})_6^{2-}} = \text{HFe}(\text{CN})_6^{3-} + \text{H}^+$	-2.6	-1.2	N	-1.8	-702.2	64

N No data.

¹Estimated from data for corresponding complexes of other divalent metal ions.²Estimated. Data given for $\text{Fe}(\text{CN})_5^{3-} + \text{CN}^- = \text{Fe}(\text{CN})_6^{4-}$ in references 59, 60 at ionic strength 1.0M.³Derived from log K = -16 for $\text{Fe}_2\text{Fe}(\text{CN})_6(\text{s}) = 2\text{Fe}^{2+} + \text{Fe}(\text{CN})_6^{4-}$ estimated from data for other divalent metal hexacyanoferrates(II).⁴Estimated.

Table D-15.-Thermodynamic data for iron(III) species at 25° C

Reaction	Log K at ionic strength (M)				-Δ _f G° of underlined species kJ·mol ⁻¹	Additional references
	0.0	0.1	1.0	3.0		
$\text{Fe}^{3+} + n\text{OH}^- = \underline{\text{Fe}(\text{OH})_n^{3-n}}$, n = 1	11.8	11.3	11.1	11.2	241.7	57
2	22.3	N	22.0	22.1	458.9	57
3	¹ 30.3	N	N	N	661.9	57
4	34.4	N	N	N	842.6	57
$2\text{Fe}^{3+} + 2\text{OH}^- = \underline{\text{Fe}_2(\text{OH})_2^{4+}}$	25.1	24.7	25.0	25.4	491.9	57
$3\text{Fe}^{3+} + 4\text{OH}^- = \underline{\text{Fe}_3(\text{OH})_4^{5+}}$	49.7	N	46.4	51.0	963.9	57
$\underline{\text{Fe}_2\text{O}_3(\text{s})} + 3\text{H}_2\text{O} = 2\text{Fe}^{3+} + 6\text{OH}^-$	-83.4	N	N	N	742.	57
$\underline{\text{FeO}(\text{OH})(\text{goe})} + \text{H}_2\text{O} = \text{Fe}^{3+} + 3\text{OH}^-$	-41.7	N	N	N	490.	57
$\underline{\text{Fe}(\text{OH})_3(\text{aged})} = \text{Fe}^{3+} + 3\text{OH}^-$	-39.	N	N	N	711.5	57
$\underline{\text{Fe}(\text{OH})_3(\text{fresh})} = \text{Fe}^{3+} + 3\text{OH}^-$	-37.	N	N	N	700.1	57
$\underline{\text{Fe}_3\text{O}_4(\text{s})} + 2\text{H}_2\text{O} = 2\text{FeO}(\text{OH})(\text{goe}) + \text{Fe}^{2+} + 2\text{OH}^-$	-18.1	N	N	N	1,015.	
$\text{Fe}^{3+} + n\text{Cl}^- = \underline{\text{FeCl}_n^{3-n}}$, n = 1	1.5	N	.6	.8	156.8	
2	2.1	N	.7	N	291.4	
$\underline{\text{FeS}(\text{s})} + \text{FeS}_2(\text{s}) + 6\text{H}^+ = 2\text{Fe}^{3+} + 3\text{H}_2\text{S}$	-25.0	N	N	N	260.	
$\text{Fe}^{3+} + n\text{SO}_4^{2-} = \underline{\text{Fe}(\text{SO}_4)_n^{3-2n}}$, n = 1	4.0	N	2.0	1.9	784.3	
2	5.4	N	N	2.1	1,536.8	
$\text{Fe}^{3+} + n\text{NCS}^- = \underline{\text{Fe}(\text{NCS})_n^{3-n}}$, n = 1	3.0	2.4	2.1	2.2	-58.6	
2	3.6	3.6	3.3	3.7	-147.9	
$\text{Fe}^{3+} + n\text{CN}^- = \underline{\text{Fe}(\text{CN})_n^{3-n}}$, n = 5	² 34.8	N	N	N	-646.4	59, 65, 66
6	³ 42.3	N	N	N	-776.0	

Table D-15.-Thermodynamic data for iron(III) species at 25° C-Continued

Reaction	Log K at ionic strength (M)			$-\Delta_f G^\circ$ of underlined species kJ·mol ⁻¹	Additional references
	0.0	0.1	1.0	3.0	
$\text{Fe}(\text{CN})_5^{2-} + \text{H}_2\text{O} = \underline{\text{Fe}(\text{CN})_5(\text{OH})^{3-}} + \text{H}^+$	⁴ -8.	N	-8.4	N	59
$\text{Fe}^{3+} + \text{Fe}(\text{CN})_6^{3-} = \underline{\text{Fe}_2(\text{CN})_6}$	⁴ 3.	2.3	1.4	N	67
$\underline{\text{Fe}_5(\text{CN})_{12}} = 3\text{Fe}^{2+} + 2\text{Fe}(\text{CN})_6^{3-}$	⁴ -40.	N	N	N	
$\underline{\text{Fe}_7(\text{CN})_{18}} = 4\text{Fe}^{3+} + 3\text{Fe}(\text{CN})_6^{4-}$	-84.	N	N	N	68

N No data.

¹Estimated from data for corresponding complexes of other trivalent metal ions.²Calculated via estimated reduction potential of +0.33 V from data at ionic strength 1.0M in references 59, 65, 66, via ionic-strength dependence of reduction potential of $\text{Fe}(\text{CN})_6^{3-}$ (reference 10).³Calculated from standard reduction potential of +0.36 V and log K for $\text{Fe}(\text{CN})_6^{4-}$.⁴Estimated.

Table D-16.-Thermodynamic data for manganese(II) species at 25° C

Reaction	Log K at ionic strength (M)				-Δ _f G° of underlined species kJ·mol ⁻¹	Additional references
	0.0	0.1	1.0	3.0		
$\text{Mn}^{2+} + \text{nOH}^- = \underline{\text{Mn}(\text{OH})_n^{2-n}}$, n = 1 2 3 4	3.4 16. 18. 8.	2.9 N N N	3.0 N N N	N N N N	407.7 579.8 748.6 905.9	
$\underline{\text{MnO}}(\text{s}) + \text{H}_2\text{O} = \text{Mn}^{2+} + 2\text{OH}^-$	-9.6				363.	
$\underline{\text{Mn}(\text{OH})_2(\text{cr})} = \text{Mn}^{2+} + 2\text{OH}^-$	-12.8	N	N	N	618.7	
$\underline{\text{Mn}(\text{OH})_2(\text{am})} = \text{Mn}^{2+} + 2\text{OH}^-$	-12.8	N	N	N	618.7	
$\text{Mn}^{2+} + \text{nCl}^- = \underline{\text{MnCl}_n^{2-n}}$, n = 1	1.1	N	-2	N	362.8	
$\underline{\text{MnS}}(\text{s}) + 2\text{H}^+ = \text{Mn}^{2+} + \text{H}_2\text{S}$	7.0	N	N	N	219.	
$\text{Mn}^{2+} + \text{nSO}_4^{2-} = \underline{\text{Mn}(\text{SO}_4)_n^{2-2n}}$, n = 1	2.3	N	.6	0.6	988.6	
$\text{Mn}^{2+} + \text{nNH}_3 = \underline{\text{Mn}(\text{NH}_3)_n^{2+}}$, n = 1 2 3 4	2.9 21.3 21.3 2.8	N N N N	N N N N	N N N N	262.6 291.4 317.9 341.6	
$\text{Mn}^{2+} + \text{HCO}_3^- = \underline{\text{Mn}(\text{HCO}_3)_n^+}$	1.3	N	N	.5	825.3	
$\text{Mn}^{2+} + \text{nCO}_3^{2-} = \underline{\text{Mn}(\text{CO}_3)_n^{2-2n}}$, n = 1	13.5	N	N	N	779.0	71
$\underline{\text{MnCO}_3(\text{s})} = \text{Mn}^{2+} + \text{CO}_3^{2-}$	-10.6	N	N	N	819.5	70
$\text{Mn}^{2+} + \text{nNCS}^- = \underline{\text{Mn}(\text{NCS})_n^{2-n}}$, n = 1	1.2	N	.6	N	145.2	
$\text{Mn}^{2+} + \text{nCN}^- = \underline{\text{Mn}(\text{CN})_n^{2-n}}$, n = 6	310.	N	N	N	-746.3	43
$\underline{\text{Mn}(\text{CN})_2(\text{s})} = \text{Mn}^{2+} + 2\text{CN}^-$	4-8.7	N	N	N	-64.1	

N No data.

¹Estimated from data for corresponding complexes of other divalent metal ions.²Estimated from data at 20° C and ionic strength 2.0M with aid of data for corresponding complexes of other divalent metals.³Extrapolated from data for lower complexes in reference 43, considering known (reference 10) low stability of this complex. Reported reduction potential of $\text{Mn}(\text{CN})_6^{3-}$, -0.24 V, is open to question (reference 10).⁴Estimated from data for divalent metal hexacyanoferrates(II).

Table D-17.-Thermodynamic data for manganese(III) species at 25° C

Reaction	Log K at ionic strength (M)				-Δ _f G° of underlined species kJ·mol ⁻¹	Additional references
	0.0	0.1	1.0	3.0		
$\text{Mn}^{3+} + n\text{OH}^- = \underline{\text{Mn}(\text{OH})_n^{3-n}}$, n = 1 2 3 4	¹ 13. ¹ 24. ¹ 31. ¹ 35.	N N N N	N N N N	14.6 28.5 N N	312.9 533.0 730.2 910.4	
$2\text{Mn}^{3+} + 2\text{OH}^- = \underline{\text{Mn}_2(\text{OH})_2^{4+}}$	¹ 31.	N	N	N	654.3	
$\underline{\text{Mn}_2\text{O}_3(\text{s})} + 3\text{H}_2\text{O} = 2\text{Mn}^{3+} + 6\text{OH}^-$	-85.0	N	N	N	881.	
$\underline{\text{MnO}(\text{OH})}(\text{man}) + \text{H}_2\text{O} = \text{Mn}^{3+} + 3\text{OH}^-$	-42.2	N	N	N	557.	71
$\underline{\text{Mn}(\text{OH})_3(\text{aged})} = \text{Mn}^{3+} + 3\text{OH}^-$	¹ -40.	N	N	N	781.6	
$\underline{\text{Mn}(\text{OH})_3(\text{fresh})} = \text{Mn}^{3+} + 3\text{OH}^-$	¹ -38.	N	N	N	770.2	
$\underline{\text{Mn}_3\text{O}_4(\text{s})} + 2\text{H}_2\text{O} = 2\text{MnO}(\text{OH}) (\text{man}) + \text{Mn}^{2+} + 2\text{OH}^-$	-17.1	N	N	N	1,283.	
$2\text{MnO}(\text{OH}) (\text{man}) = \underline{\text{MnO}_2(\text{pyr})} + \text{Mn}^{2+} + 2\text{OH}^-$	-18.1	N	N	N	465.	
$2\text{MnO}(\text{OH}) (\text{man}) = \underline{\text{MnO}_2(\text{ppt})} + \text{Mn}^{2+} + 2\text{OH}^-$	-19.8	N	N	N	455.3	71
$\text{Mn}^{3+} + \text{nCl}^- = \underline{\text{MnCl}_n^{3-n}}$, n = 1 2	¹ 1.8 ¹ 2.5	N N	N N	1.1 N	222.9 358.1	
$\underline{\text{MnS}(\text{s})} + \text{MnS}_2(\text{s}) + 6\text{H}^+ = 2\text{Mn}^{3+} + 3\text{H}_2\text{S}$	34.7	N	N	N	444.	
$\text{Mn}^{3+} + \text{nSO}_4^{2-} = \underline{\text{Mn}(\text{SO}_4)_n^{3-2n}}$, n = 1 2	¹ 4.0 ¹ 5.4	N N	N N	N N	848.7 1,601.2	
$\text{Mn}^{3+} + \text{nCN}^- = \underline{\text{Mn}(\text{CN})_n^{3-n}}$, n = 5 6	² 34. ³ 35.	N N	N N	N N	-586.5 -753.2	72

Table D-17.-Thermodynamic data for manganese(III) species at 25° C-Continued

Reaction	Log K at ionic strength (M)			-Δ _f G° of underlined species kJ·mol ⁻¹	Additional references
	0.0	0.1	1.0	3.0	
$\text{Mn}(\text{CN})_5^{2-} + \text{H}_2\text{O} = \underline{\text{Mn}(\text{CN})_5(\text{OH})^{3-}} + \text{H}^+$	¹ -9.	N	N	-400.7	
$\underline{\text{Mn}_2(\text{CN})_6(\text{s})} = 2\text{Mn}^{3+} + 6\text{CN}^-$	⁴ -43.	N	N	-626.2	
$\underline{\text{Mn}_3(\text{CN})_{12}(\text{s})} = 3\text{Mn}^{2+} + 2\text{Mn}(\text{CN})_6^{3-}$	⁵ -20.	N	N	-699.2	
$2\text{Mn}(\text{CN})_6^{3-} + 6\text{H}^+ = \underline{\text{Mn}(\text{CN})_6^{2-}} + \text{Mn}_2^{2+} + 6\text{HCN}$	>0.	N	N	⁶ -900.	73, 74

N No data.

¹Estimated from data for corresponding complexes of other trivalent metal ions.²Estimated, based on observed synthesis of solid derivatives (reference 10).³Estimated as in reference 10 with log K = -40 for solubility of Mn(OH)₃ precipitate.⁴Estimated from observed insolubility (reference 73) via log K = -8 for Mn₂(CN)₆³⁺ + Mn(CN)₆³⁻.⁵Estimated from data for divalent metal hexacyanoferrates(III).⁶Rough estimate from occurrence of stated reaction and observed decomposition of K₂Mn(CN)₆ in water (reference 10).

Table D-18.-Thermodynamic data for chromium(III) species at 25° C

Reaction	Log K at ionic strength (M)				-Δ _f G° of underlined species kJ·mol ⁻¹	Additional references
	0.0	0.1	1.0	3.0		
$\text{Cr}^{3+} + n\text{OH}^- = \underline{\text{Cr}(\text{OH})_n^{3-n}}$, n = 1	10.0	9.8	9.5	N	440.4	77
2	118.	17.3	21.5	N	643.3	77
3	125.	N	N	N	840.6	
4	130.	N	N	N	1,026.4	
$2\text{Cr}^{3+} + 2\text{OH}^- = \underline{\text{Cr}_2(\text{OH})_2^{4+}}$	122.6	N	22.4	N	895.6	77
$3\text{Cr}^{3+} + 4\text{OH}^- = \underline{\text{Cr}_3(\text{OH})_4^{5+}}$	147	N	46.4	N	1,575.5	77
$\underline{\text{Cr}_2\text{O}_3(\text{s})} + 3\text{H}_2\text{O} = 2\text{Cr}^{3+} + 6\text{OH}^-$	-65.6	N	N	N	1,059.	
$\underline{\text{CrO}(\text{OH})(\text{s})} + \text{H}_2\text{O} = \text{Cr}^{3+} + 3\text{OH}^-$	1-34.	N	N	N	654.8	
$\underline{\text{Cr}(\text{OH})_3(\text{aged})} = \text{Cr}^{3+} + 3\text{OH}^-$	1-32.	N	N	N	880.6	
$\underline{\text{Cr}(\text{OH})_3(\text{fresh})} = \text{Cr}^{3+} + 3\text{OH}^-$	-30.	N	N	N	869.1	
$\text{Cr}^{3+} + \text{nCl}^- = \underline{\text{CrCl}_n^{3-n}}$, n = 1	1.5	N	-5	-0.2	360.1	
2	1.6	N	N	N	491.8	
$\underline{\text{Cr}_2\text{S}_3(\text{s})} + 6\text{H}^+ = 2\text{Cr}^{3+} + 3\text{H}_2\text{S}$	33.7	N	N	N	343.	
$\text{Cr}^{3+} + \text{nSO}_4^{2-} = \underline{\text{Cr}(\text{SO}_4)_n^{3-2n}}$, n = 1	14.0	N	N	N	993.3	
2	15.4	N	N	N	1,745.8	
$\text{Cr}^{3+} + \text{nNH}_3 = \underline{\text{Cr}(\text{NH}_3)_n^{3+}}$, n = 3fac	27.8	N	N	N	350.0	
3mer	27.2	N	N	N	346.6	
4cis	39.5	N	N	N	386.2	
4tr	38.6	N	N	N	381.1	
5	310.8	N	N	N	420.1	
6	312.	N	N	N	453.5	
$\text{Cr}(\text{NH}_3)_3^{3+} + \text{H}_2\text{O} = \underline{\text{Cr}(\text{NH}_3)_3(\text{OH})^{2+}}$	4-4.5	N	-5.0	N	561.5	78
+ H ⁺	4-4.0	N	-4.5	N	561.0	78
fac						
mer						

Table D-18.--Thermodynamic data for chromium(III) species at 25° C--Continued

Reaction	Log K at ionic strength (M)			-Δ _f G° of underlined species kJ.mol ⁻¹	Additional references
	0.0	0.1	1.0	3.0	
$\text{Cr}(\text{NH}_3)_3(\text{OH})^{2+} + \text{H}_2\text{O} =$					
$\text{Cr}(\text{NH}_3)_3(\text{OH})_2^+ + \text{H}^+$					
fac	4-7.1	N	-7.3	758.2	78
mer	4-6.9	N	-7.1	758.8	78
$\text{Cr}(\text{NH}_3)_3(\text{OH})_2^+ + \text{H}_2\text{O} =$					
fac	4-9.3	N	-9.3	942.3	78
mer	4-9.2	N	-9.2	943.5	78
$\text{Cr}(\text{NH}_3)_4^{3+} + \text{H}_2\text{O} = \text{Cr}(\text{NH}_3)_3(\text{OH})^{2+} + \text{H}^+$					
cis	4-4.5	N	-5.0	597.7	78
trans	4-3.9	N	-4.4	596.0	78
$\text{Cr}(\text{NH}_3)_4(\text{OH})^{2+} + \text{H}_2\text{O} =$					
cis	4-7.3	N	-7.5	793.3	78
trans	4-7.6	N	-7.8	789.8	78
$\text{Cr}(\text{NH}_3)_5^{3+} + \text{H}_2\text{O} = \text{Cr}(\text{NH}_3)_3(\text{OH})^{2+} + \text{H}^+$					
	4-4.7	-5.1	-5.2	630.5	50, 78
$\text{Cr}^{3+} + \text{nNCS}^- = \text{Cr}(\text{NCS})_n^{3-n}, n = 1, 2$					
	3.1	N	N	151.0	
	13.6	N	N	61.1	
$\text{Cr}^{3+} + \text{nCN}^- = \text{Cr}(\text{CN})_n^{3-n}, n = 5, 6$					
	528.	N	29.1	-476.2	53
	533.	N	34.	-620.0	
$\text{Cr}(\text{CN})_5^{2-} + \text{H}_2\text{O} = \text{Cr}(\text{CN})_5(\text{OH})^{3-} + \text{H}^+$					
	5-9.	-8.8	-9.0	-290.3	79

N No data.

¹Estimated from data for corresponding complexes of other trivalent metal ions.²Estimated from data for tetrammine and pentammine complexes and trends in formation log K values for other metal ammine complexes.³Estimated from data at ionic strength 4.5 M assuming near-zero ionic strength dependence; compare data for NH₃ complexes of divalent metal ions.⁴Estimated from ionic-strength dependence of hydrolysis reactions of metal ions having the same charges and similar sizes.⁵Estimated.

Table D-19.--Thermodynamic data for thallium(I) species at 25° C

Reaction	Log K at ionic strength (<u>M</u>)				-Δ _f G° of underlined species kJ·mol ⁻¹	Additional references
	0.0	0.1	1.0	3.0		
$\text{Tl}^+ + \text{NOH}^- = \underline{\text{Tl}(\text{OH})_n}^{1-n}$, $n = 1$	0.8	N	0.3	0.1	193.5	
$\text{Tl}^+ + n\text{Cl}^- = \underline{\text{TlCl}_n}^{1-n}$, $n = 1$ 2	.5 .0	N N	.0 -.1	-.1 -1.0	165.7 294.0	
$\underline{\text{TlCl}} = \text{Tl}^+ + \text{Cl}^-$	-3.8	N	-3.2	-3.1	184.9	80
$\underline{\text{Tl}_2\text{S}(\text{s})} + 2\text{H}^+ = 2\text{Tl}^+ + \text{H}_2\text{S}$	-.4	N	-.7	N	93.	
$\text{Tl}^+ + n\text{SH}^- = \underline{\text{Tl}(\text{SH})_n}^{1-n}$, $n = 1$	¹ 5.3	N	2.3	N	49.6	
$2\text{Tl}^+ + n\text{SH}^- = \underline{\text{Tl}_2(\text{SH})_n}^{2-n}$, $n = 1$	¹ 6.6	N	5.8	N	88.6	
$2\text{Tl}^+ + 2\text{SH}^- + 2\text{OH}^- = \underline{\text{Tl}_2\text{O}(\text{SH})_2}^{2-}$ + H_2O	¹ 18.0	N	16.7	N	276.6	
$2\text{Tl}^+ + 3\text{SH}^- + \text{OH}^- = \underline{\text{Tl}_2\text{S}(\text{SH})_2}^{2-} + \text{H}_2\text{O}$	¹ 16.3	N	15.0	N	455.9	
$\text{Tl}^+ + n\text{S}_2\text{O}_3^{2-} = \underline{\text{Tl}(\text{S}_2\text{O}_3)_n}^{1-2n}$, $n = 1$ 2	¹ 2.3 ¹ 2.8	N N	1.6 1.9	N N	567.2 1,092.6	
$\text{Tl}^+ + \text{SO}_4^{2-} = \underline{\text{Tl}(\text{SO}_4)}^{1-}$	1.4	N	.4	-.1	784.1	
$\text{Tl}^+ + n\text{NCS}^- = \underline{\text{Tl}(\text{NCS})_n}^{1-n}$, $n = 1$ 2	.6 ¹ 0.0	N N	.2 0.0	.1 -.1	-57.7 -153.8	
$\underline{\text{TlNCS}} = \text{Tl}^+ + \text{NCS}^-$	-3.8	N	N	-3.2	-39.4	

N No data.

¹Estimated from ionic-strength dependence of log K for corresponding Cu and Ag complexes.

Table D-20.--Thermodynamic data for thallium(III) species at 25° C

Reaction	Log K at ionic strength (M)				-Δ _f G° of underlined species kJ·mol ⁻¹	Additional references
	0.0	0.1	1.0	3.0		
$\text{Tl}^{3+} + \text{nOH}^- = \underline{\text{Tl}(\text{OH})_n^{3-n}}, n = 1$	13.4	12.8	12.7	13.1	18.8	
2	26.6	25.2	25.4	25.8	251.4	
3	38.7	37.5	N	N	477.8	
4	41.0	N	N	39.4	648.2	
$\underline{\text{Tl}_2\text{O}_3(\text{s})} + 3\text{H}_2\text{O} = 2\text{Tl}^{3+} + 6\text{OH}^-$	-89.4	N	N	-90.0	312.	
$\text{Tl}^{3+} + \text{nCl}^- = \underline{\text{TlCl}_n^{3-n}}, n = 1$	7.7	N	N	7.1	-39.8	
2	13.5	N	N	12.5	124.5	
3	16.5	N	N	15.8	272.8	
4	18.3	N	N	18.0	414.3	
$\text{TlCl}^{2+} + \text{H}_2\text{O} = \underline{\text{TlCl}(\text{OH})^{2+}} + \text{H}^+$	12.	N	N	1.9	185.9	
$\text{Tl}^{3+} + \text{nSO}_4^{2-} = \underline{\text{Tl}(\text{SO}_4)_n^{3-2n}}, n = 1$	24.7	N	N	2.3	556.3	
2	26.3	N	N	N	1,310.0	
$\text{Tl}^{3+} + \text{nCN}^- = \underline{\text{Tl}(\text{CN})_n^{3-n}}, n = 1$	313.	N	N	413.2	-313.2	81
2	326.	N	N	426.5	-411.4	81
3	334.	N	N	435.2	-538.1	81
4	340.	N	N	442.6	-676.3	81

N No data.

¹Estimated by comparison with data for analogous Hg(II) complexes.²Estimated from data for corresponding rare earth, Fe, and In complexes.³Estimated assuming same ionic-strength dependence as for corresponding halide complexes.⁴Ionic strength 4.0M.

Table D-21.-Thermodynamic data for lead(II) species at 25° C

Reaction	Log K at ionic strength (M)				-Δ _f G° of underlined species kJ·mol ⁻¹	Additional references
	0.0	0.1	1.0	3.0		
$\text{Pb}^{2+} + n\text{OH}^- = \underline{\text{Pb}(\text{OH})_n^{2-n}}$, n = 1 2 3	6.4 10.9 13.9	6.0 N N	N N N	6.3 10.9 13.7	217.8 400.8 575.2	
$2\text{Pb}^{2+} + \text{OH}^- = \underline{\text{Pb}_2(\text{OH})^{3+}}$	7.6	N	N	7.8	248.7	
$3\text{Pb}^{2+} + 4\text{OH}^- = \underline{\text{Pb}_3(\text{OH})_4^{2+}}$	32.1	N	N	34.0	884.4	
$4\text{Pb}^{2+} + 4\text{OH}^- = \underline{\text{Pb}_4(\text{OH})_4^{4+}}$	36.0	N	N	37.5	930.7	
$6\text{Pb}^{2+} + 8\text{OH}^- = \underline{\text{Pb}_6(\text{OH})_8^{4+}}$	68.4	N	N	71.3	1,792.8	
$\text{PbO}(\text{tetr}) + \text{H}_2\text{O} = \text{Pb}^{2+} + 2\text{OH}^-$	-15.3	N	N	N	188.9	
$\text{PbO}(\text{orth}) + \text{H}_2\text{O} = \text{Pb}^{2+} + 2\text{OH}^-$	-15.2	N	N	N	187.9	
$\text{Pb}(\text{OH})_2(\text{am}) = \text{Pb}^{2+} + 2\text{OH}^-$	-14.9	N	N	N	423.6	
$\text{Pb}^{2+} + n\text{Cl}^- = \underline{\text{PbCl}_n^{2-n}}$, n = 1 2 3 4	1.6 2.2 1.8 1.1	N N N N	0.9 1.2 1.1 N	1.1 1.6 1.9 1.0	164.3 299.0 427.9 555.1	
$\underline{\text{PbCl}_2(\text{s})} = \text{Pb}^{2+} + 2\text{Cl}^-$	-4.8	N	N	-5.0	314.1	82
$\underline{\text{Pb}(\text{OH})\text{Cl}(\text{s})} = \text{Pb}^{2+} + \text{OH}^- + \text{Cl}^-$	-13.4	N	N	N	389.0	
$\underline{\text{Pb}_2(\text{OH})_3\text{Cl}(\text{s})} = 2\text{Pb}^{2+} + 3\text{OH}^- + \text{Cl}^-$	-16.9	N	N	N	747.6	83
$\underline{\text{PbS}(\text{s})} + 2\text{H}^+ = \text{Pb}^{2+} + \text{H}_2\text{S}$	-7.9	N	N	N	97.	
$\text{Pb}^{2+} + n\text{S}_2\text{O}_3^{2-} = \underline{\text{Pb}(\text{S}_2\text{O}_3)_n^{2-2n}}$, n = 1 2	3.6 6.5	N N	N N	2.4 4.9	567.0 1,106.1	
$\underline{\text{Pb}(\text{S}_2\text{O}_3)_1(\text{s})} = \text{Pb}^{2+} + \text{S}_2\text{O}_3^{2-}$	-8.3	N	N	N	594.5	
$\text{Pb}^{2+} + n\text{SO}_4^{2-} = \underline{\text{Pb}(\text{SO}_4)_n^{2-2n}}$, n = 1	2.7	2.1	N	N	783.9	
$\underline{\text{PbSO}_4(\text{s})} = \text{Pb}^{2+} + \text{SO}_4^{2-}$	7.8	7.0	6.2	N	813.0	84

Table D-21.-Thermodynamic data for lead(II) species at 25° C-Continued

Reaction	Log K at ionic strength (M)				-Δ _f G° of underlined species kJ·mol ⁻¹	Additional references
	0.0	0.1	1.0	3.0		
$\frac{\text{Pb}_2\text{O}(\text{SO}_4)(\text{s})}{2\text{OH}^- + \text{SO}_4^{2-}} + \text{H}_2\text{O} = 2\text{Pb}^{2+}$	-27.0	N	N	N	1,024.	84
$\frac{\text{Pb}_3\text{O}_2(\text{SO}_4)(\text{s})}{+ 4\text{OH}^- + \text{SO}_4^{2-}} + 2\text{H}_2\text{O} = 3\text{Pb}^{2+}$	-41.8	N	N	N	1,210.	84
$\frac{\text{Pb}_5\text{O}_4(\text{SO}_4)(\text{s})}{+ 8\text{OH}^- + \text{SO}_4^{2-}} + 4\text{H}_2\text{O} = 5\text{Pb}^{2+}$	-75.5	N	N	N	1,605.	84
$\text{Pb}^{2+} + \text{HCO}_3^- = \underline{\text{Pb}(\text{HCO}_3)^+}$	13.	N	N	N	628.0	
$\text{Pb}^{2+} + n\text{CO}_3^{2-} = \underline{\text{Pb}(\text{CO}_3)_n^{2-2n}}$, n = 1 n = 2	26. 29.	N N	N N	N N	586.2 1,131.4	
$\text{PbCO}_3(\text{s}) = \text{Pb}^{2+} + \text{CO}_3^{2-}$	-12.0	N	N	-11.2	674.1	
$\frac{\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2(\text{s})}{3\text{Pb}^{2+} + 2\text{OH}^- + 2\text{CO}_3^{2-}} =$	-47.	-46.	N	N	1,710.9	85
$\frac{\text{Pb}_{10}\text{O}(\text{OH})_6(\text{CO}_3)_6(\text{s})}{10\text{Pb}^{2+} + 8\text{OH}^- + 6\text{CO}_3^{2-}} + \text{H}_2\text{O} =$	-120.8	N	N	N	5,118.7	84
$\text{Pb}^{2+} + n\text{NCS}^- = \underline{\text{Pb}(\text{NCS})_n^{2-n}}$, n = 1 2 3	1.2 1.5 1.2	N N N	N N N	.8 1.0 1.0	-61.9 -152.8 -247.3	

N No data.

¹Estimated from data for corresponding complexes of other divalent metal ions.²Estimated from data at ionic strength 0.3M and data for corresponding complexes of other divalent metal ions.

Table D-22.--Thermodynamic data for magnesium(II) species at 25° C

Reaction	Log K at ionic strength (M)				-Δ _f G° of underlined species kJ·mol ⁻¹	Additional references
	0.0	0.1	1.0	3.0		
$\text{Mg}^{2+} + \text{NOH}^- = \underline{\text{Mg}(\text{OH})_n^{2-n}}, n = 1$	2.8	N	N	2.2	629.3	
$\underline{\text{Mg}(\text{OH})_2(\text{cr})} = \text{Mg}^{2+} + 2\text{OH}^-$	-11.1	N	N	-11.1	834.0	
$\underline{\text{Mg}(\text{OH})_2(\text{am})} = \text{Mg}^{2+} + 2\text{OH}^-$	-9.3	N	N	N	823.7	
$\text{Mg}^{2+} + n\text{SO}_4^{2-} = \underline{\text{Mg}(\text{SO}_4)_n^{2-2n}}, n = 1$	2.2	1.5	0.8	N	1,213.1	
$\underline{\text{MgCO}_3(\text{s})} = \text{Mg}^{2+} + \text{CO}_3^{2-}$	-7.5	N	N	N	1,026.8	
$\underline{\text{MgCO}_3 \cdot 3\text{H}_2\text{O}(\text{s})} = \text{Mg}^{2+} + \text{CO}_3^{2-} + 3\text{H}_2\text{O}$	-4.7	N	N	N	1,722.4	
$\underline{\text{MgCO}_3 \cdot 5\text{H}_2\text{O}(\text{s})} = \text{Mg}^{2+} + \text{CO}_3^{2-} + 5\text{H}_2\text{O}$	-4.5	N	N	N	2,195.7	
$\text{Mg}^{2+} + \text{CO}_3^{2-} = \underline{\text{Mg}(\text{CO}_3)_1}$	2.9	N	N	1.7	1,000.6	
$\text{Mg}^{2+} + \text{HCO}_3^- = \underline{\text{Mg}(\text{HCO}_3)_1^+}$	1.0	N	N	0.1	1,048.6	

N No data.

Table D-23.-Thermodynamic data for calcium(II) species at 25° C

Reaction	Log K at ionic strength (M)				-Δ _f G° of underlined species kJ·mol ⁻¹	Additional references
	0.0	0.1	1.0	3.0		
$\text{Ca}^{2+} + \text{NOH}^- = \underline{\text{Ca}(\text{OH})_n^{2-n}}$, n = 1	1.3	1.0	N	0.7	717.8	
$\text{Ca}(\text{OH})_2(\text{cr}) = \text{Ca}^{2+} + 2\text{OH}^-$	-5.2	N	N	N	897.4	
$\underline{\text{CaSO}_4(\text{s})} = \text{Ca}^{2+} + \text{SO}_4^{2-}$	-4.4	N	N	N	1,321.7	
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}(\text{s}) = \text{Ca}^{2+} + \text{SO}_4^{2-} + 2\text{H}_2\text{O}$	-4.6	N	2.9	3.2	1,798.3	
$\text{Ca}^{2+} + \text{nSO}_4^{2-} = \underline{\text{Ca}(\text{SO}_4)_n^{2-2n}}$, n = 1	2.3	1.5	1.0	N	1,310.7	
$\underline{\text{CaCO}_3(\text{s,cal})} = \text{Ca}^{2+} + \text{CO}_3^{2-}$	-8.5	N	N	N	1,129.6	
$\underline{\text{CaCO}_3(\text{s,ara})} = \text{Ca}^{2+} + \text{CO}_3^{2-}$	-8.3	N	N	N	1,128.5	
$\underline{\text{CaCO}_3(\text{s,vat})} = \text{Ca}^{2+} + \text{CO}_3^{2-}$	-7.9	N	N	N	1,126.2	
$\underline{\text{CaCO}_3 \cdot \text{H}_2\text{O}(\text{s})} = \text{Ca}^{2+} + \text{CO}_3^{2-} + \text{H}_2\text{O}$	-7.6	N	N	N	1,361.7	
$\text{Ca}^{2+} + \text{CO}_3^{2-} = \underline{\text{Ca}(\text{CO}_3)}$	3.2	N	N	N	1,099.4	
$\text{Ca}^{2+} + \text{HCO}_3^- = \underline{\text{Ca}(\text{HCO}_3)^+}$	1.3	N	N	N	1,147.4	

N No data.

Table D-24.-Thermodynamic data for gallium(III)
and indium(III) species at 25° C

(Values for CN⁻ species are estimated)

Reaction	Log K, 25° C, zero ionic strength	
	Ga	In
$M^{3+} + nOH^- = M(OH)_n^{3-n}, n = 1$	11.6	10.1
2	21.8	20.2
3	31.7	29.5
4	39.4	33.8
$M(OH)_3(am) = M^{3+} + 3OH^-$	37.	N
$M(OH)_3(cr) = M^{3+} + 3OH^-$	N	36.9
$MO(OH)(cr) + H_2O = M^{3+} + 3OH^-$	39.1	N
$M^{3+} + nCN^- = M(CN)_n^{3-n}, n = 1$	4.	4.
2	8.	8.
3	11.	11.
4	14.	13.

N No data.

Table D-25.-Standard Gibbs free energies of
formation of heavy-metal selenides at 25° C

Compound	$-\Delta_f G^\circ$ kJ·mol ⁻¹	Additional references
ZnSe	174	87
CdSe	141	88
HgSe	38	89
Cu ₂ Se	71	90
CuSe	45	98
Ag ₂ Se	51	
AuSe	10	
NiSe	76	91
NiSe ₂	112	91
PbSe	99	92

APPENDIX E.—EQUILIBRIUM PREDOMINANCE AREA DIAGRAMS

This appendix contains a compilation of equilibrium predominance area diagrams (EPAD). Information on their construction, capabilities, limitations, and use is given in chapters 4 and 11. The diagrams presented here were selected for usefulness in precious metals processing and mine closure operations. All of the diagrams are drawn for a temperature of 25° C and a pressure of 100 kPa (1 bar).

Diagrams are included for free cyanide and carbonate (figures E-1 and E-2), which show selected partial-pressure isobars for HCN and CO₂, respectively. The Eh-pH diagram for NCO⁻/CN⁻ is also included (figure E-3).

A few selected Eh-pH diagrams for sulfur and selenium in the absence and presence of cyanide (figures E-4 through E-9) are included, and they show the conditions under which SCN⁻ and SeCN⁻ are expected to be stable.

The diagrams for the metal systems compiled in this appendix are summarized in table E-1. As shown in table E-1, pM-pH and pCN-pH diagrams are listed for different values of pCN and pM, respectively. For reference, pCN = 5.0 = 0.26 ppm CN⁻, and pM = 5.0 = 0.65 ppm Zn, 1.12 ppm Cd, 2.01 ppm Hg, 0.64 ppm Cu, 1.08 ppm Ag, 1.97 ppm Au, 0.59 ppm Ni, or 0.56 ppm Fe. The pCN-pH diagrams for solution species show only the predominant solution species regardless of the presence of solid phases. A number of pM-pH and pCN-pH diagrams for selected concentrations of auxiliary species that may exist in process or waste solutions, namely Cl⁻, SCN⁻, S₂O₃²⁻, CO₃²⁻, and [Fe(CN)₆]⁴⁻, are also provided. Also included are pM-pCN

diagrams for selected pH values ranging from 7 to 12. These, along with the pM-pH and pCN-pH diagrams, form the three sets of sections through the pM-pH-pCN composition volume. Some Eh-pH diagrams for pCN = 2.0 and pM = 2.0 are provided; these are compositions typical for precious metals cementation or electrowinning from the pregnant solutions.

No diagrams are given for Cu(II) with CN⁻ because Cu(II) is rapidly reduced to Cu(I) cyanide species by CN⁻.

The cyanide chemistry of iron is dominated by the kinetically inert Fe(CN)₆^{q-} (q = 3 or 4), so most of the EPAD one might generate for iron would be of limited use at best. For both Fe(II) and Fe(III), pM-pH diagrams with no ligands and with p[Fe(CN)₆⁴⁻] = 4.0 are provided, as is done for several other metal ions. A pM-pH diagram with pCO₃ = 3.0 is provided for Fe(II), analogous to corresponding diagrams for other divalent metal ions.

Diagrams are not provided for cobalt or chromium because the cyanide chemistry of those metals is kinetically controlled, and EPAD would be of limited, if not misleading, significance. As described in chapter 8, Co(II) in the presence of CN⁻ is very easily oxidized by O₂ to the very inert Co(CN)₆³⁻.

Diagrams are not provided for manganese because manganese is of minor importance in cyanide operations, the cyanide complexes of manganese are not very stable, and the data for the manganese cyanide complexes are not known accurately.

Table E-1.-Compilation of equilibrium predominance area diagrams in this appendix¹

Variables in diagram	Zn 2+	Cd 2+	Hg 2+	Cu 1+	Cu 2+	Ag 1+	Au 1+	Ni 2+
pH-pM, no ligands	y	y	² n	² n	y	² n	² n	y
pH-pM, pCO ₃ = 3.0	y	y	³ n	³ n	y	³ n	³ n	y
pH-pM, pCN = 2.0, 3.0, 4.0, 5.0	y	y	y	y	⁴ n	y	y	y
pH-pM, pCN = 2.0, pSH = 6.0	y	y	y	y	⁴ n	y	² n	y
pH-pM, pCN = 5.0, pCO ₃ = 3.0	y	y	³ n	³ n	⁴ n	³ n	³ n	y
pH-pM, pCN = 5.0, pCl = 3.0	³ n	³ n	y	³ n	⁴ n	y	³ n	³ n
pH-pM, pCN = 5.0, pSCN = 4.0	³ n	³ n	y	y	⁴ n	y	y	³ n
pH-pM, pCN = 5.0, pS ₂ O ₃ = 4.0	³ n	³ n	y	y	⁴ n	y	y	³ n
pH-pM, pCN = 5.0, p[Fe(CN) ₆ ⁴⁻] = 4.0	y	y	⁵ n	⁵ n	y	⁵ n	⁵ n	y
pCN-pH, solution species only	y	y	y	y	⁴ n	y	y	y
pCN-pH, pM = 2.0, 3.0, 4.0, 5.0	y	y	⁶ y	y	⁴ n	y	y	y
pCN-pH, pM = 4.0, p[Fe(CN) ₆ ⁴⁻] = 4.0	y	y	⁵ n	⁵ n	⁴ n	⁵ n	⁵ n	y
pCN-pH, pCl = 3.0, solution species only	³ n	³ n	y	³ n	⁴ n	y	y	³ n
pCN-pH, pSCN = 4.0, solution species only	³ n	³ n	y	y	⁴ n	y	y	³ n
pCN-pH, pS ₂ O ₃ = 4.0, solution species only	³ n	³ n	y	y	⁴ n	y	y	³ n
pM-pCN, pH = 12.0, 11.0, 10.0, 9.0, 8.0, 7.0	y	y	y	y	⁴ n	⁷ y	⁷ y	y
Eh-pH, pM = 2.0, pCN = 2.0	y	y	y	⁸ n	y	y	y	y

¹y = diagram included, n = diagram not included.²Diagram is of no practical importance.³Species containing auxiliary ligand do not appear in diagram.⁴Redox reactions occur.⁵Uncomplexed metal cation and [Fe(CN)₆]⁴⁻ are unstable with respect to removal of CN⁻ from [Fe(CN)₆]⁴⁻ by the metal cation.⁶Diagrams for pHg = 4.0 and 5.0 are the same as the diagram for solution species only.⁷Diagrams for pH 12.0 and 10.0 are the same as the diagram for pH 11.0.⁸See the diagram for Cu(II).

Figure E-1

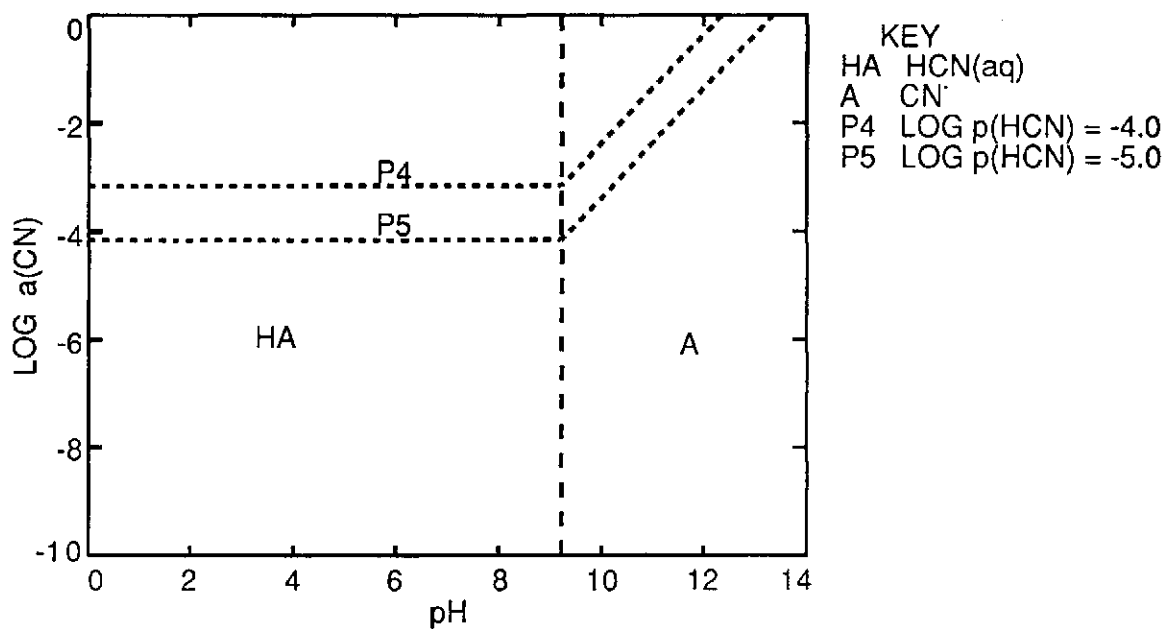
*pL-pH diagram for free cyanide.*

Figure E-2

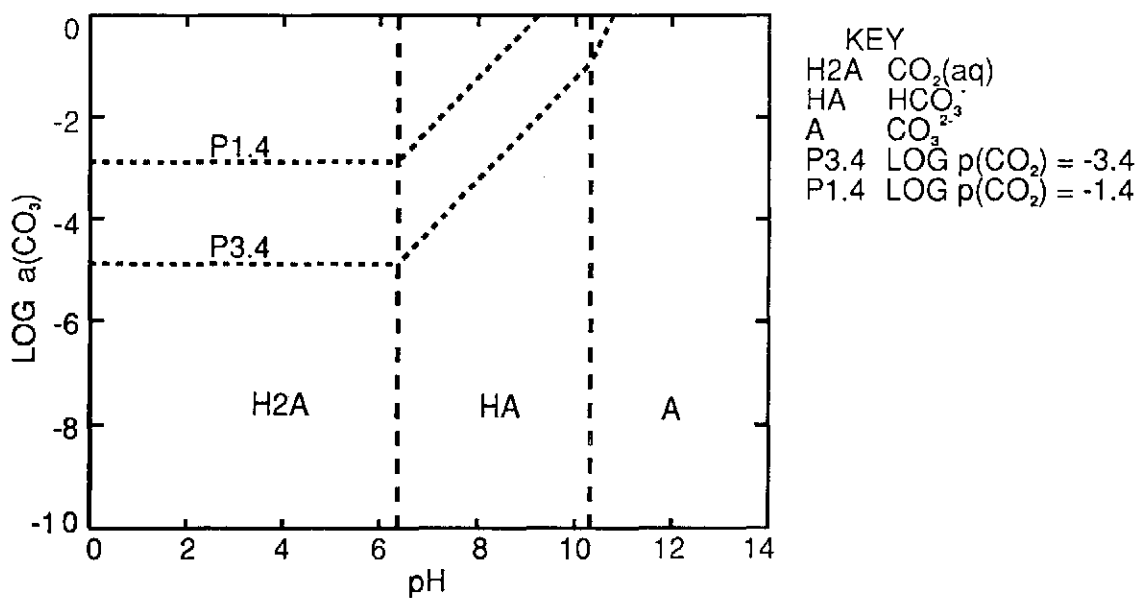
*pL-pH diagram for free carbonic acid.*

Figure E-3

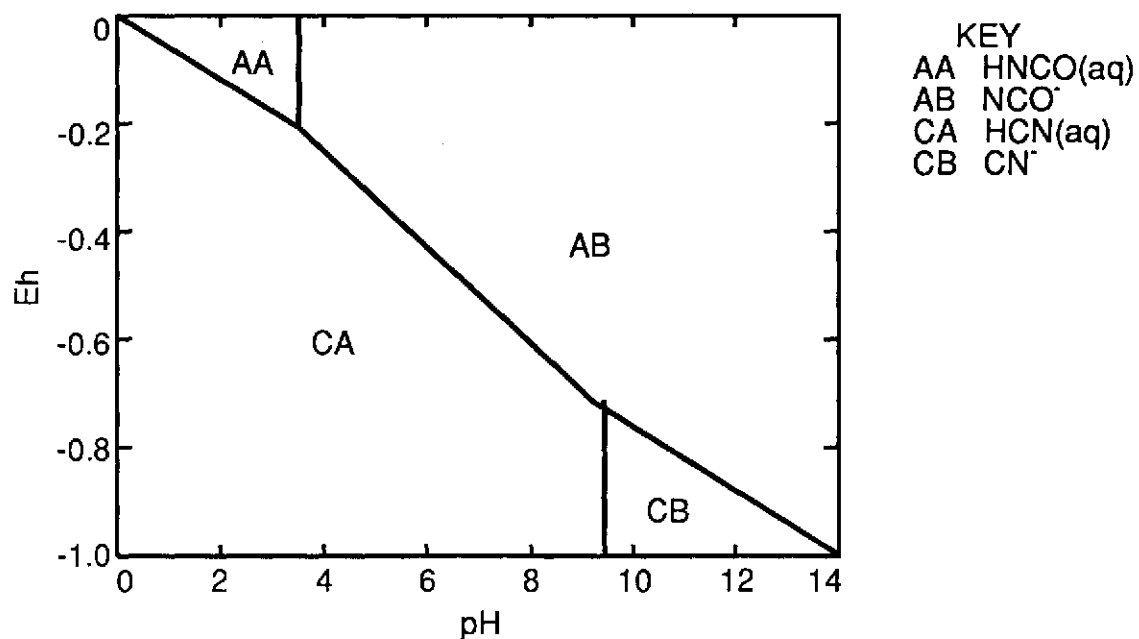
*Eh-pH diagram for free cyanate and cyanide.*

Figure E-4

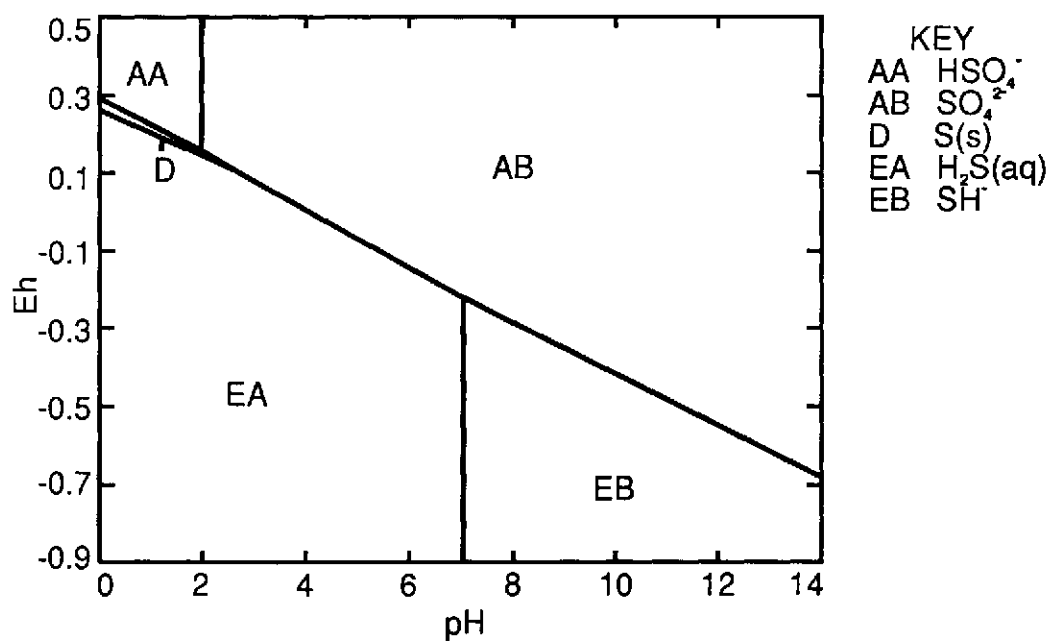
*Eh-pH diagram for sulfur.*

Figure E-5

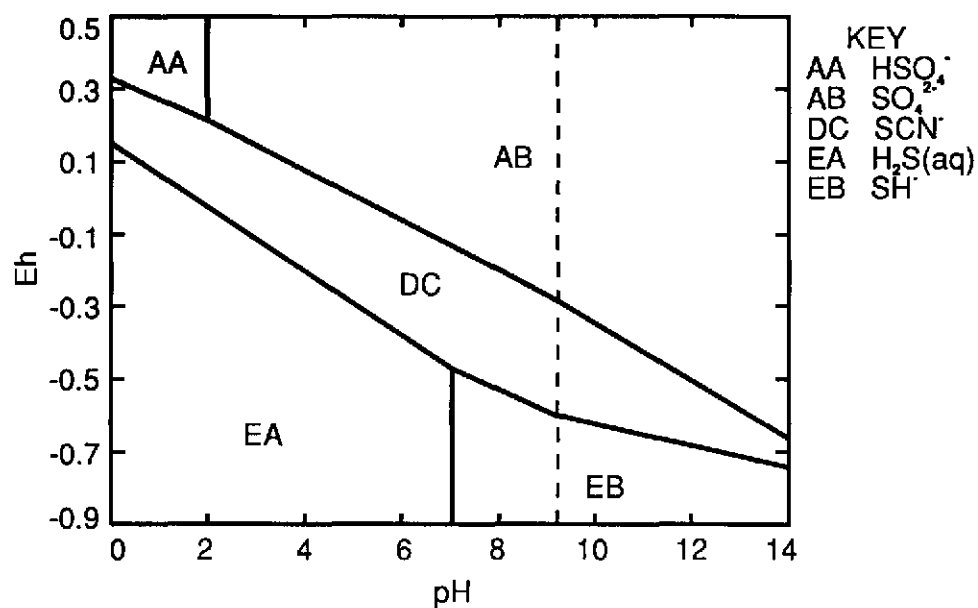
*Eh-pH diagram for sulfur with $pCN = 5.0$.*

Figure E-6

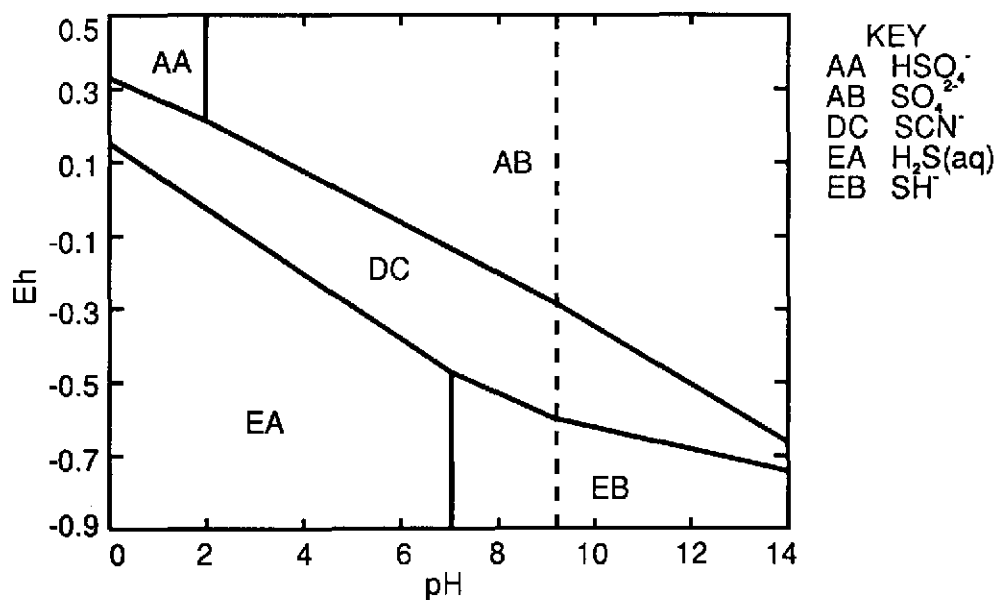
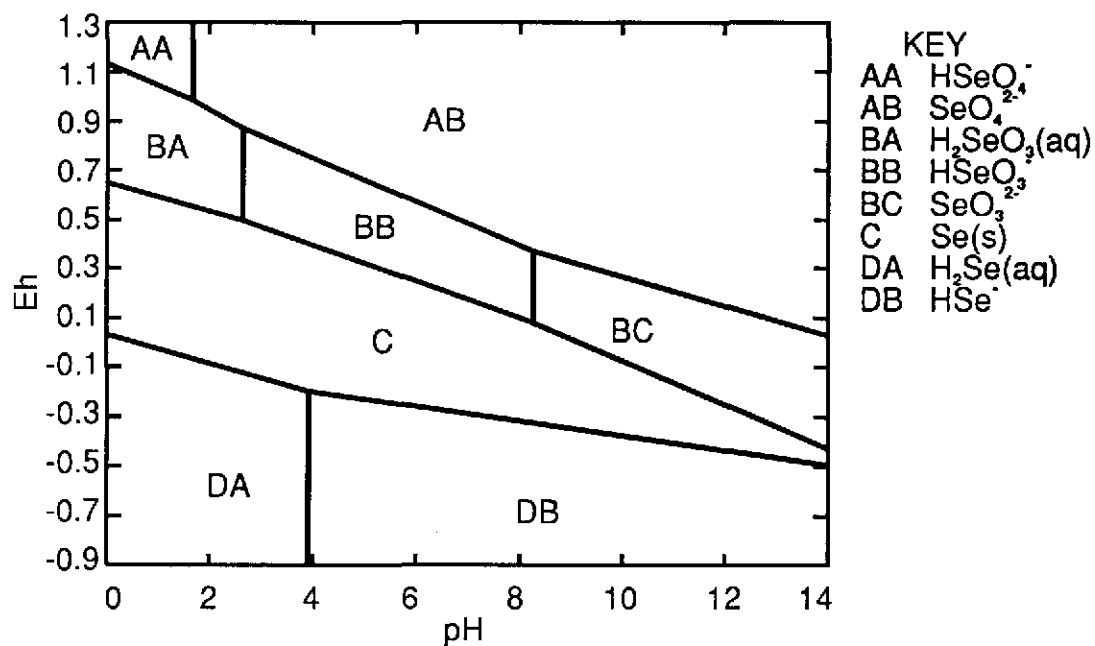
*Eh-pH diagram for sulfur with $pCN = 2.0$.*

Figure E-7



Eh-pH diagram for selenium.

Figure E-8

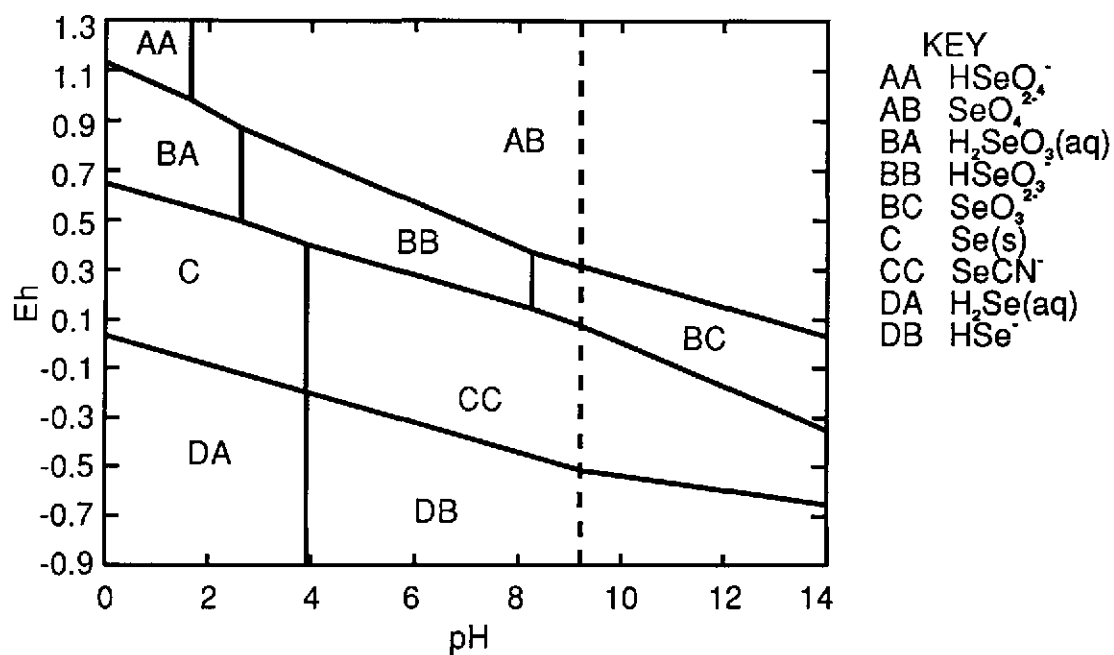
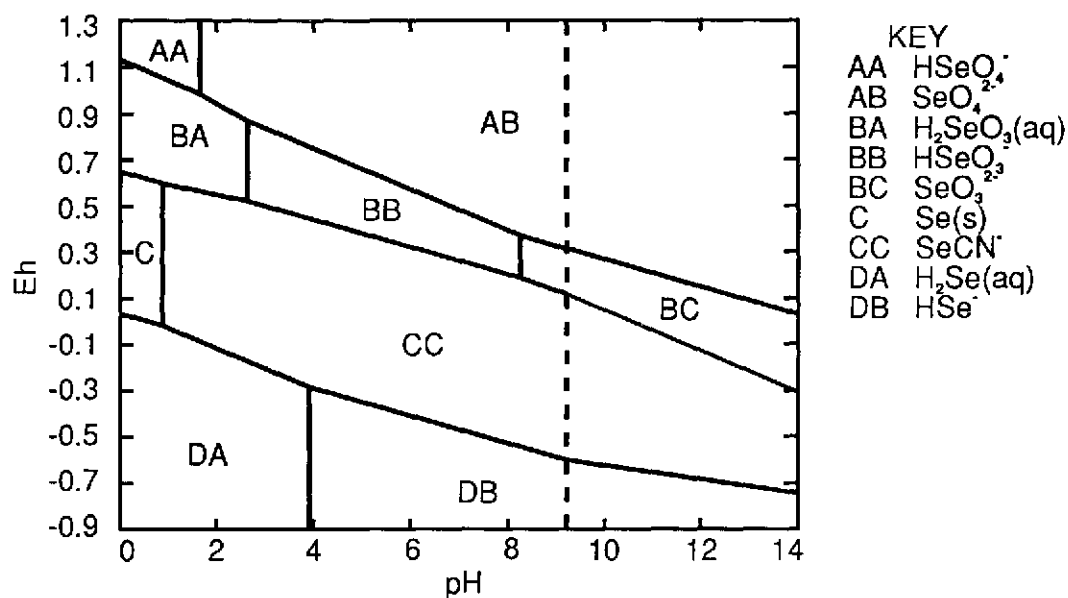
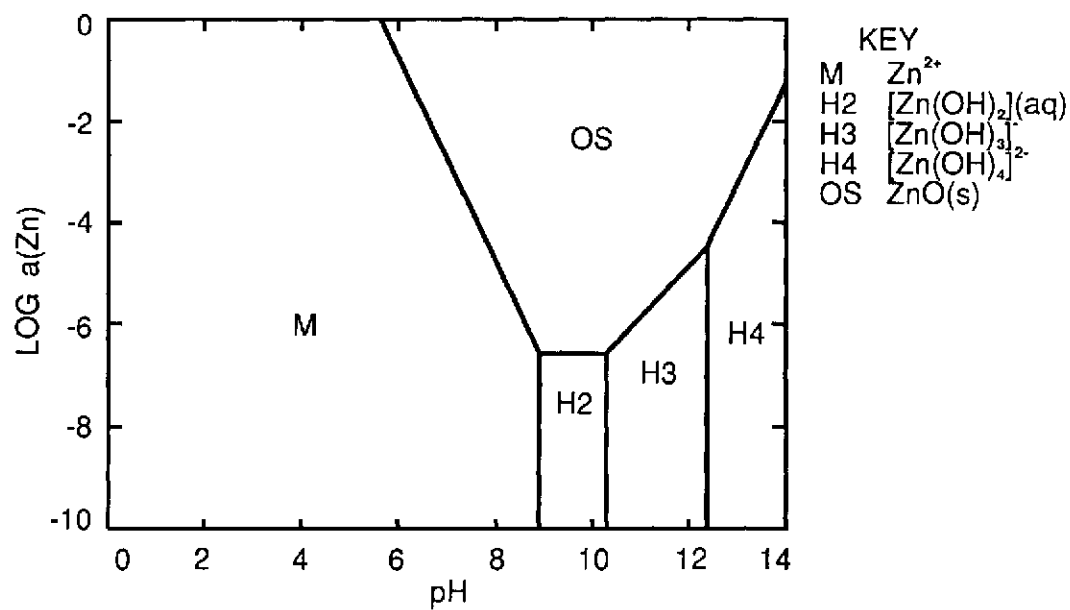
Eh-pH diagram for selenium with $p\text{CN} = 5.0$.

Figure E-9



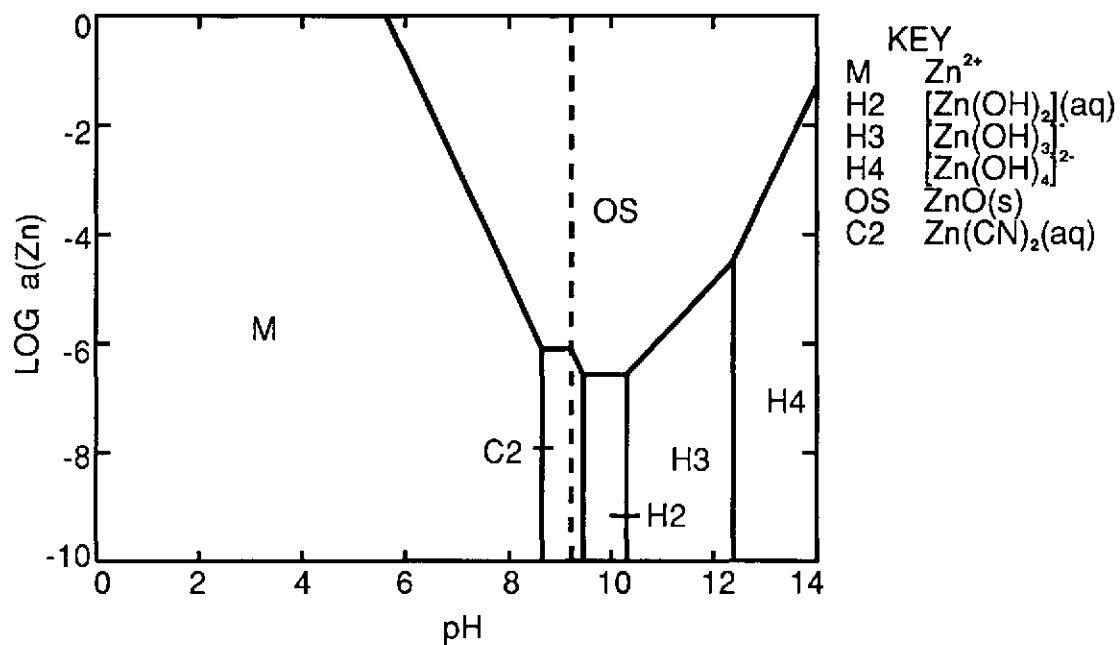
Eh-pH diagram for selenium with $p\text{CN} = 2.0$.

Figure E-10



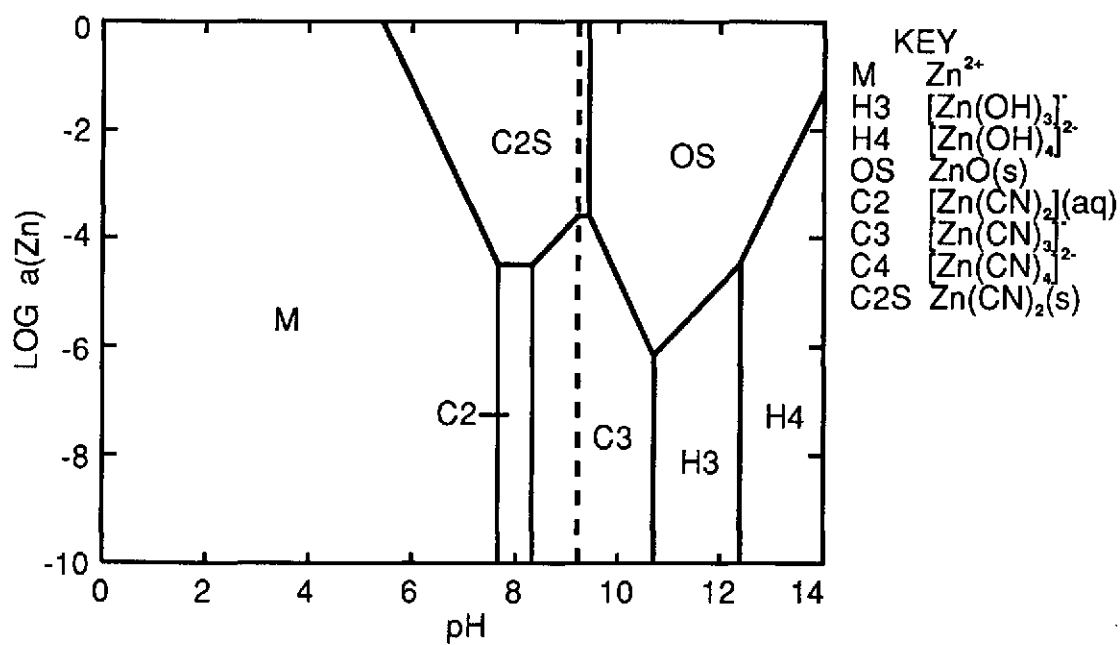
pZn-pH diagram with no ligands.

Figure E-11



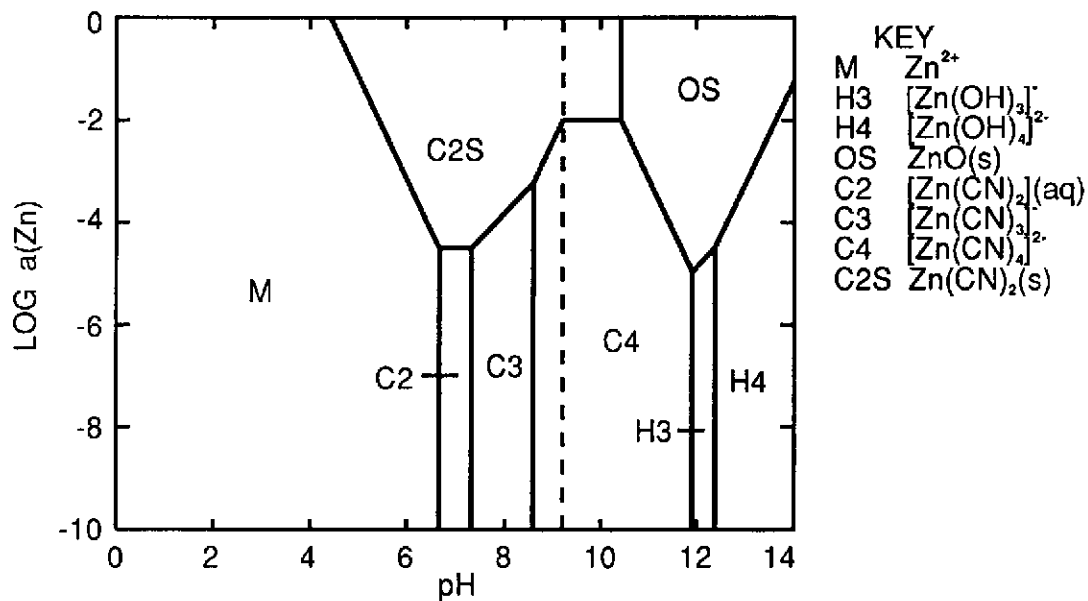
pZn-pH diagram for $pCN = 5.0$.

Figure E-12



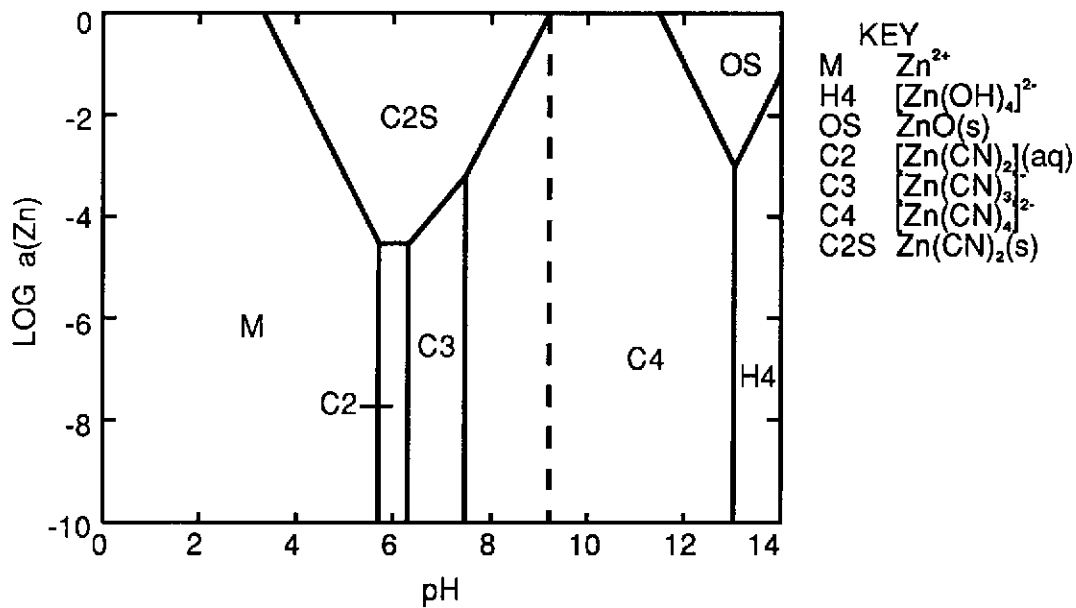
pZn-pH diagram for $pCN = 4.0$.

Figure E-13



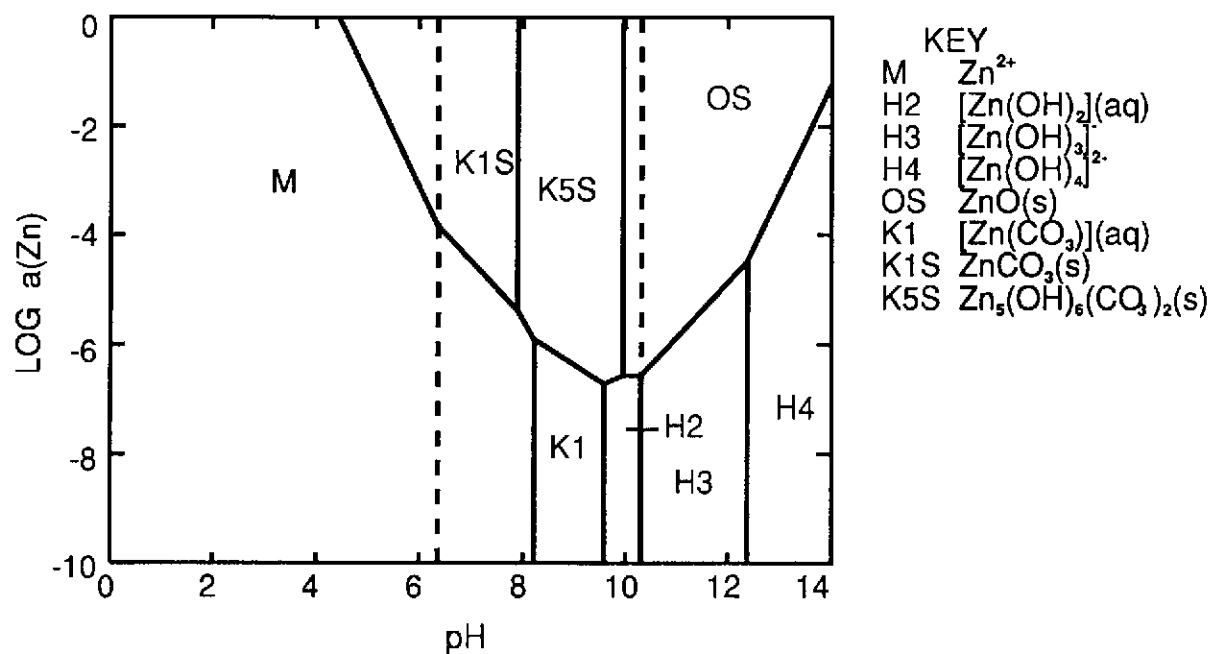
pZn-pH diagram for $p\text{CN} = 3.0$.

Figure E-14



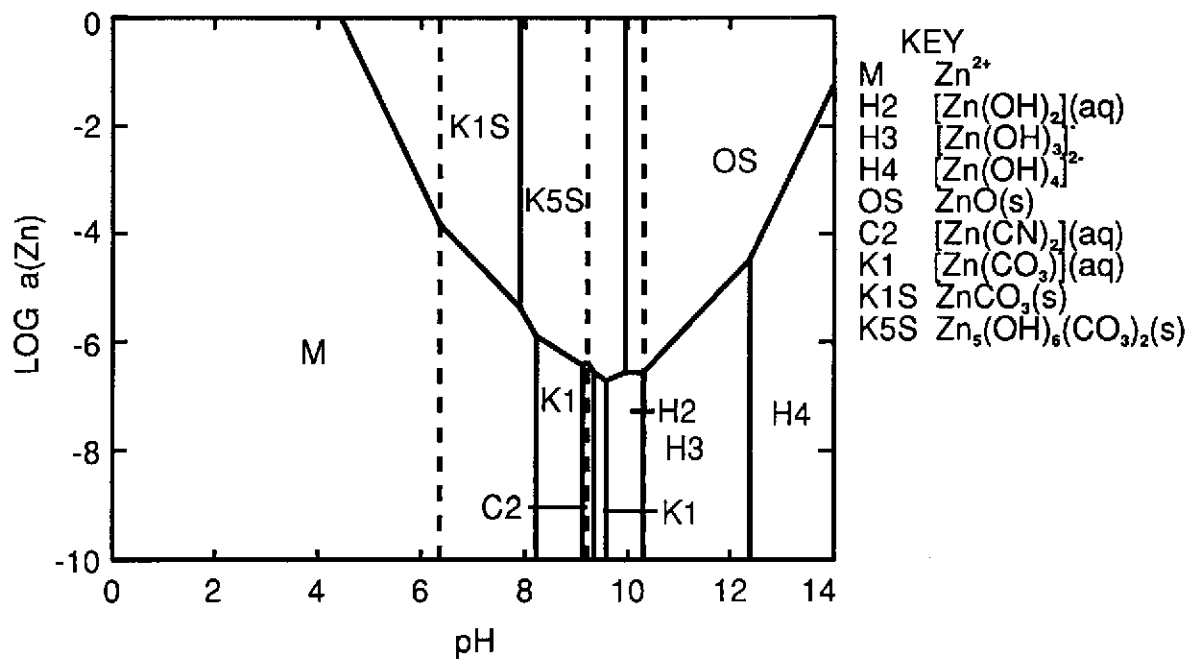
pZn-pH diagram for $p\text{CN} = 2.0$.

Figure E-15



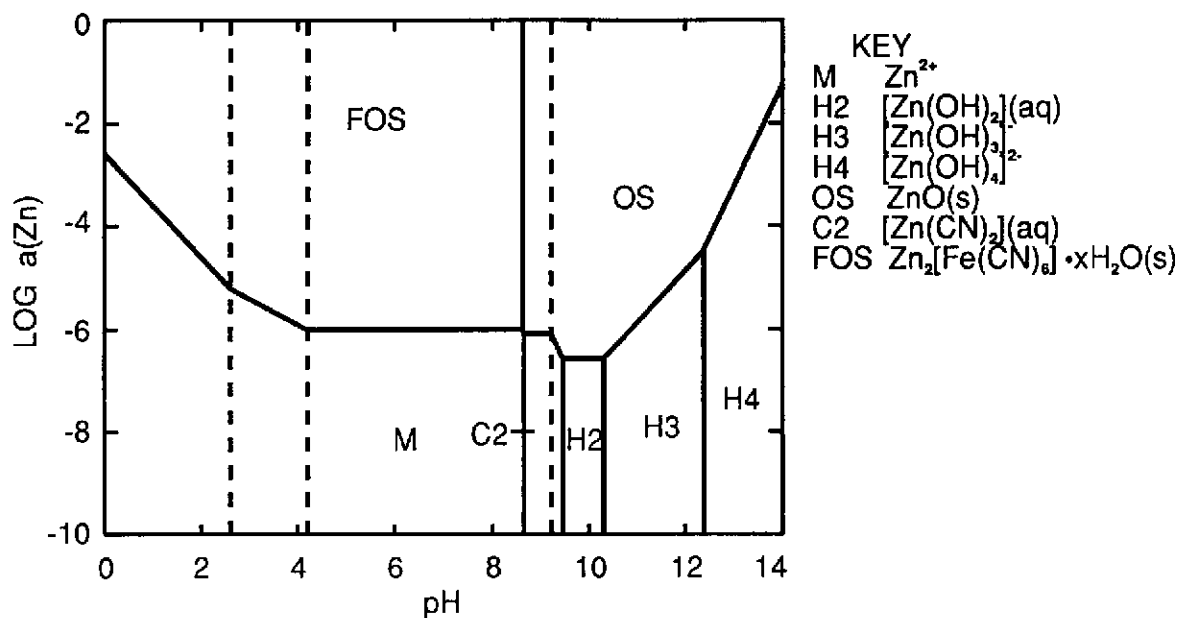
pZn-pH diagram for $p\text{CO}_3 = 3.0$.

Figure E-16



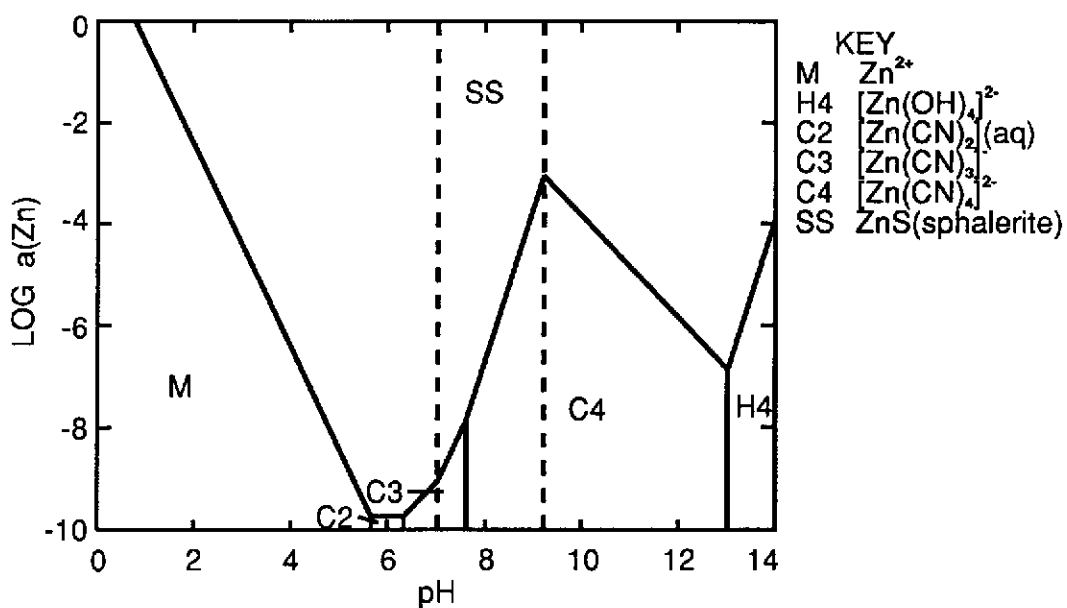
pZn-pH diagram for $p\text{CN} = 5.0$ and $p\text{CO}_3 = 3.0$.

Figure E-17



pZn - pH diagram for $pCN = 5.0$ and $p[Fe(CN)_6^{4-}] = 4.0$.

Figure E-18



pZn - pH diagram for $pCN = 2.0$ and $pSH = 6.0$.

Figure E-19

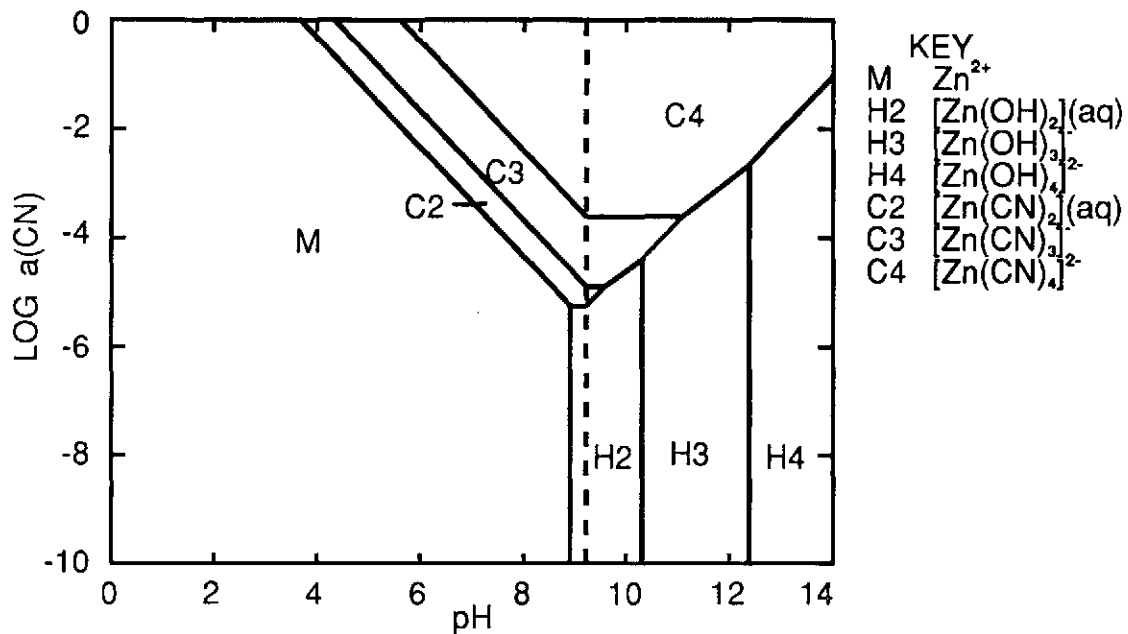
*pCN-pH diagram for zinc solution species.*

Figure E-20

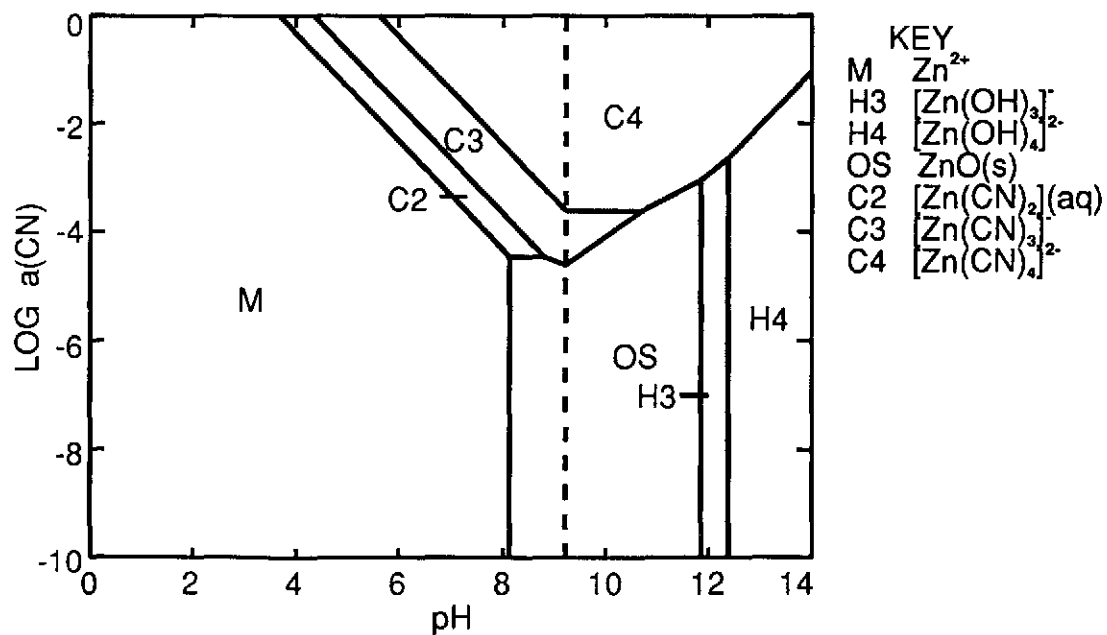
*pCN-pH diagram for $p\text{Zn} = 5.0$.*

Figure E-21

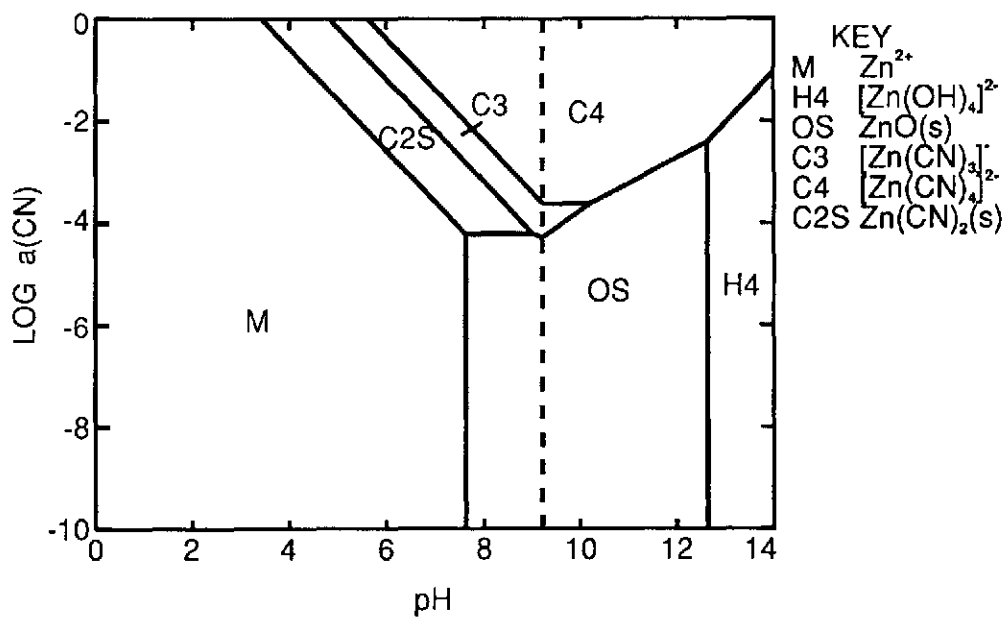


Figure E-22

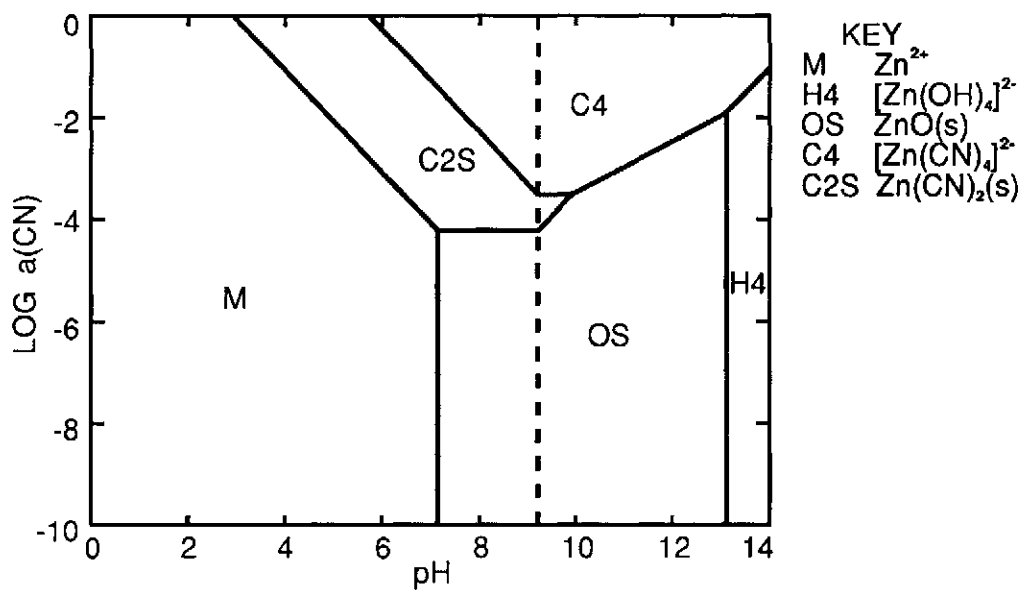
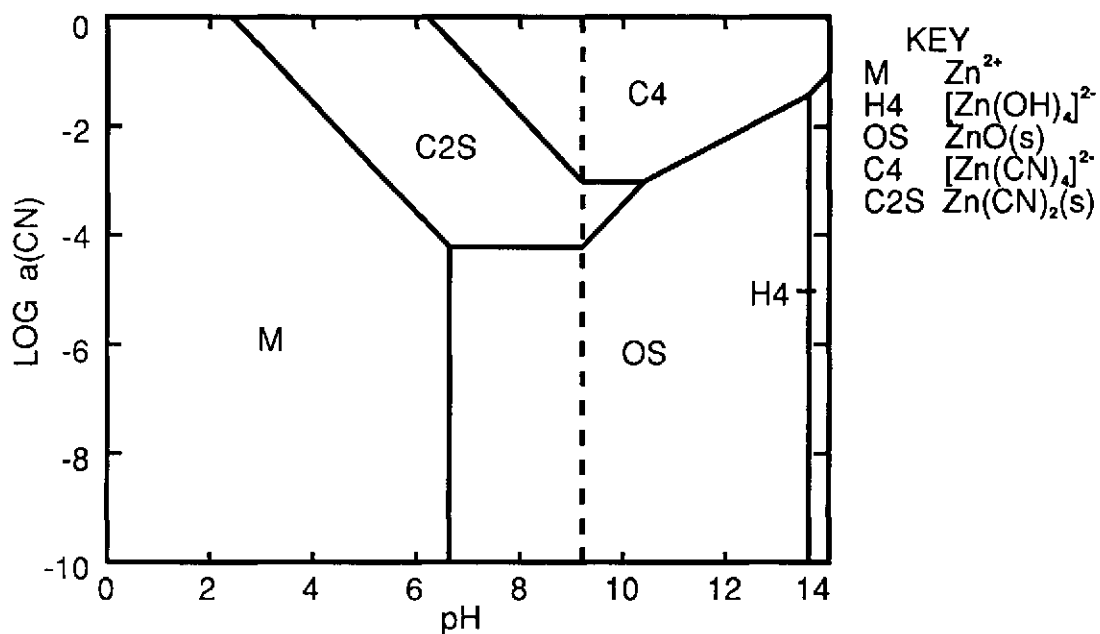
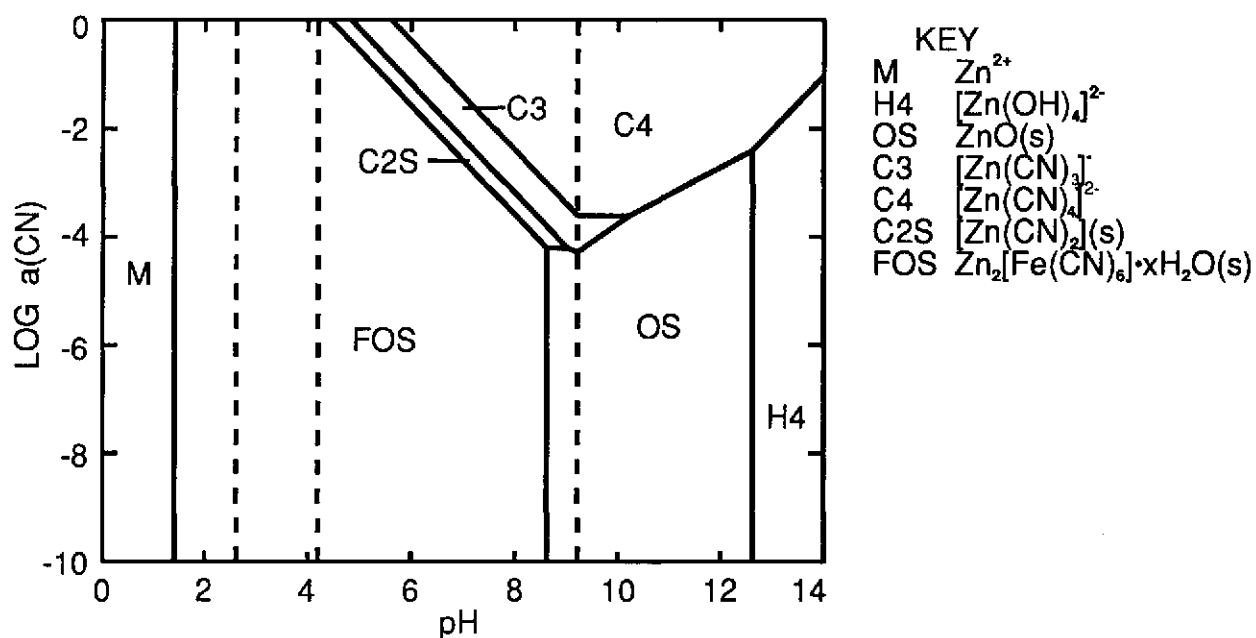


Figure E-23



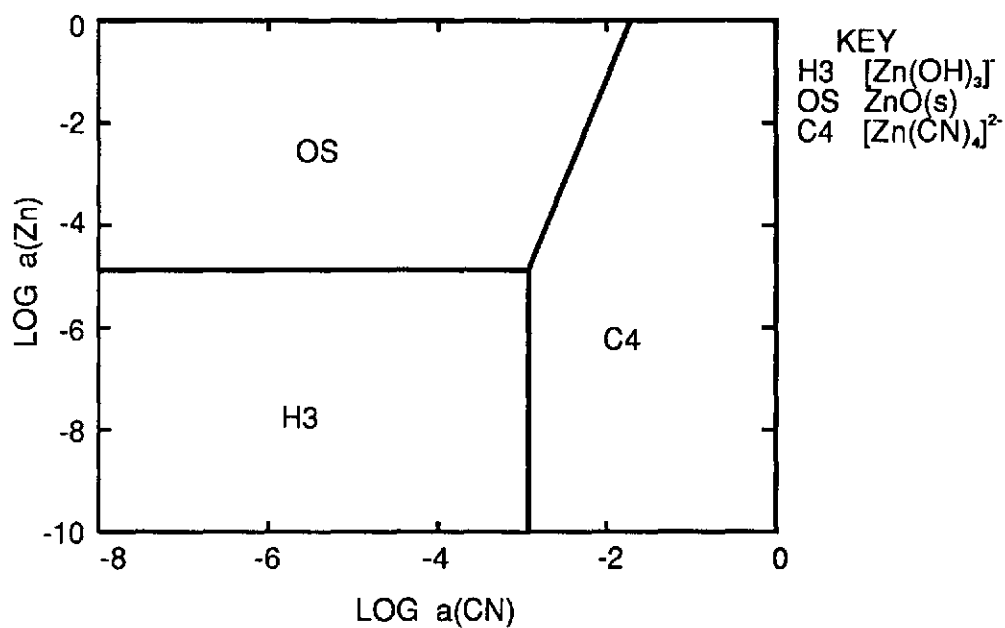
pCN-pH diagram for $p\text{Zn} = 2.0$.

Figure E-24



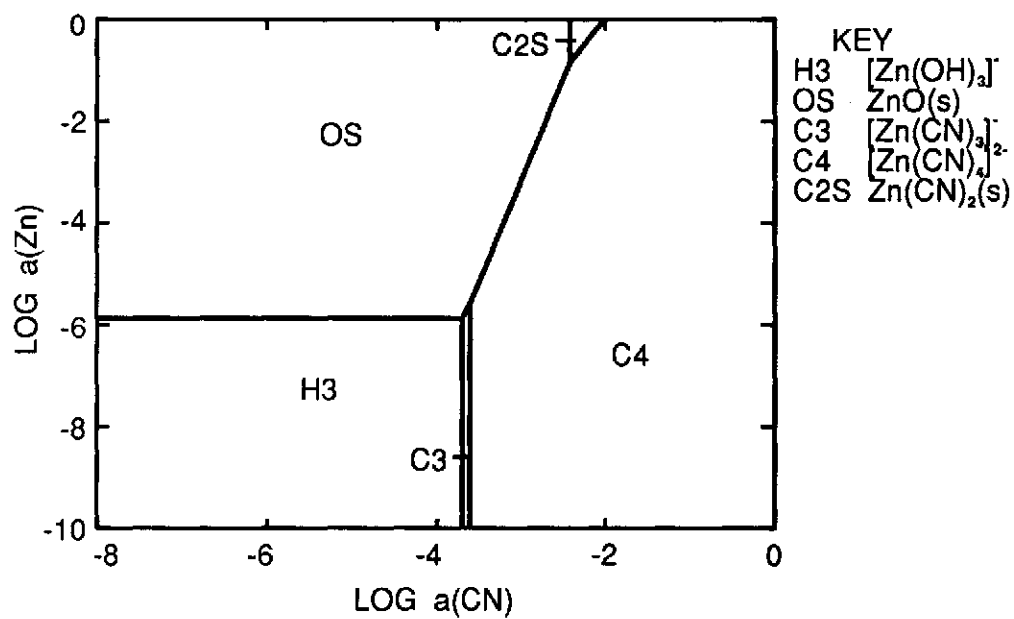
pCN-pH diagram for $p\text{Zn} = 4.0$ and $p[\text{Fe}(\text{CN})_6]^{3-} = 4.0$.

Figure E-25



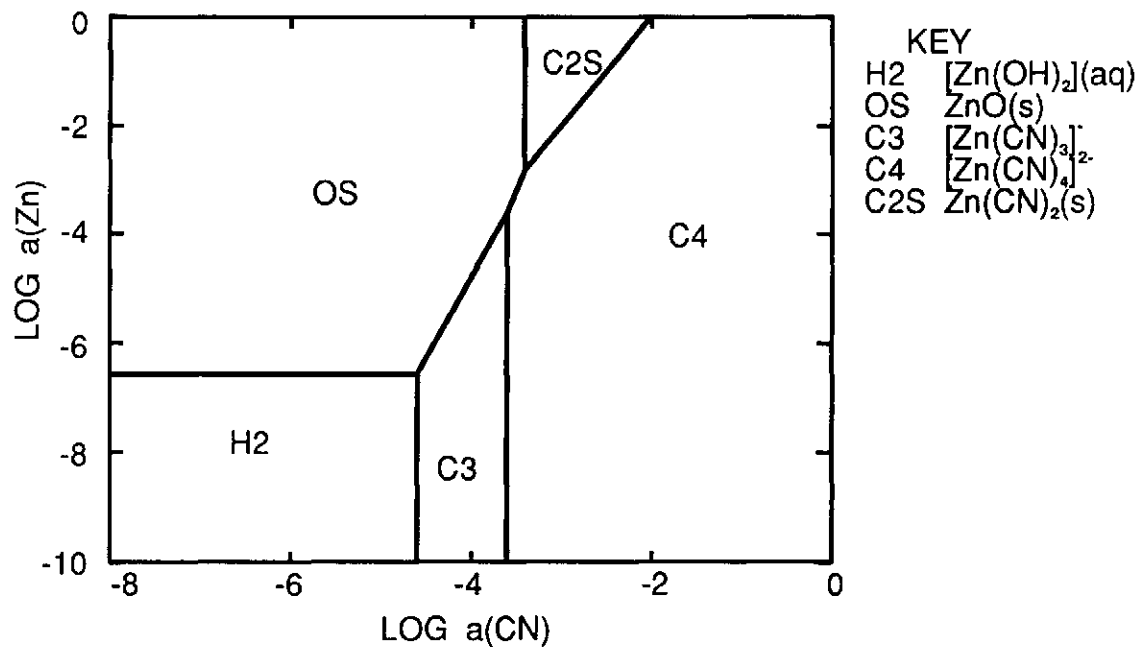
pZn - pCN diagram for $pH = 12.0$.

Figure E-26



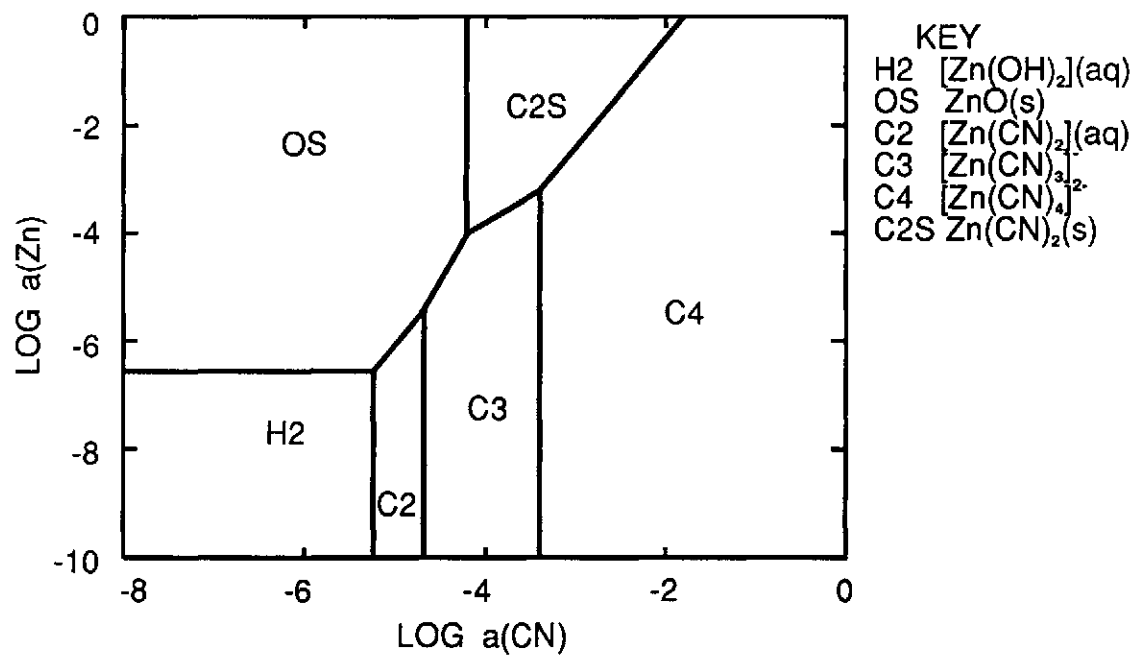
pZn - pCN diagram for $pH = 11.0$.

Figure E-27



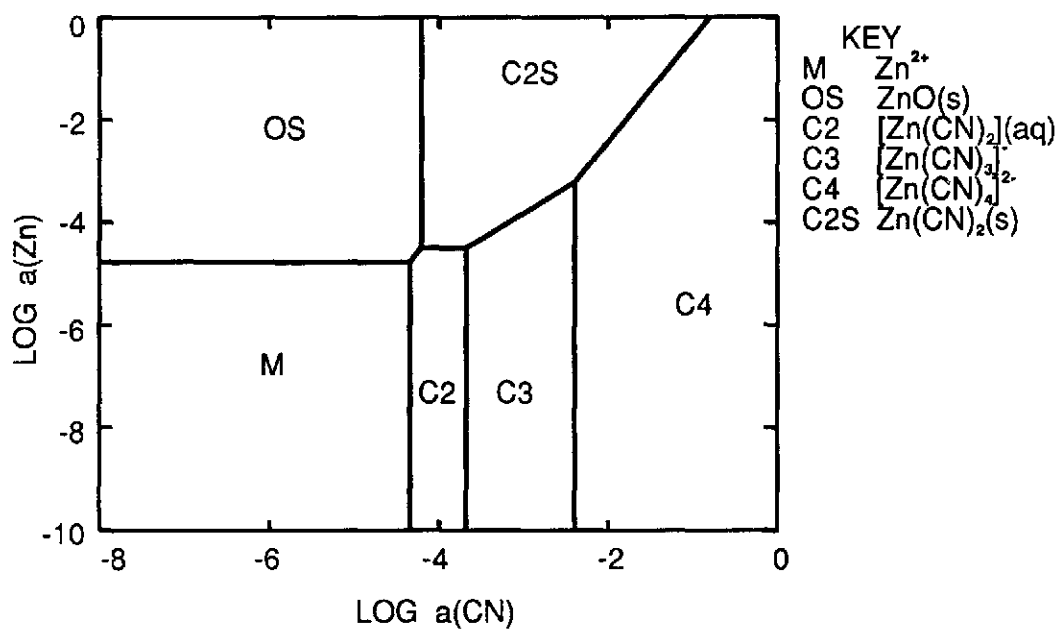
pZn-pCN diagram for pH = 10.0.

Figure E-28



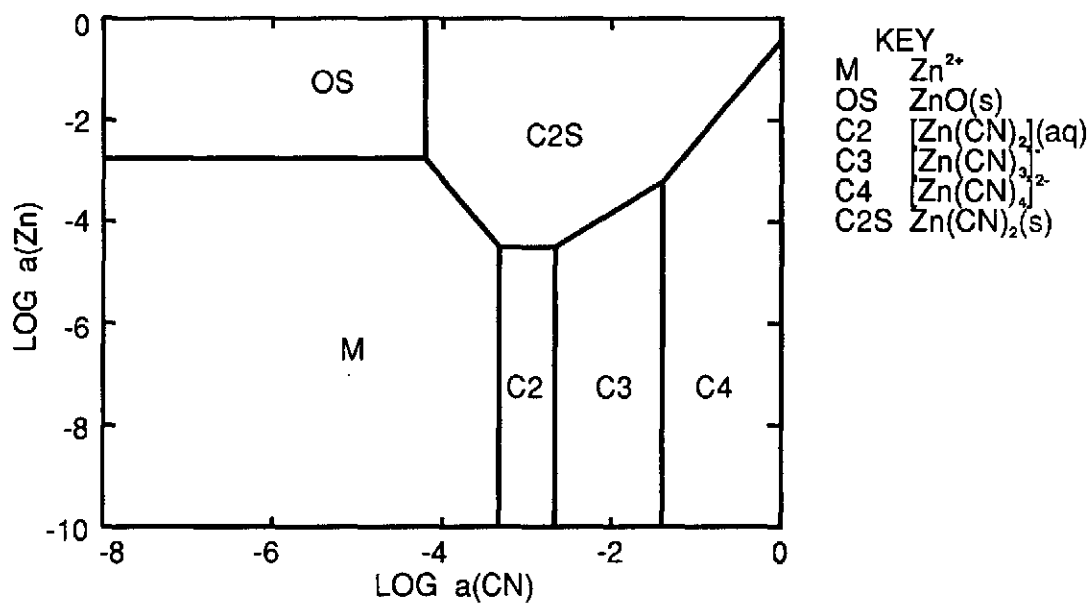
pZn-pCN diagram for pH = 9.0.

Figure E-29



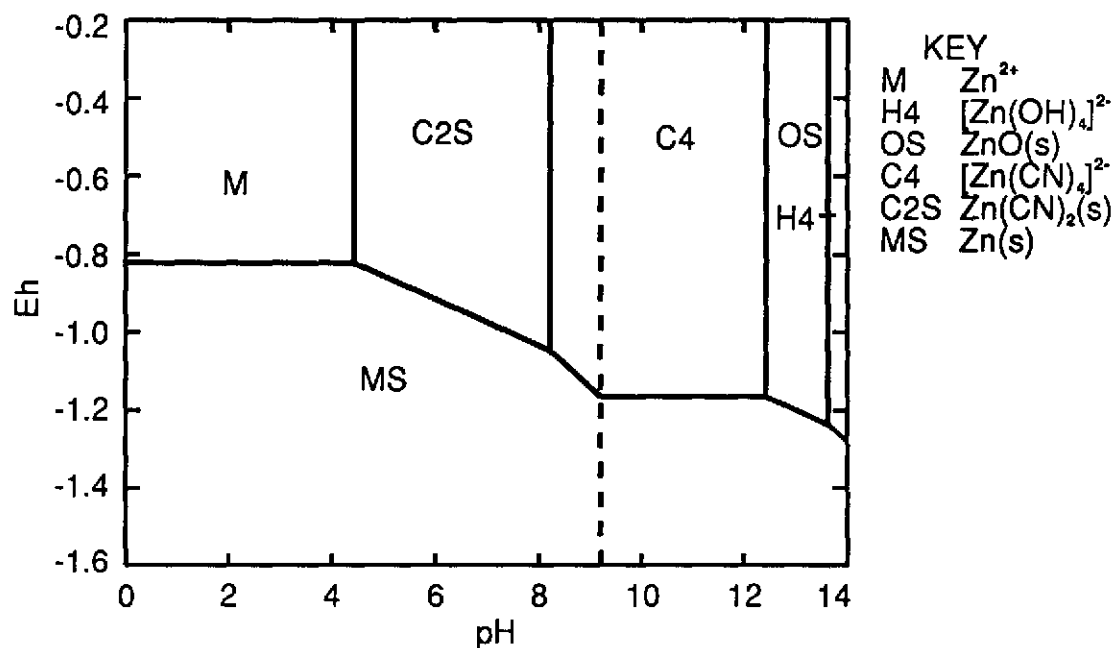
pZn - pCN diagram for $pH = 8.0$.

Figure E-30



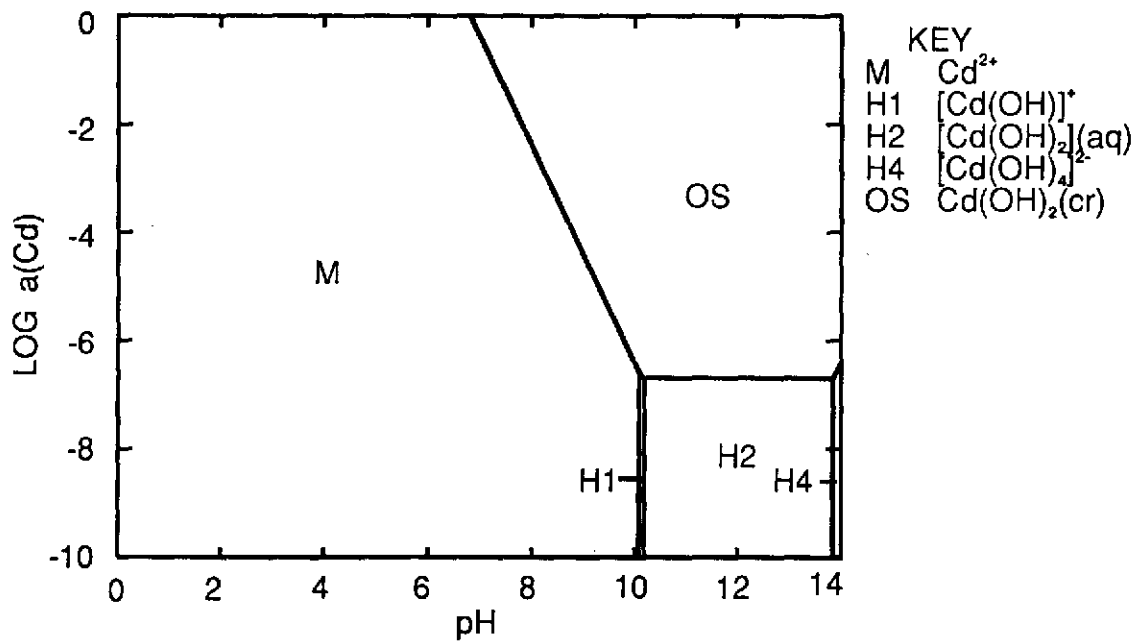
pZn - pCN diagram for $pH = 7.0$.

Figure E-31



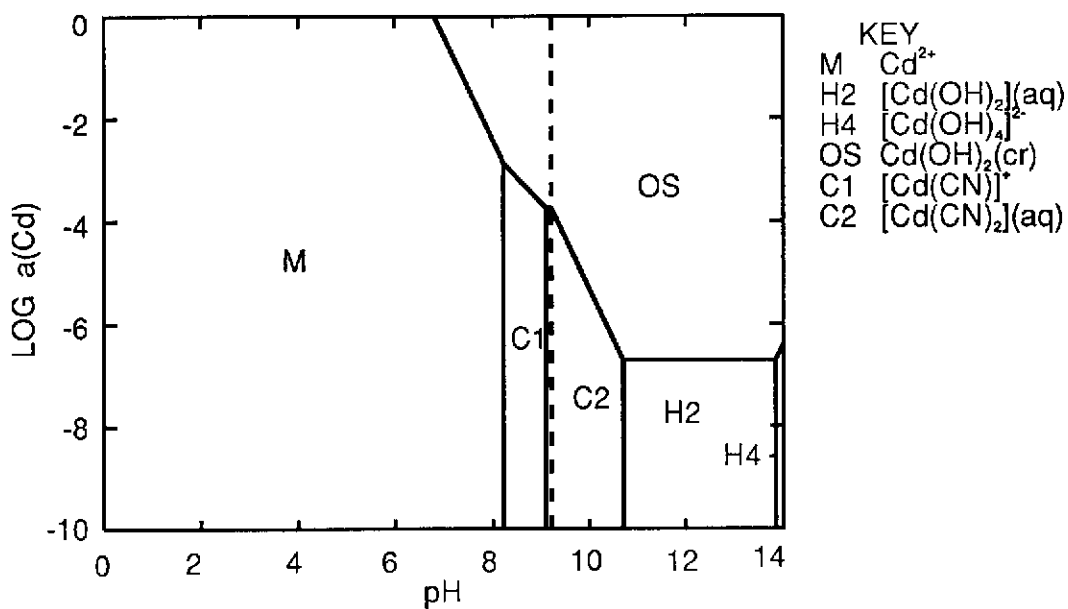
Eh-pH diagram for $p\text{Zn} = 2.0$ and $p\text{CN} = 2.0$.

Figure E-32



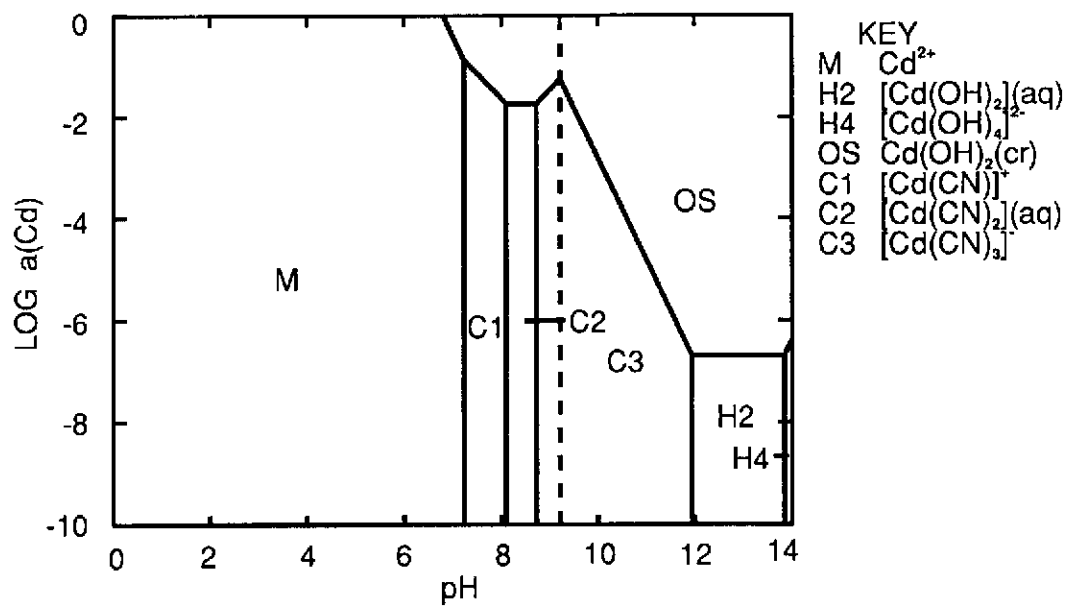
pCd-pH diagram with no ligands.

Figure E-33



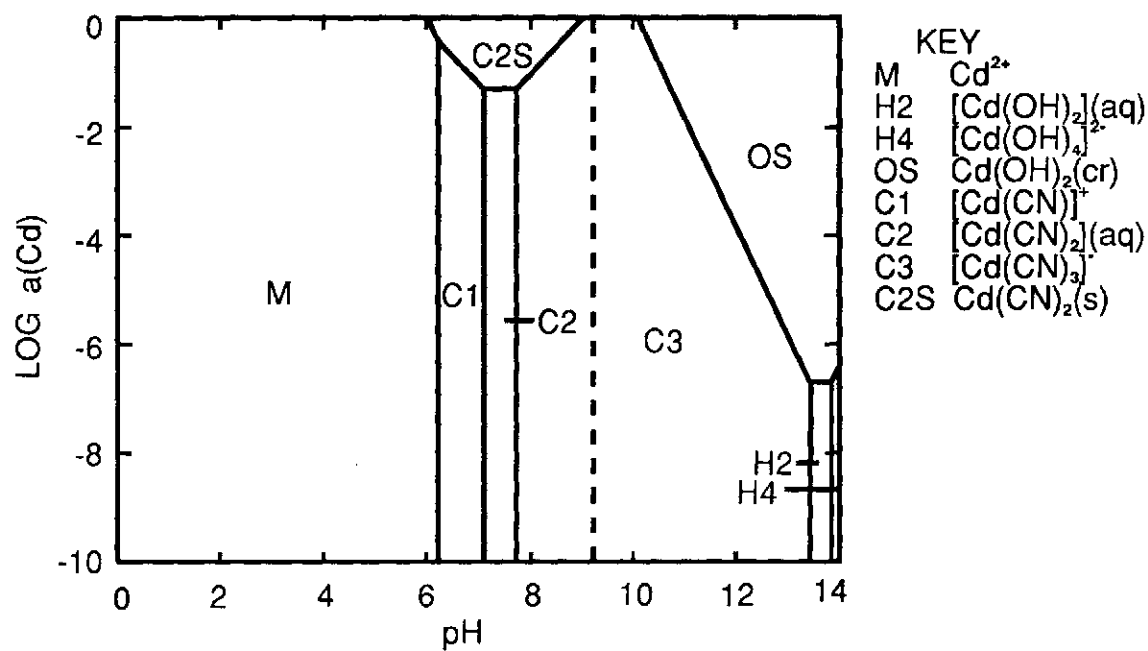
pCd-pH diagram for $p\text{CN} = 5.0$.

Figure E-34



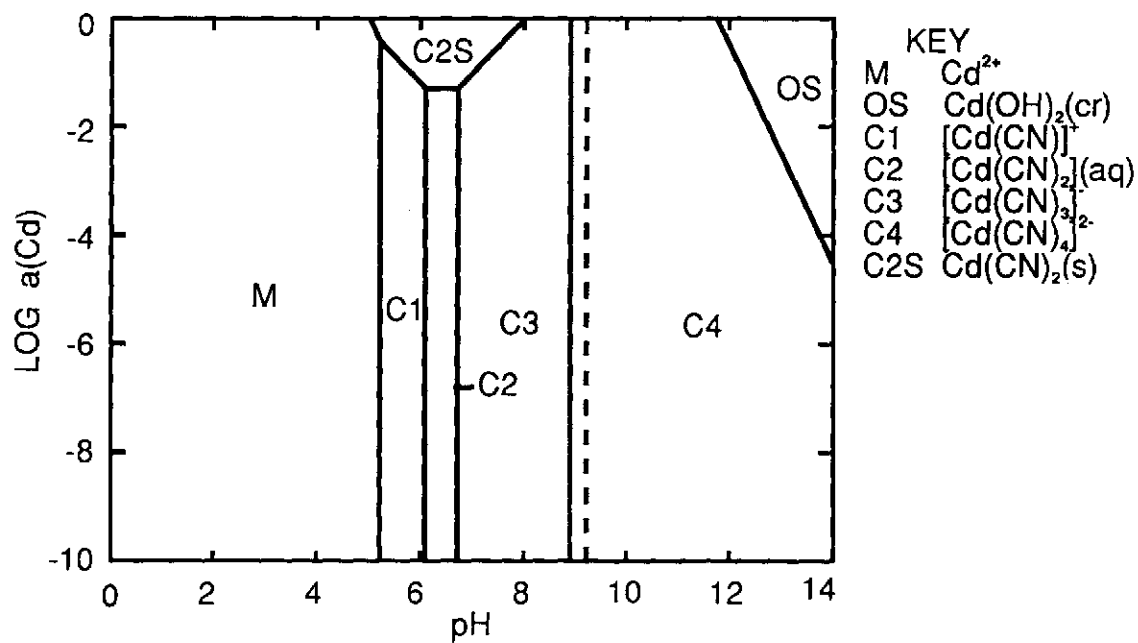
pCd-pH diagram for $p\text{CN} = 4.0$.

Figure E-35



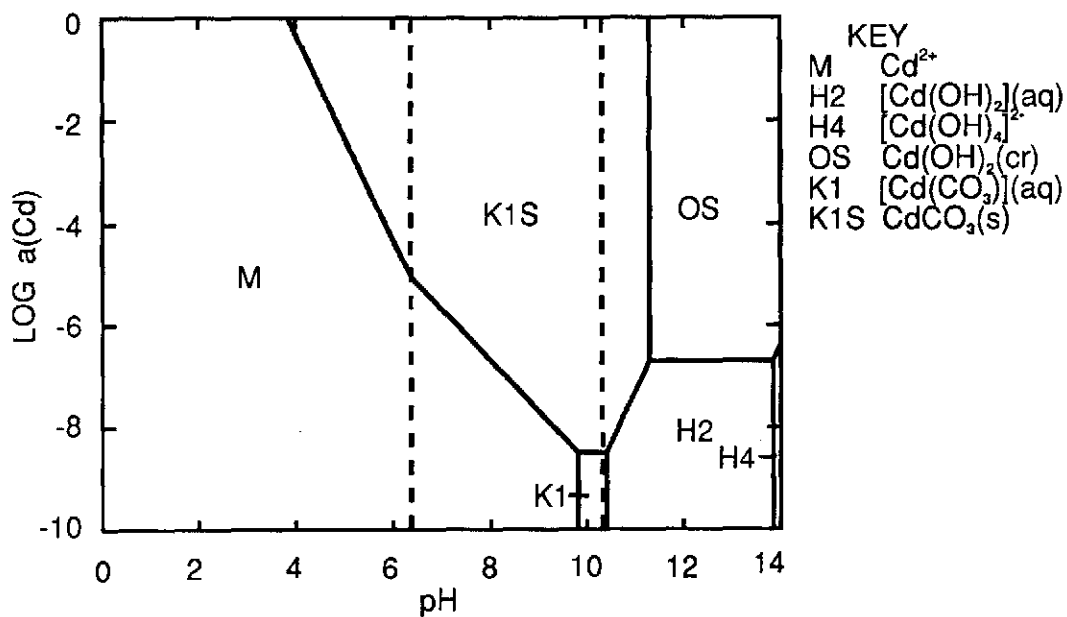
pCd-pH diagram for $p\text{CN} = 3.0$.

Figure E-36



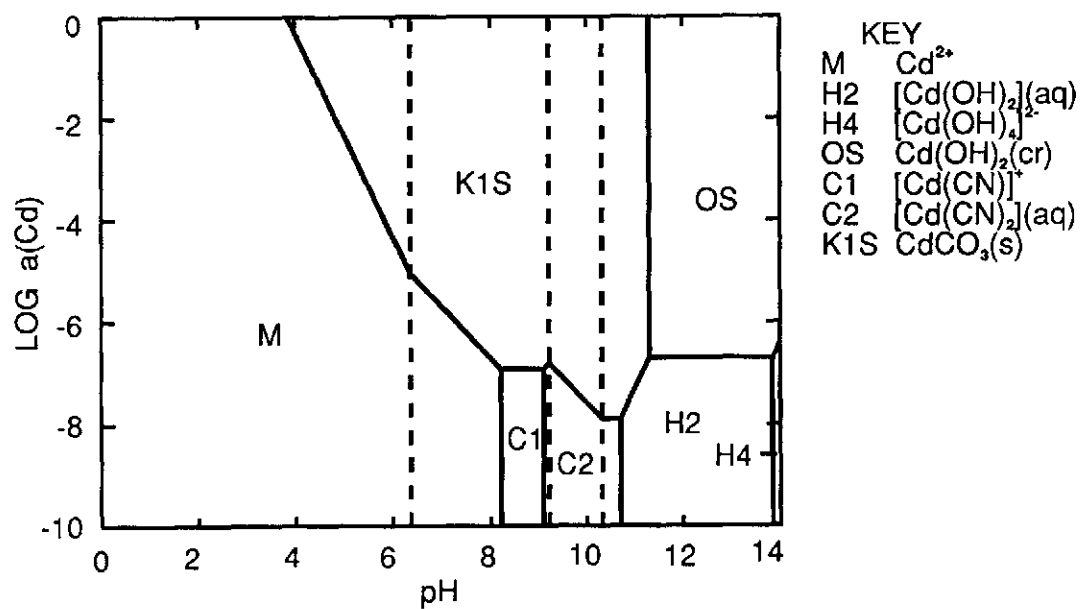
pCd-pH diagram for $p\text{CN} = 2.0$.

Figure E-37



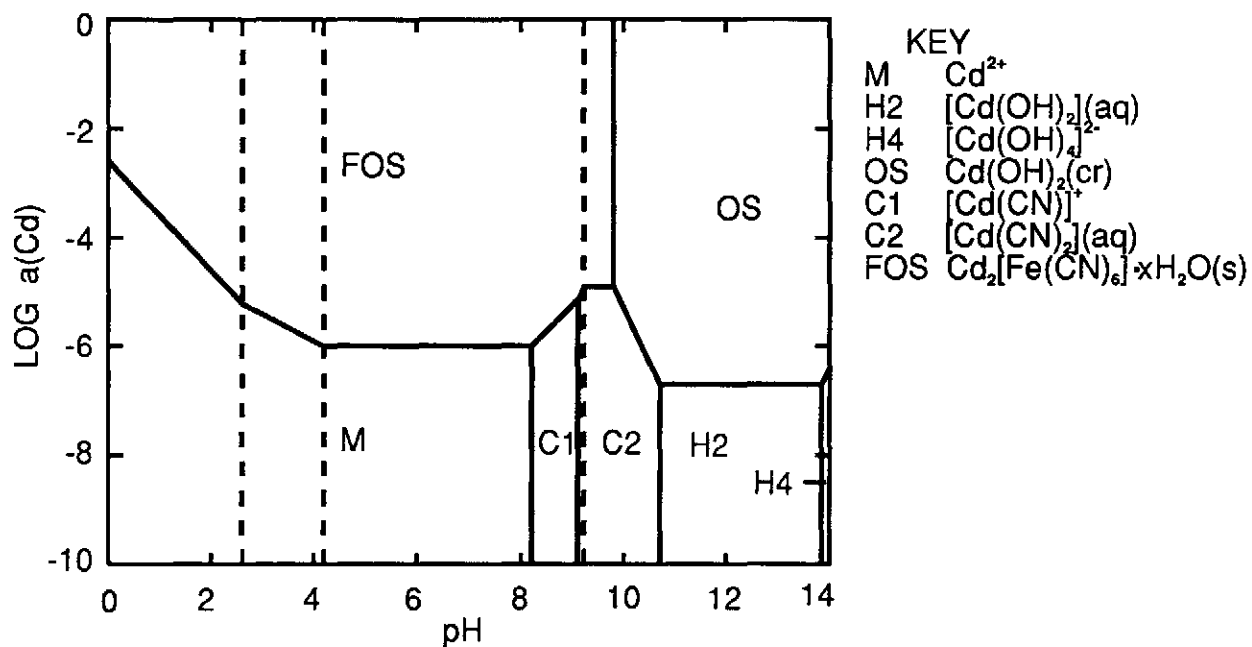
pCd-pH diagram for $p\text{CO}_3 = 3.0$.

Figure E-38



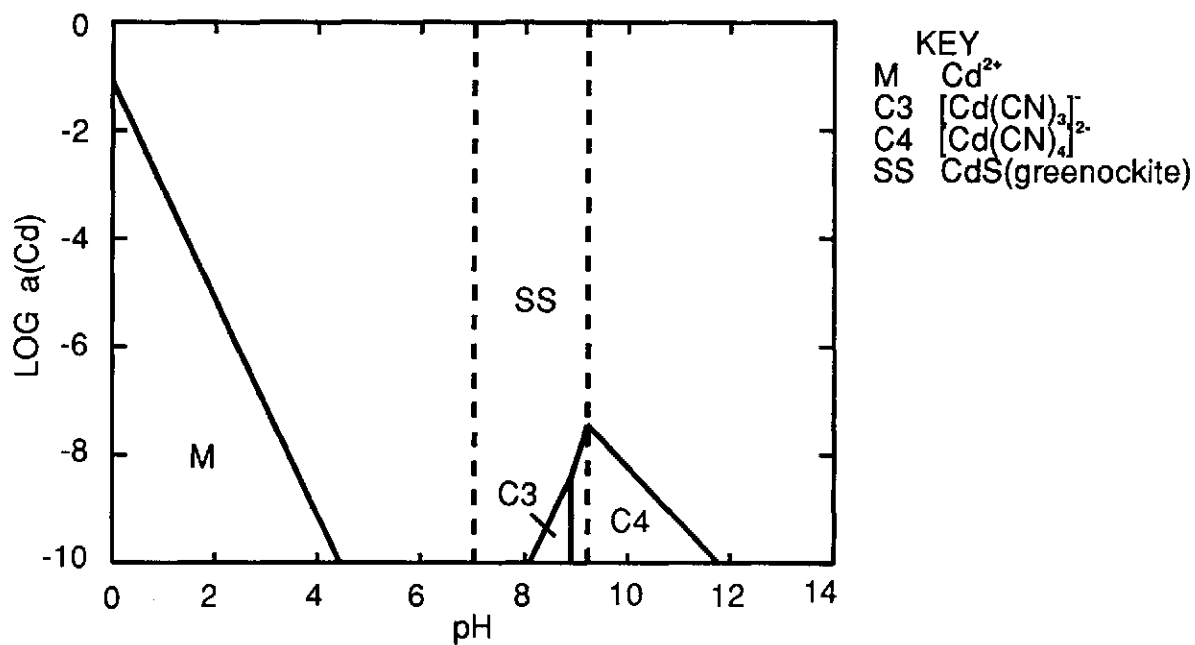
pCd-pH diagram for $p\text{CN} = 5.0$ and $p\text{CO}_3 = 3.0$.

Figure E-39



pCd-pH diagram for $pCN = 5.0$ and $p[Fe(CN)_6^{4-}] = 4.0$.

Figure E-40



pCd-pH diagram for $pCN = 2.0$ and $pSH = 6.0$.

Figure E-41

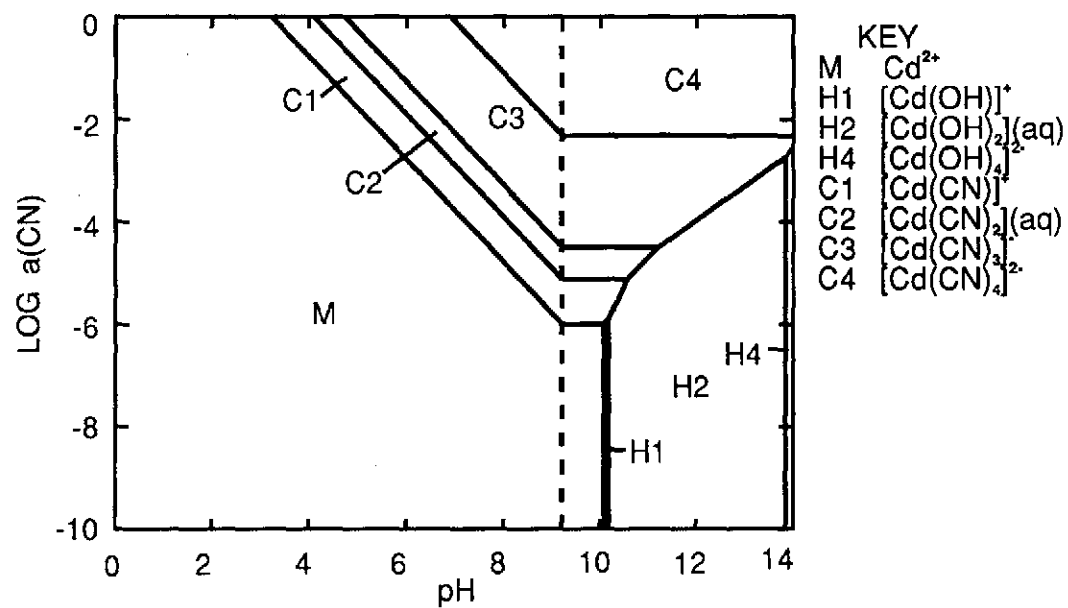
*pCN-pH diagram for cadmium solution species.*

Figure E-42

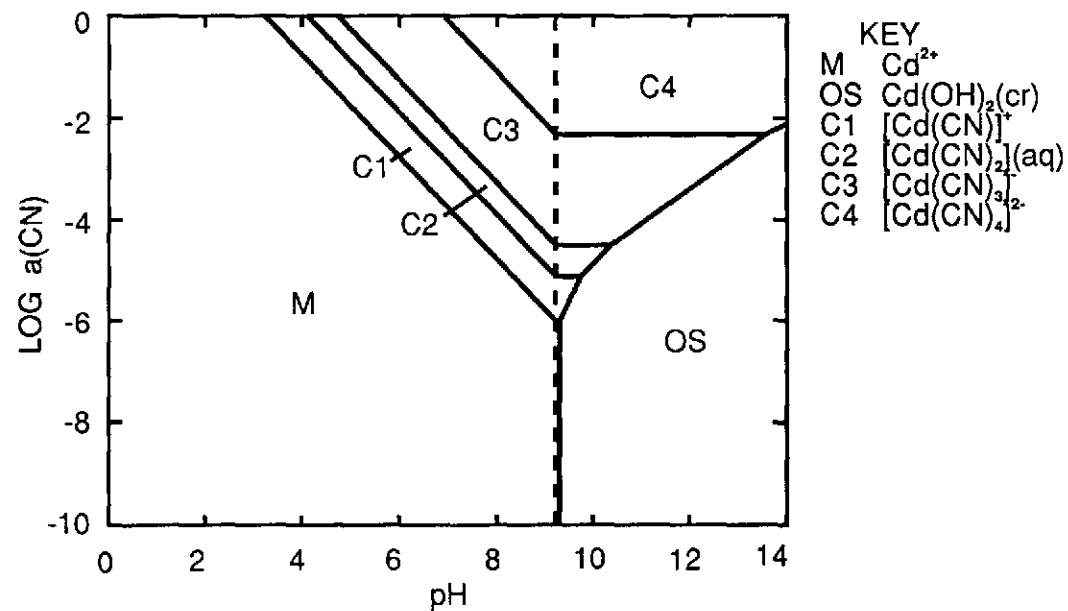
*pCN-pH diagram for $p\text{Cd} = 5.0$.*

Figure E-43

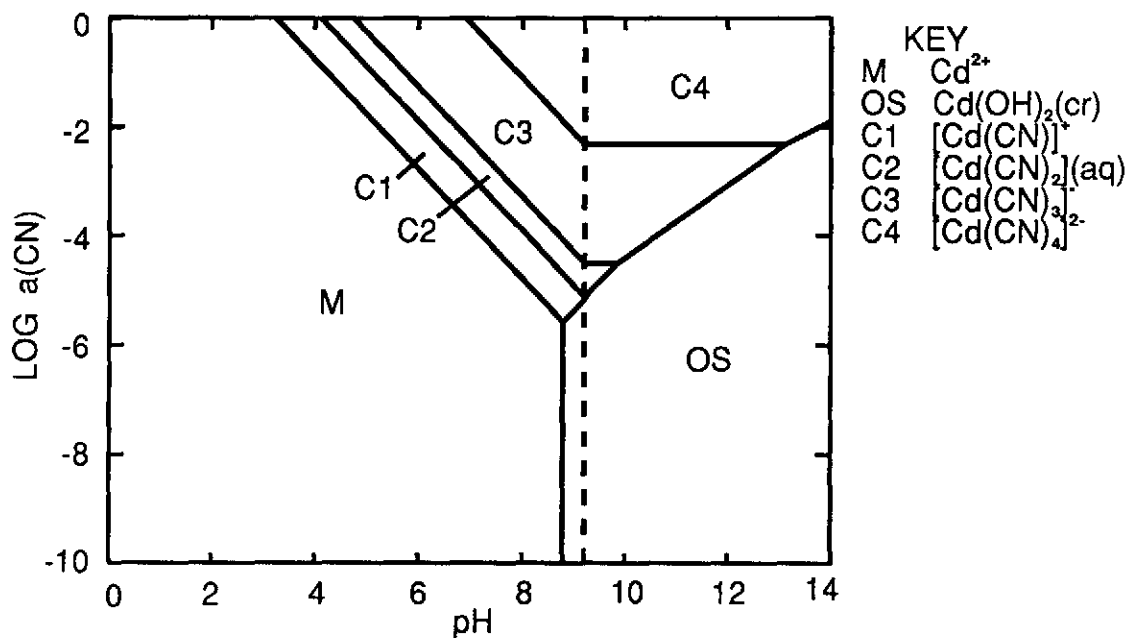
*pCN-pH diagram for $pCd = 4.0$.*

Figure E-44

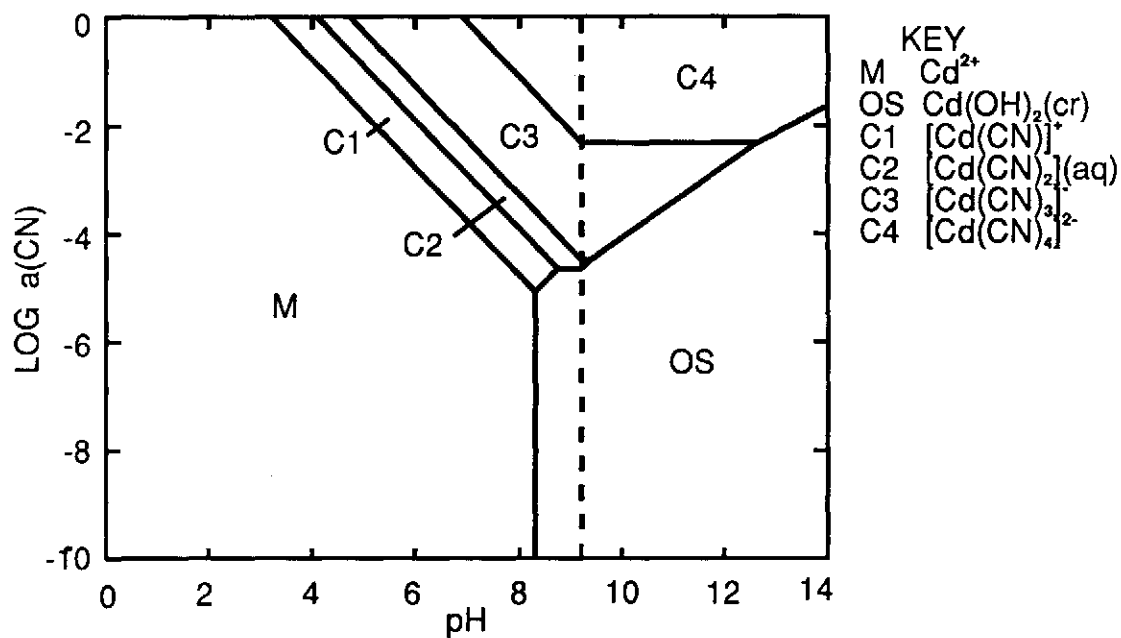
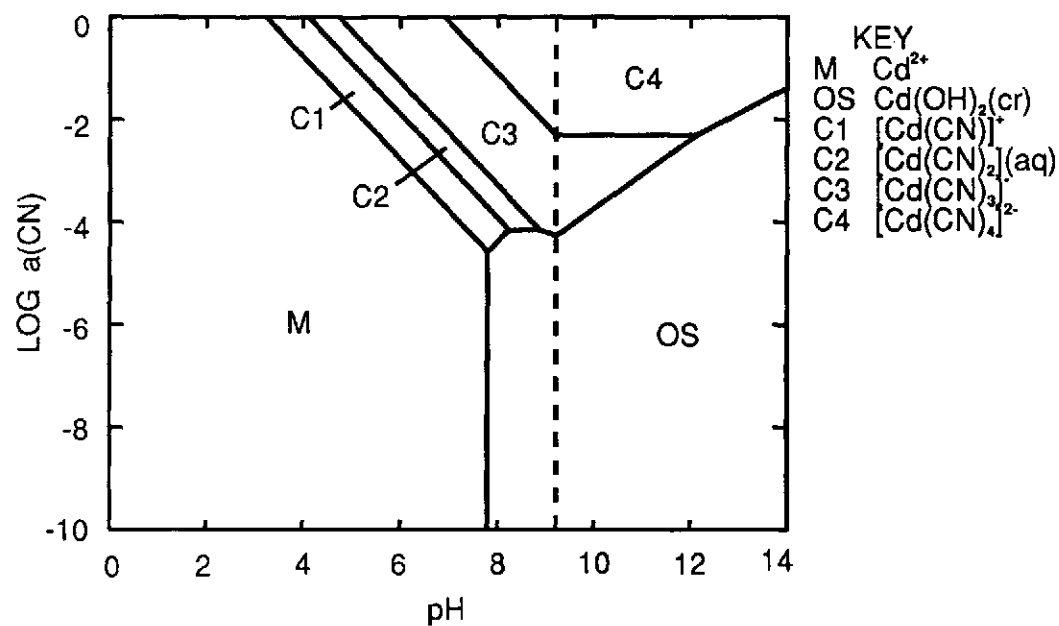
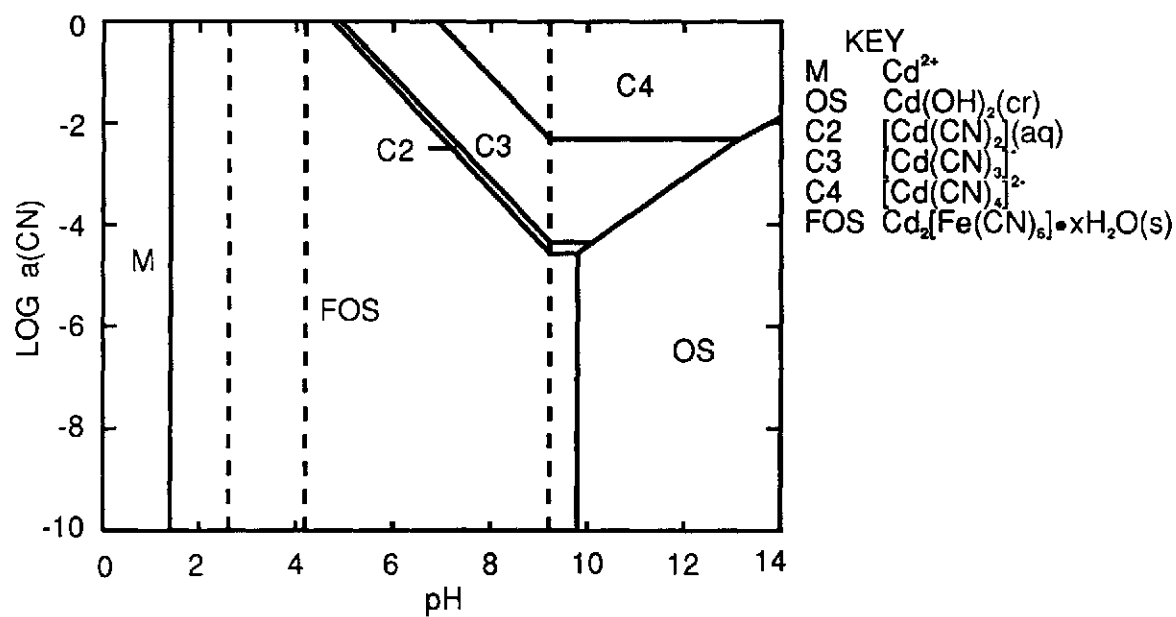
*pCN-pH diagram for $pCd = 3.0$.*

Figure E-45



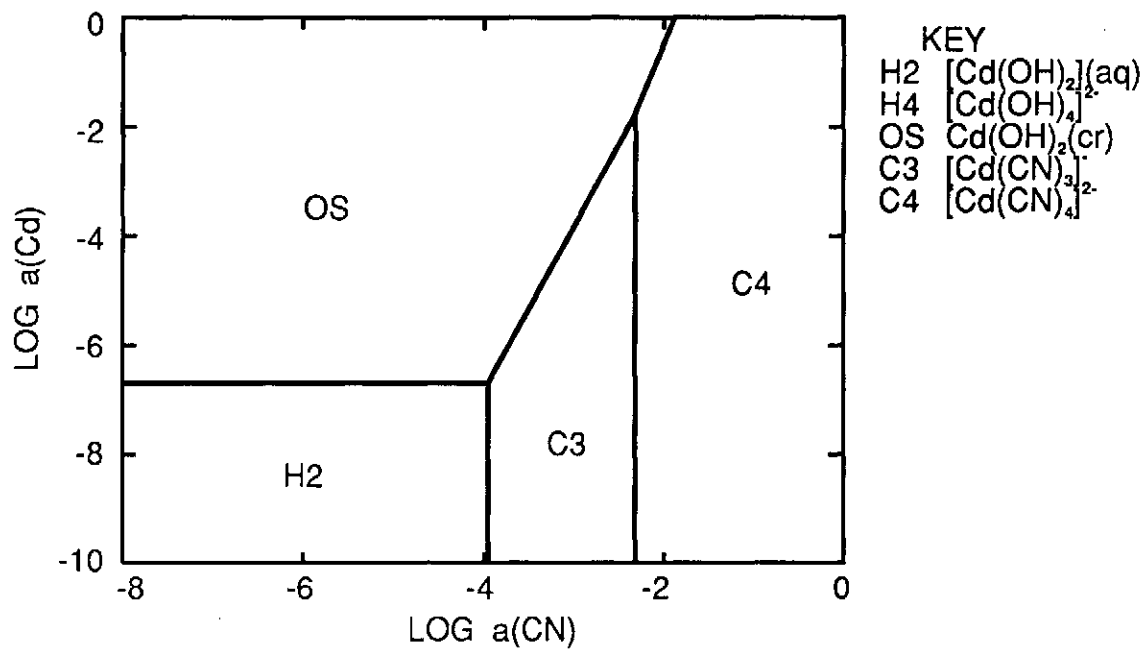
pCN-pH diagram for $p\text{Cd} = 2.0$.

Figure E-46



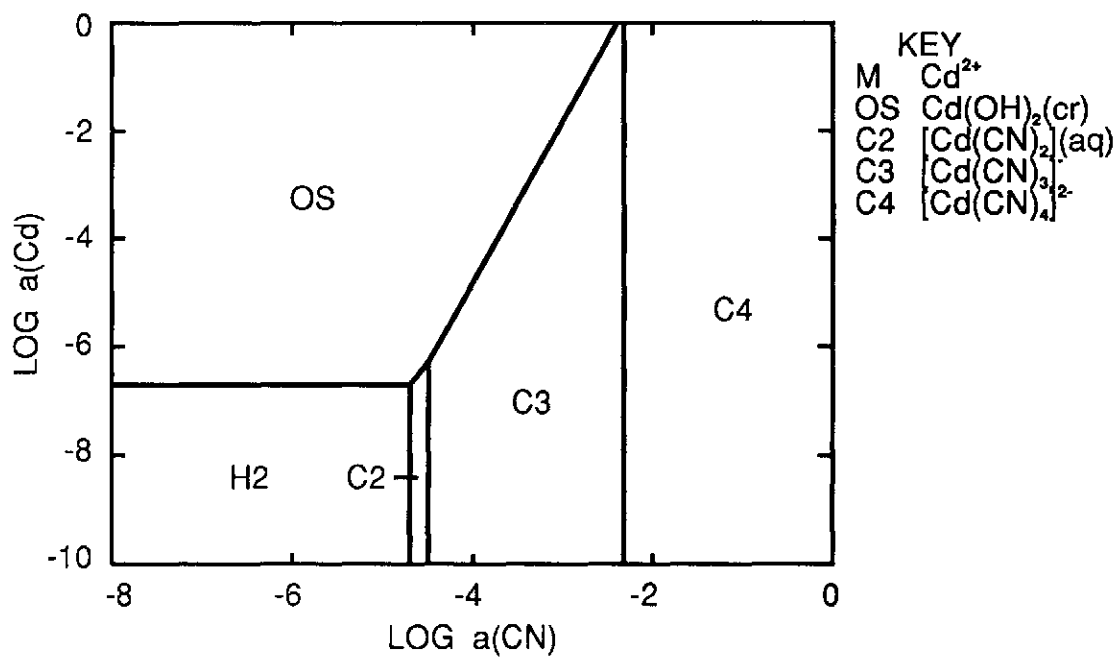
pCN-pH diagram for $p\text{Cd} = 4.0$ and $p[\text{Fe}(\text{CN})_6^{4-}] = 4.0$.

Figure E-47



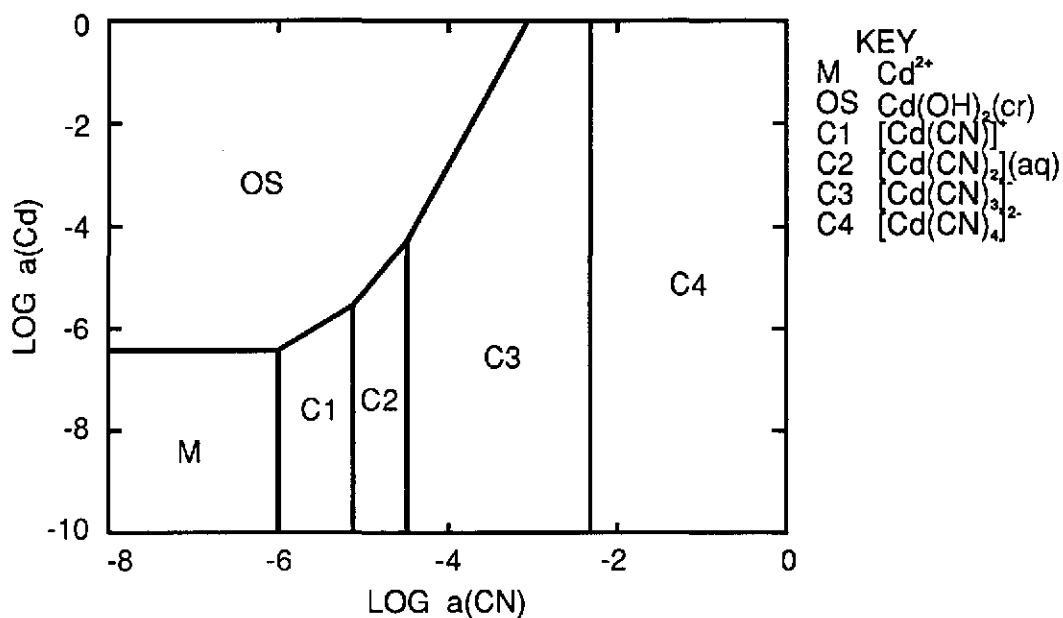
$p\text{Cd}$ - $p\text{CN}$ diagram for $\text{pH} = 12.0$.

Figure E-48



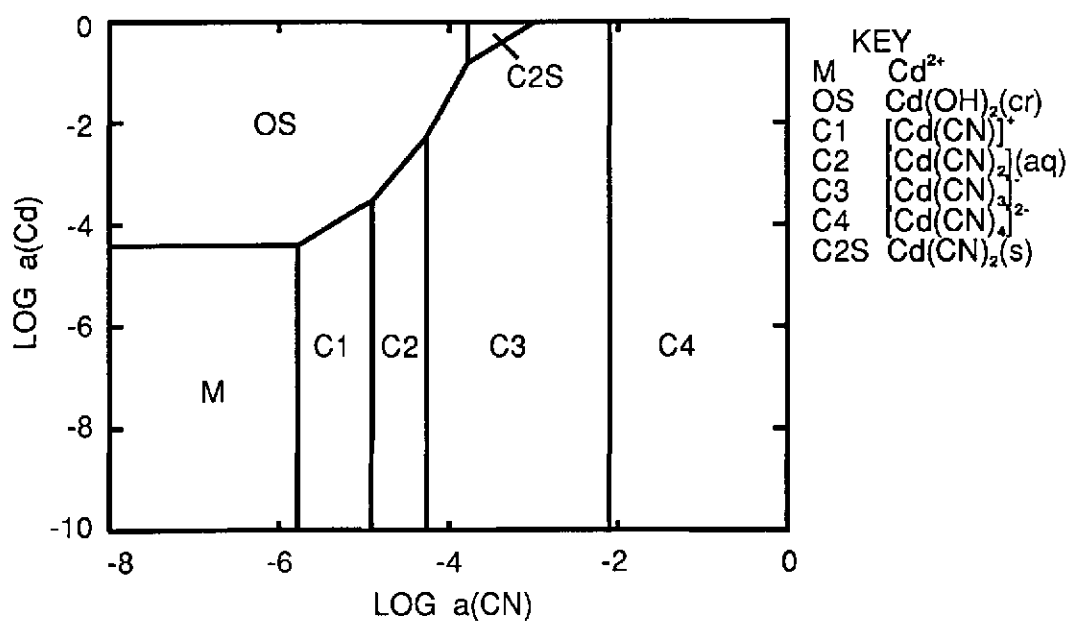
$p\text{Cd}$ - $p\text{CN}$ diagram for $\text{pH} = 11.0$.

Figure E-49



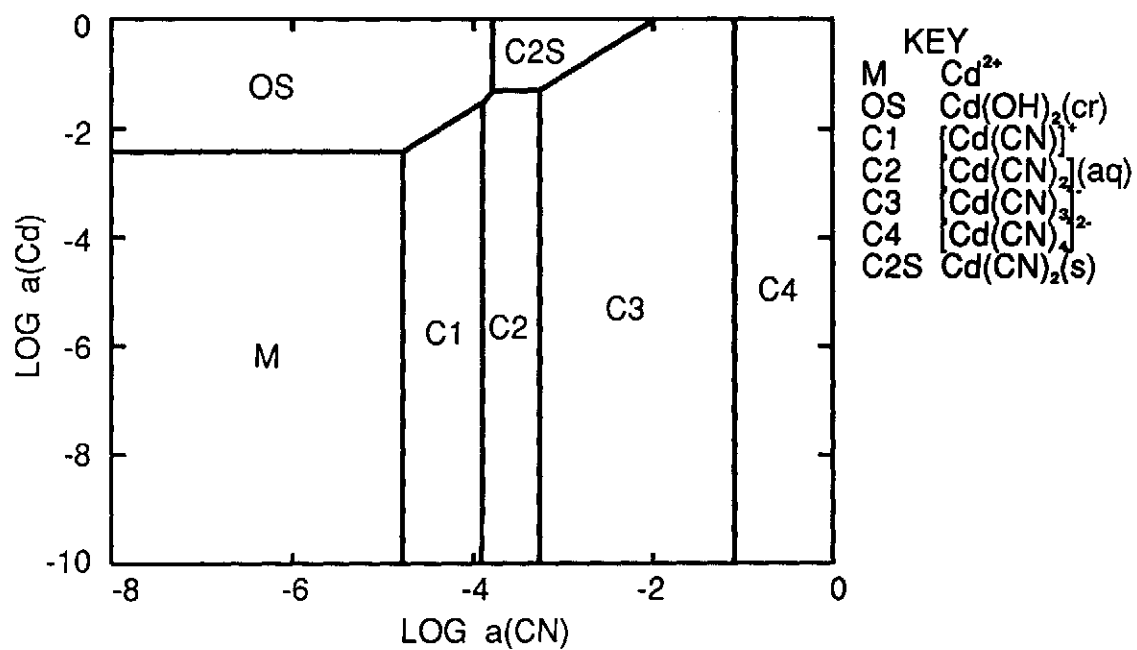
pCd-pCN diagram for pH = 10.0.

Figure E-50



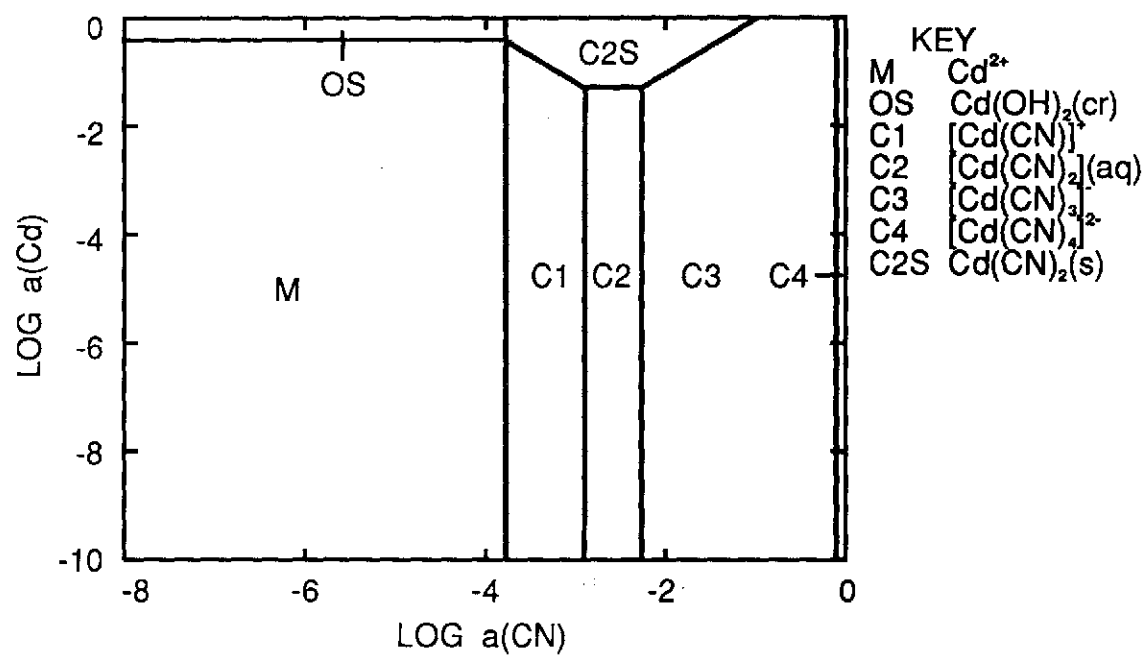
pCd-pCN diagram for pH = 9.0.

Figure E-51



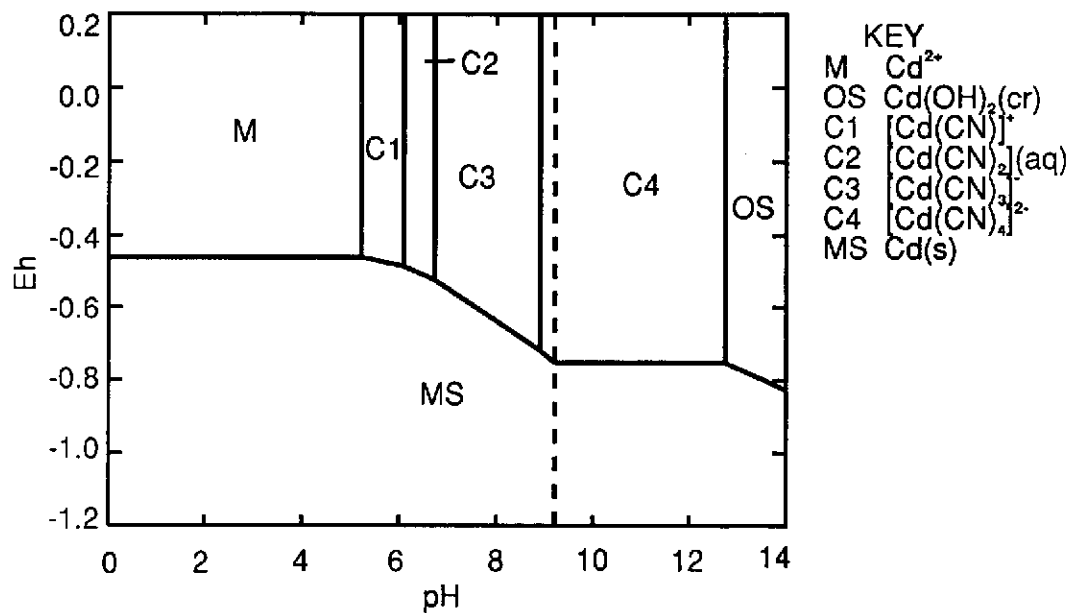
$p\text{Cd}$ - $p\text{CN}$ diagram for $\text{pH} = 8.0$.

Figure E-52



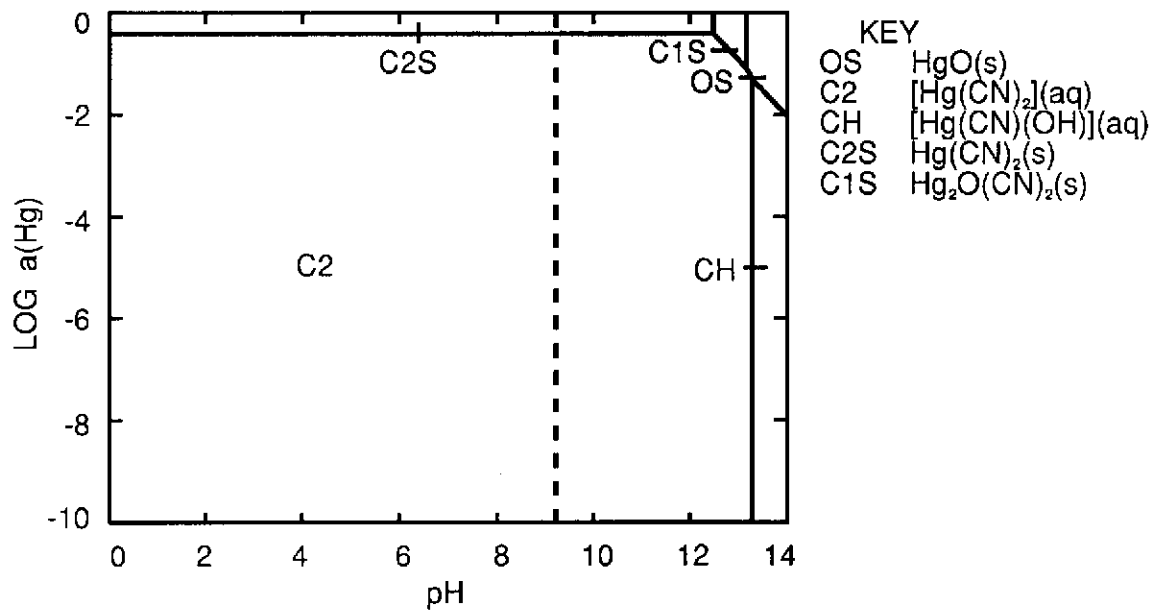
$p\text{Cd}$ - $p\text{CN}$ diagram for $\text{pH} = 7.0$.

Figure E-53



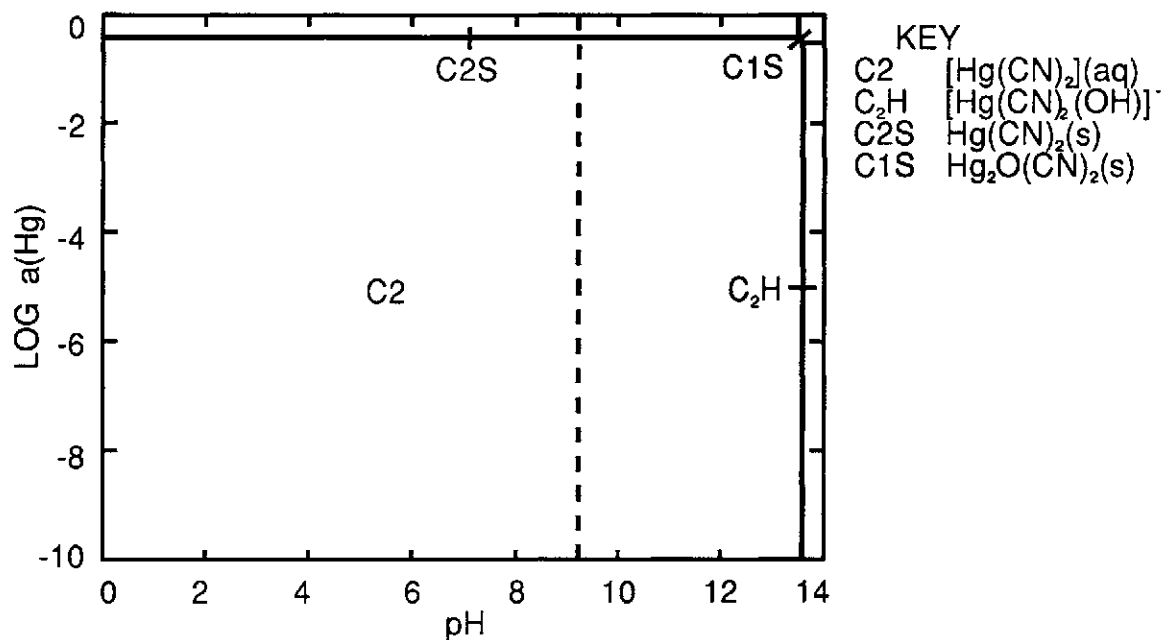
Eh-pH diagram for $p\text{Cd} = 2.0$ and $p\text{CN} = 2.0$.

Figure E-54



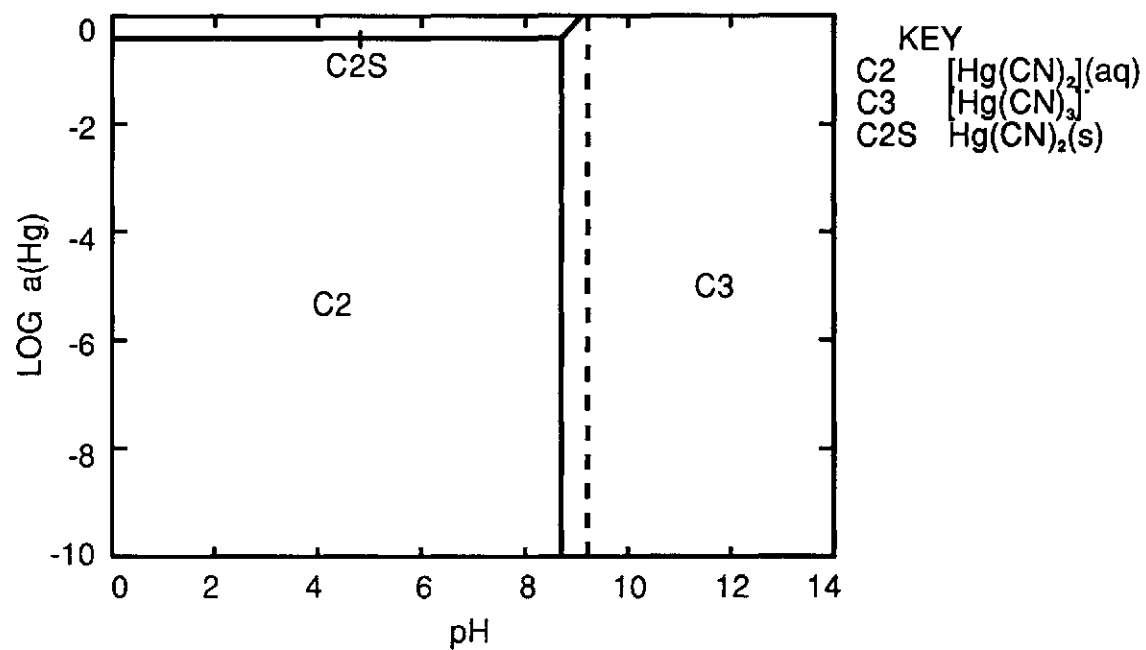
pHg-pH diagram for $p\text{CN} = 5.0$.

Figure E-55



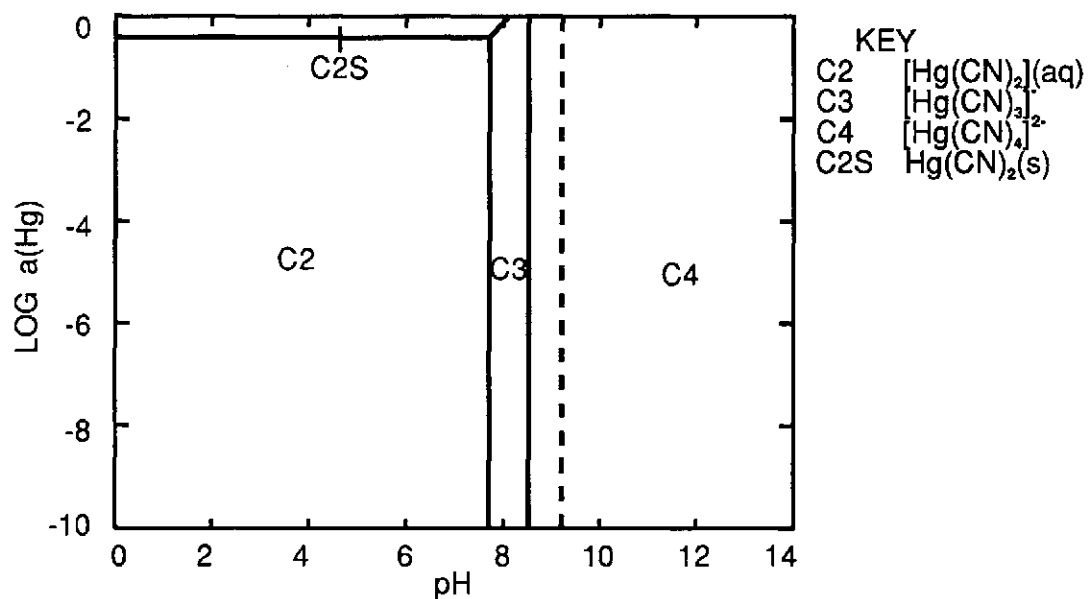
pHg-pH diagram for $p\text{CN} = 4.0$.

Figure E-56



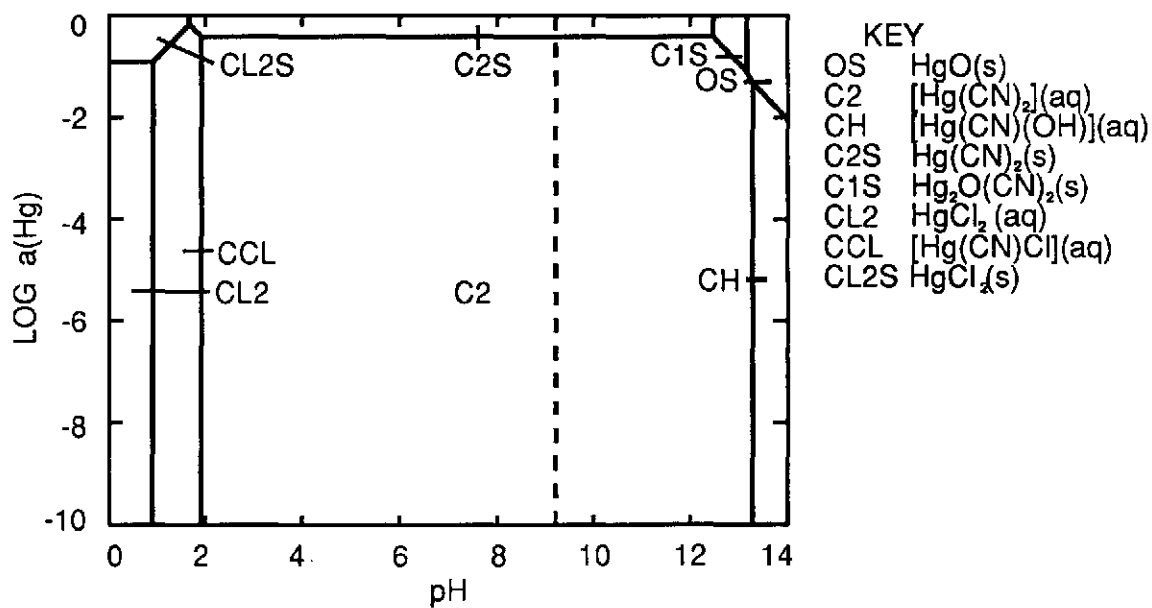
pHg-pH diagram for $p\text{CN} = 3.0$.

Figure E-57



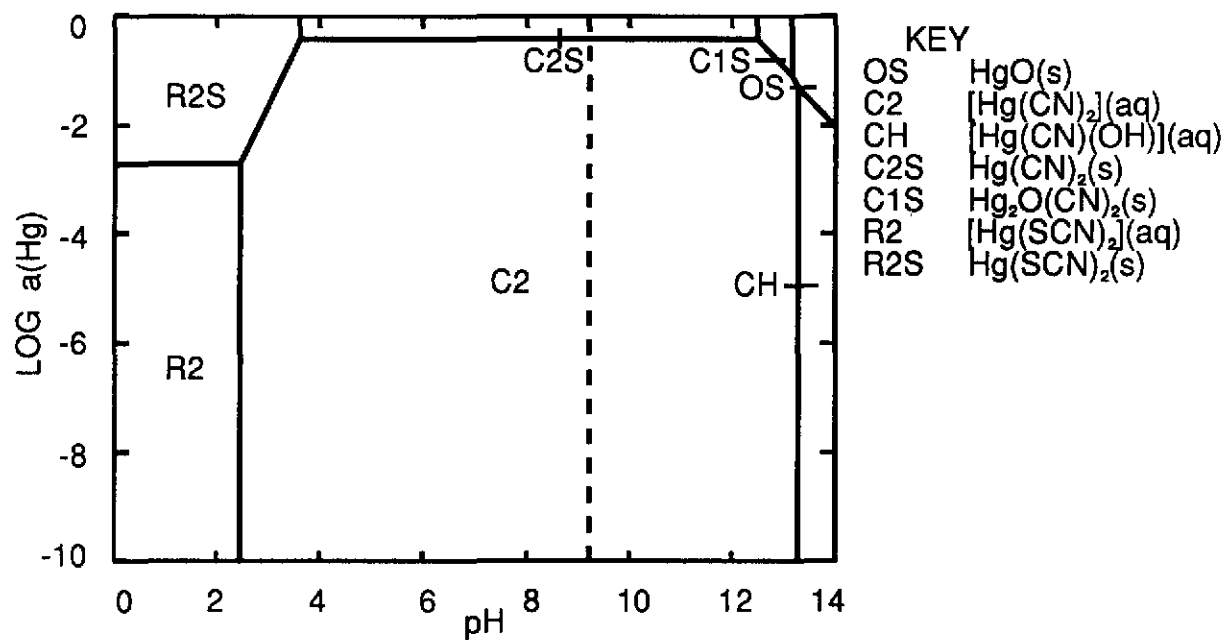
pHg-pH diagram for $p\text{CN} = 2.0$.

Figure E-58



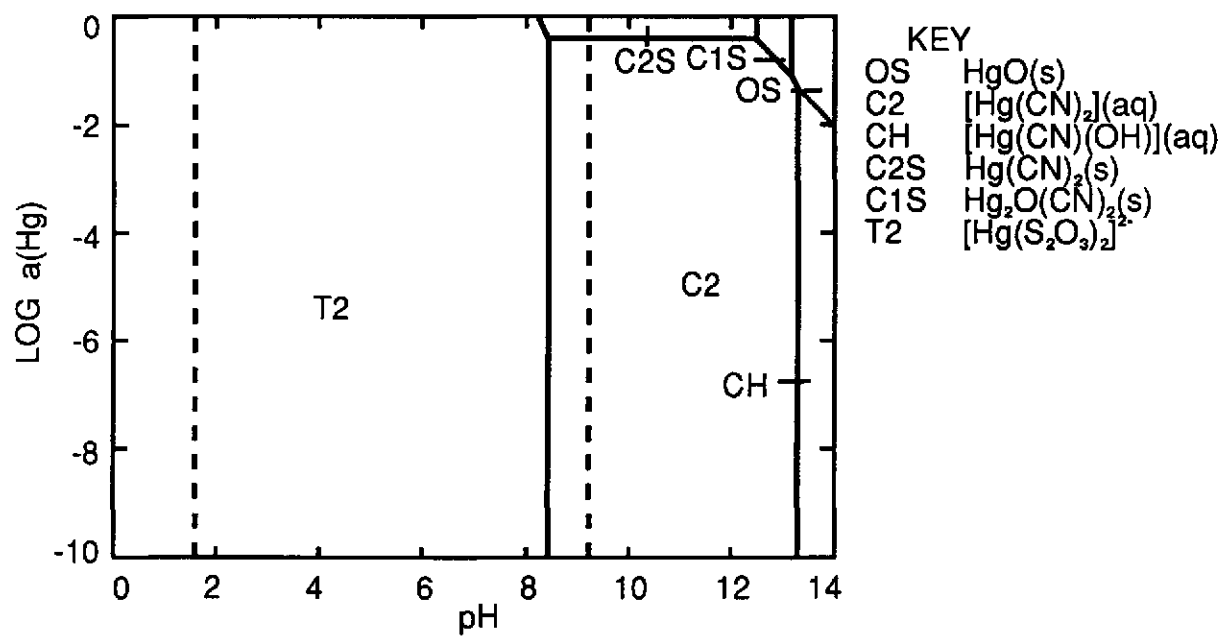
pHg-pH diagram for $p\text{CN} = 5.0$ and $p\text{Cl} = 3.0$.

Figure E-59



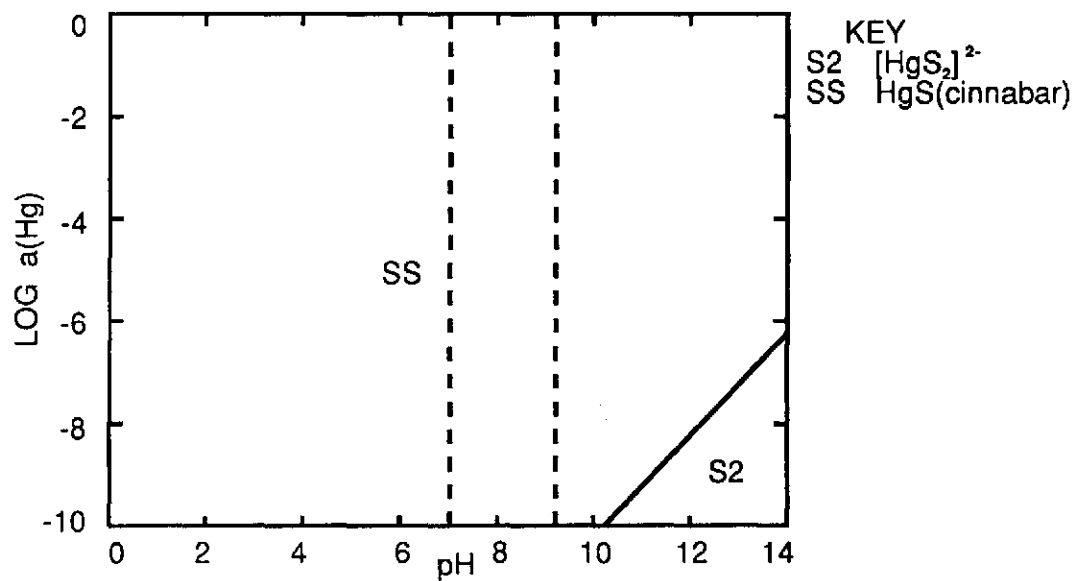
pHg-pH diagram for $p\text{CN} = 5.0$ and $p\text{SCN} = 4.0$.

Figure E-60



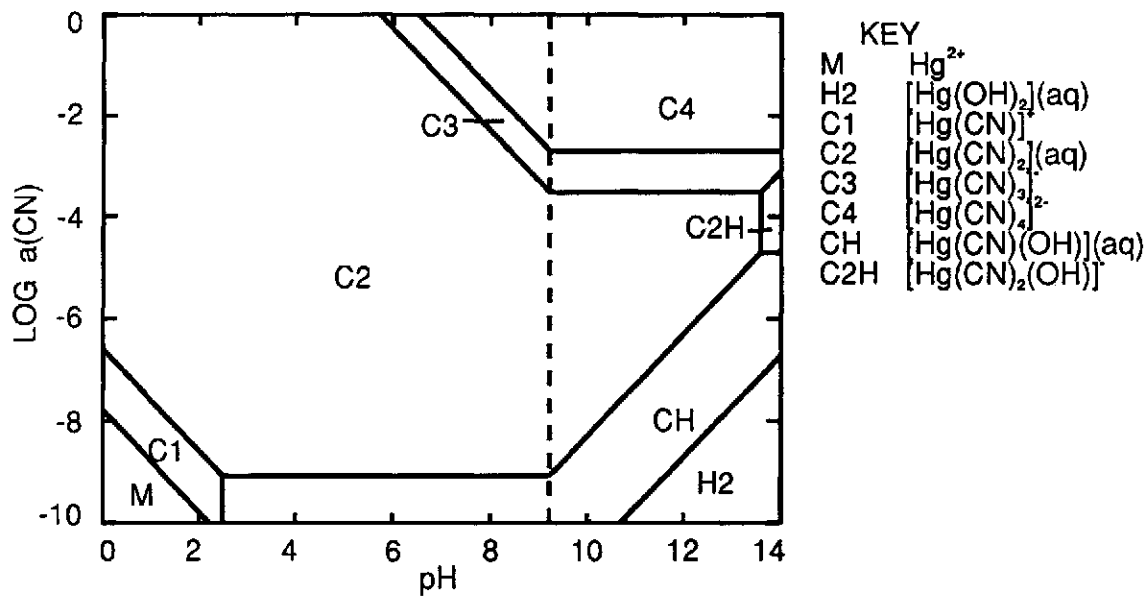
pHg-pH diagram for $p\text{CN} = 5.0$ and $p\text{S}_2\text{O}_3 = 4.0$.

Figure E-61



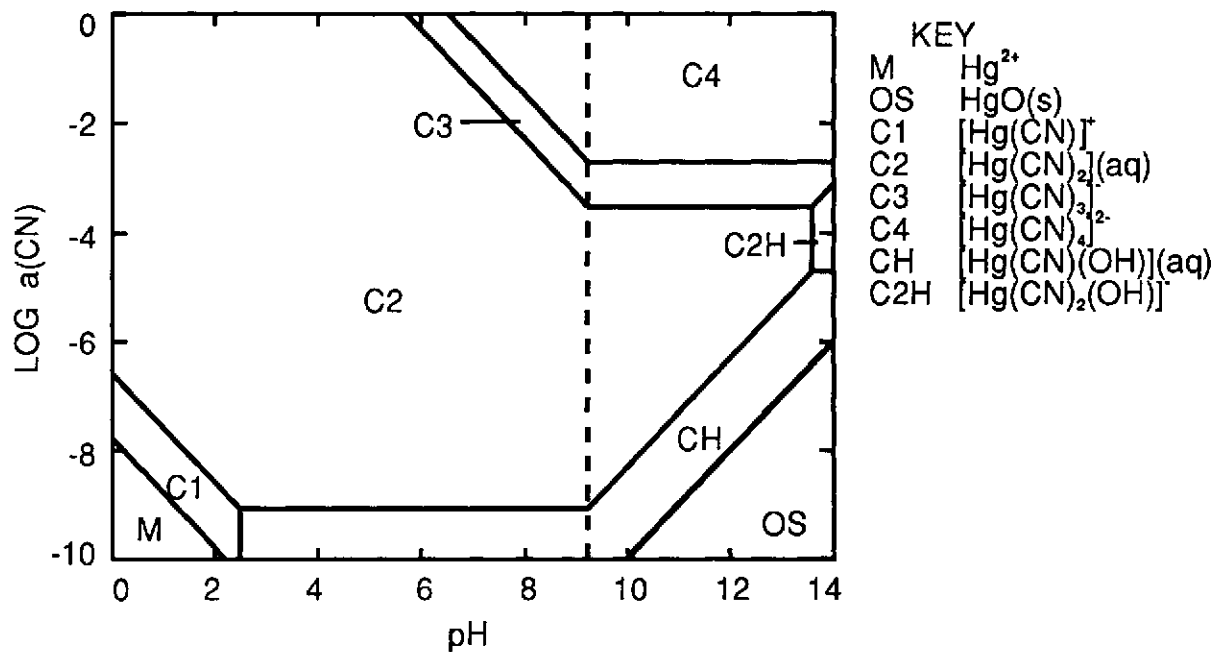
pHg-pH diagram for $p\text{CN} = 2.0$ and $p\text{SH} = 6.0$.

Figure E-62



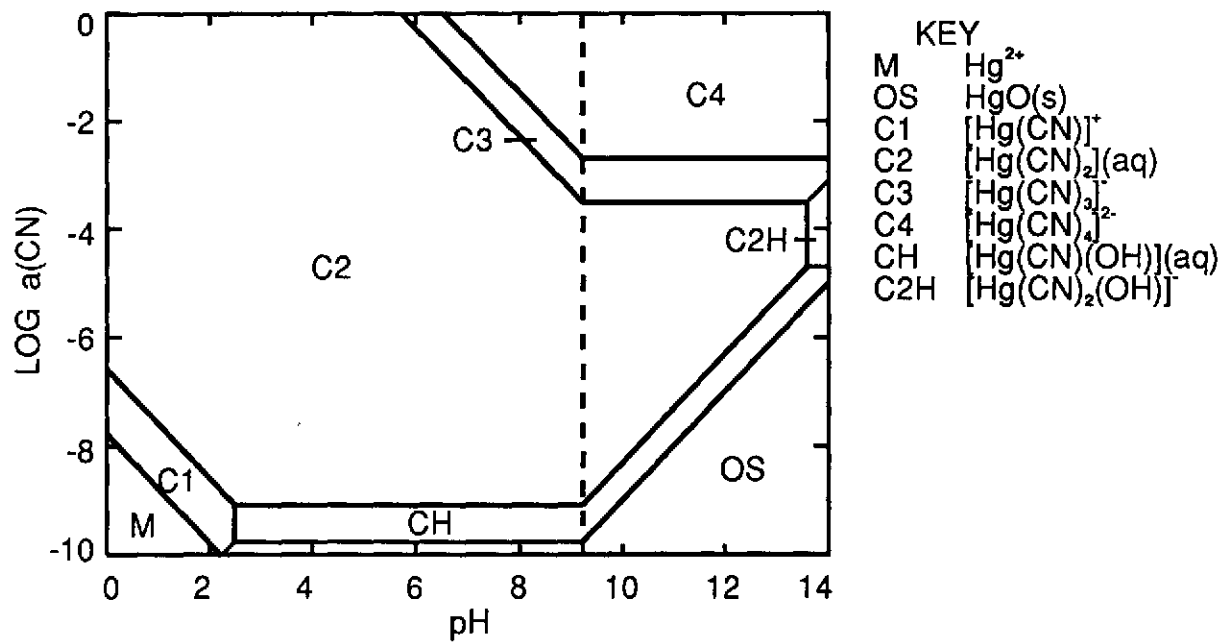
pCN-pH diagram for mercury solution species.

Figure E-63



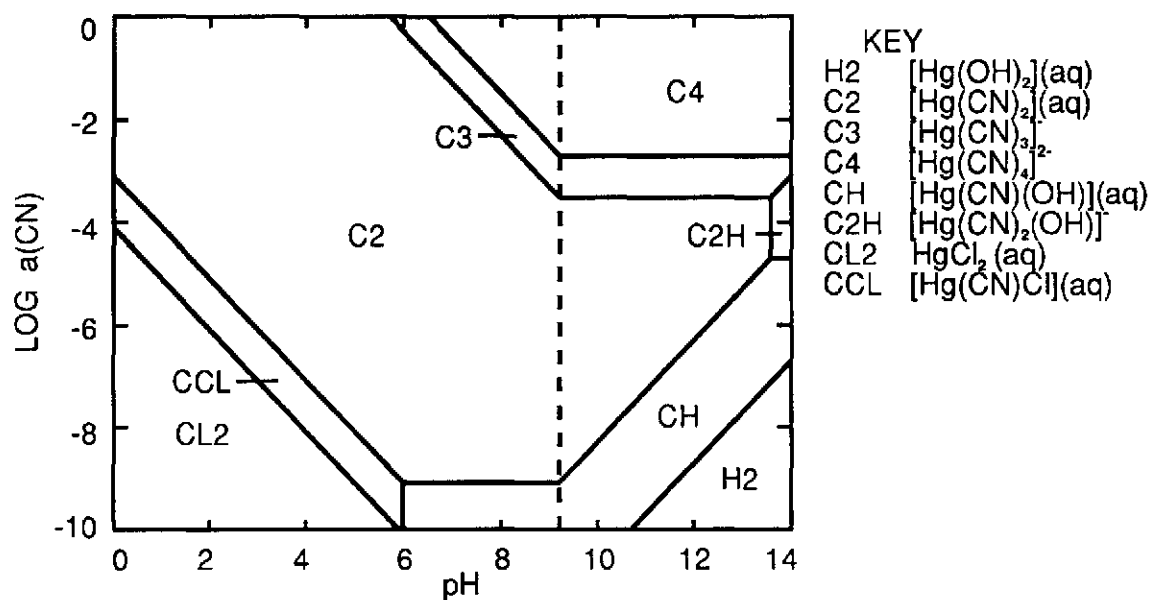
pCN-pH diagram for $\text{pH}_g = 3.0$.

Figure E-64



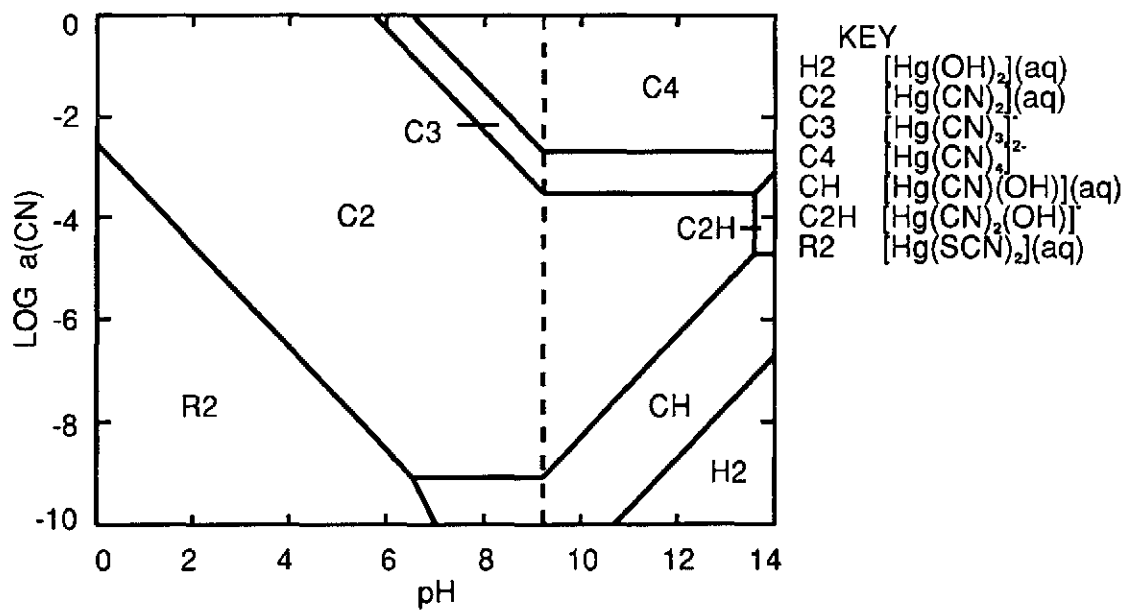
pCN-pH diagram for $\text{pH}_g = 2.0$.

Figure E-65



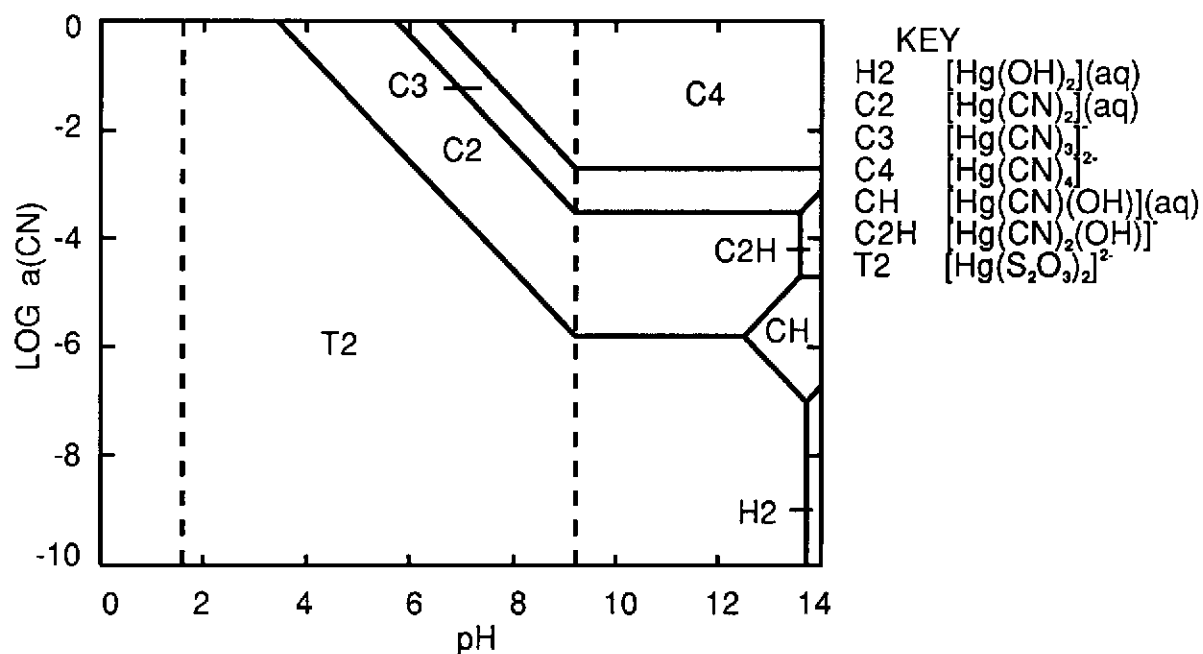
pCN-pH diagram for mercury solution species with $p\text{Cl} = 3.0$.

Figure E-66



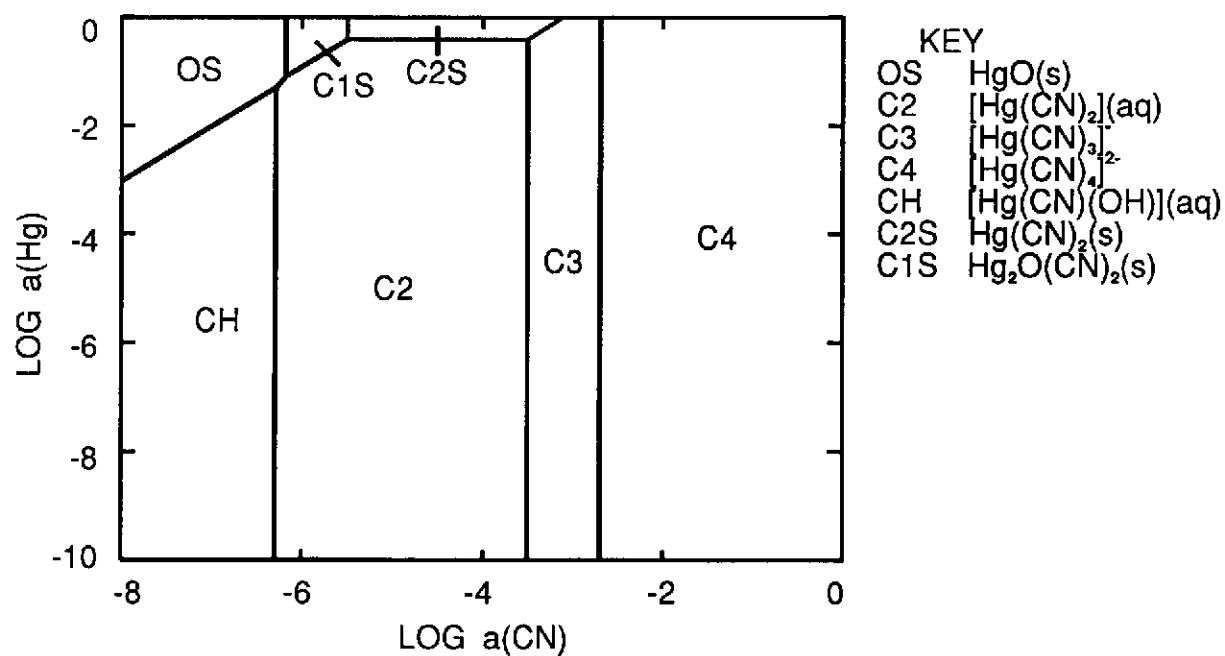
pCN-pH diagram for mercury solution species with $p\text{SCN} = 4.0$.

Figure E-67



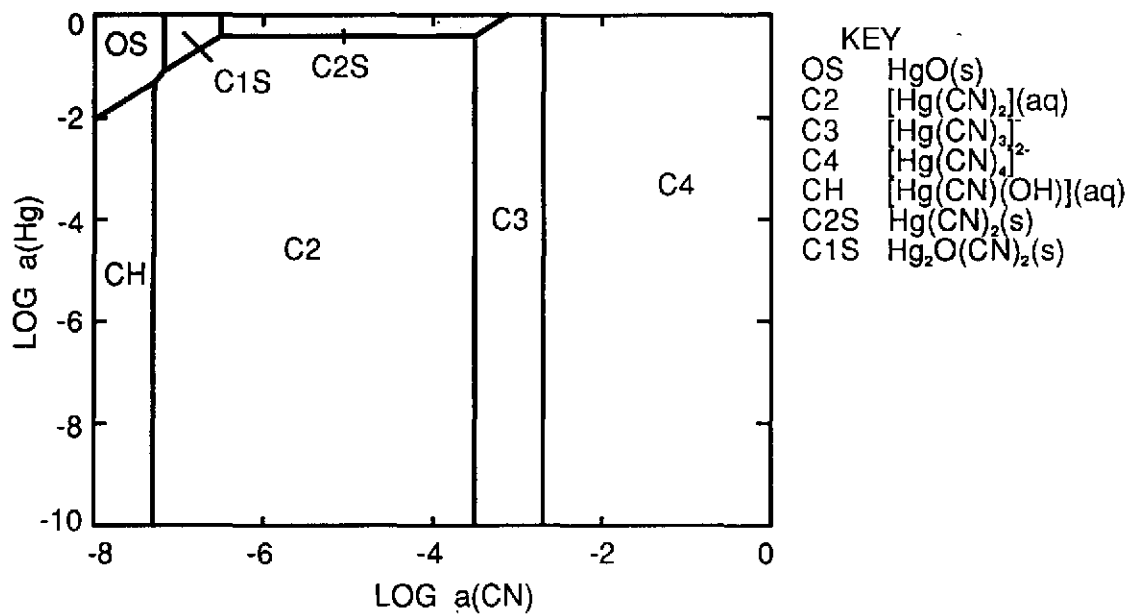
pCN-pH diagram for mercury solution species with $p\text{S}_2\text{O}_3 = 4.0$.

Figure E-68



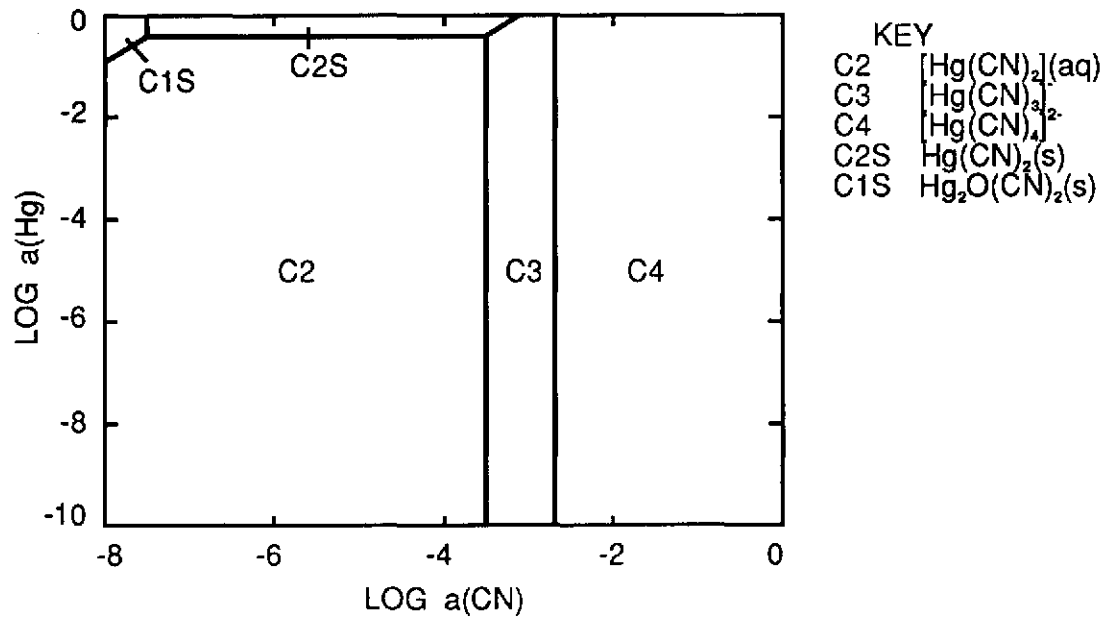
pHg-pCN diagram for $\text{pH} = 12.0$.

Figure E-69



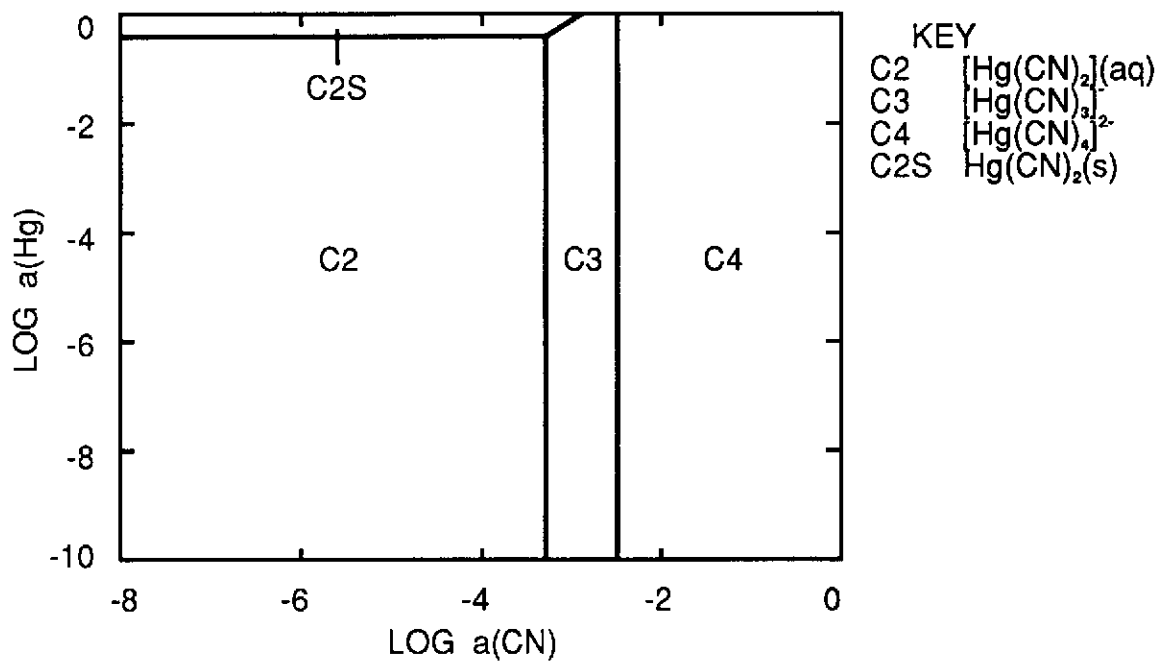
pHg-pCN diagram for pH = 11.0.

Figure E-70



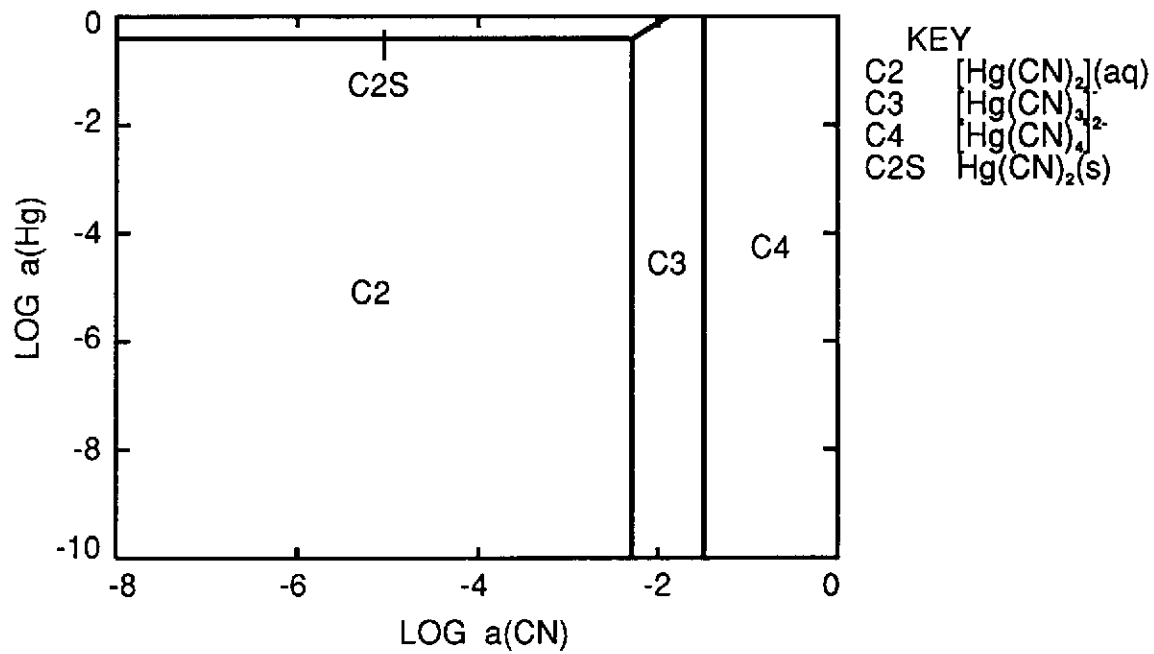
pHg-pCN diagram for pH = 10.0.

Figure E-71



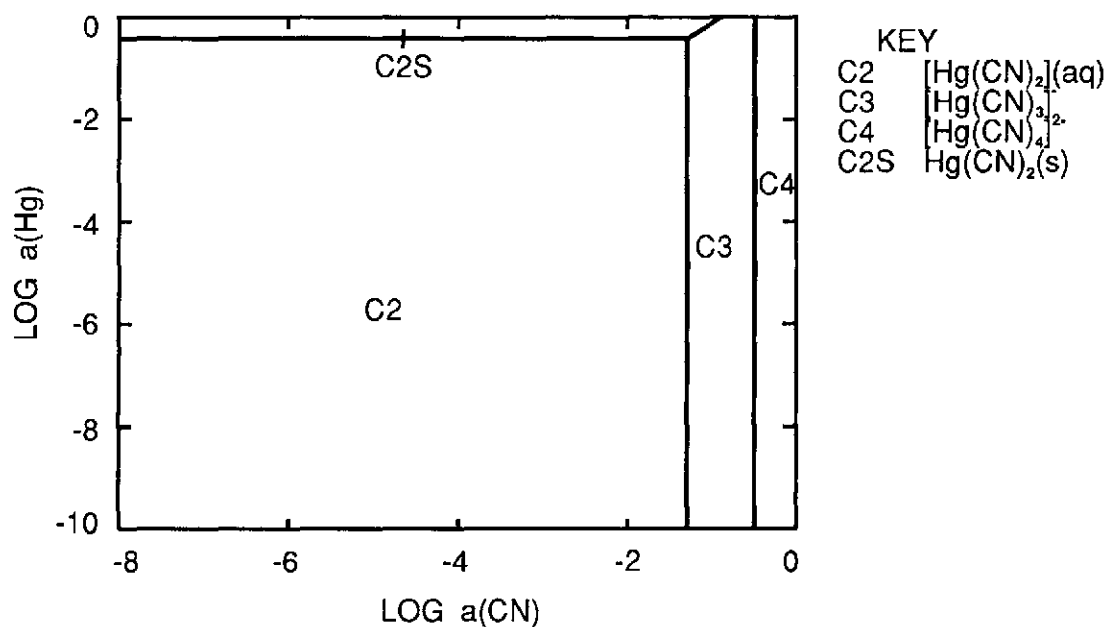
pHg-pCN diagram for pH = 9.0.

Figure E-72



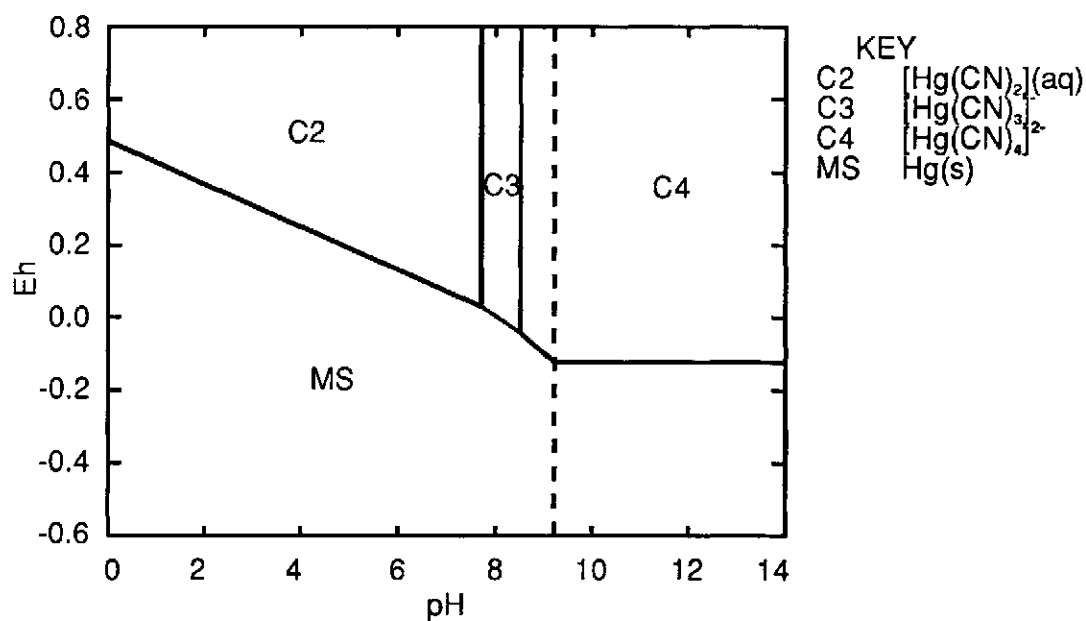
pHg-pCN diagram for pH = 8.0.

Figure E-73



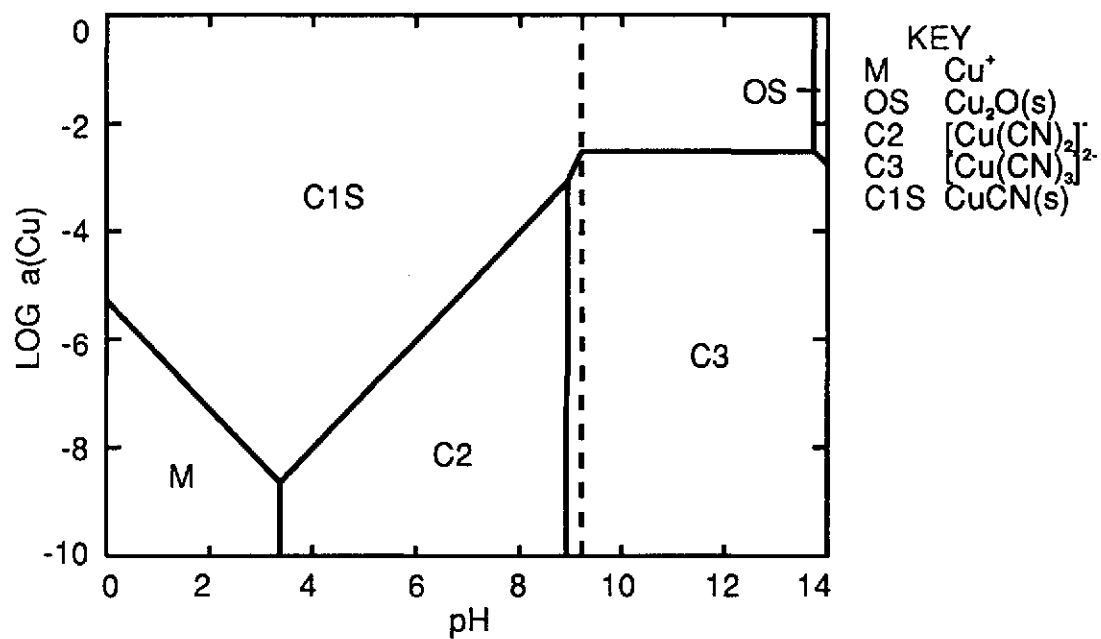
pHg-pCN diagram for pH = 7.0.

Figure E-74



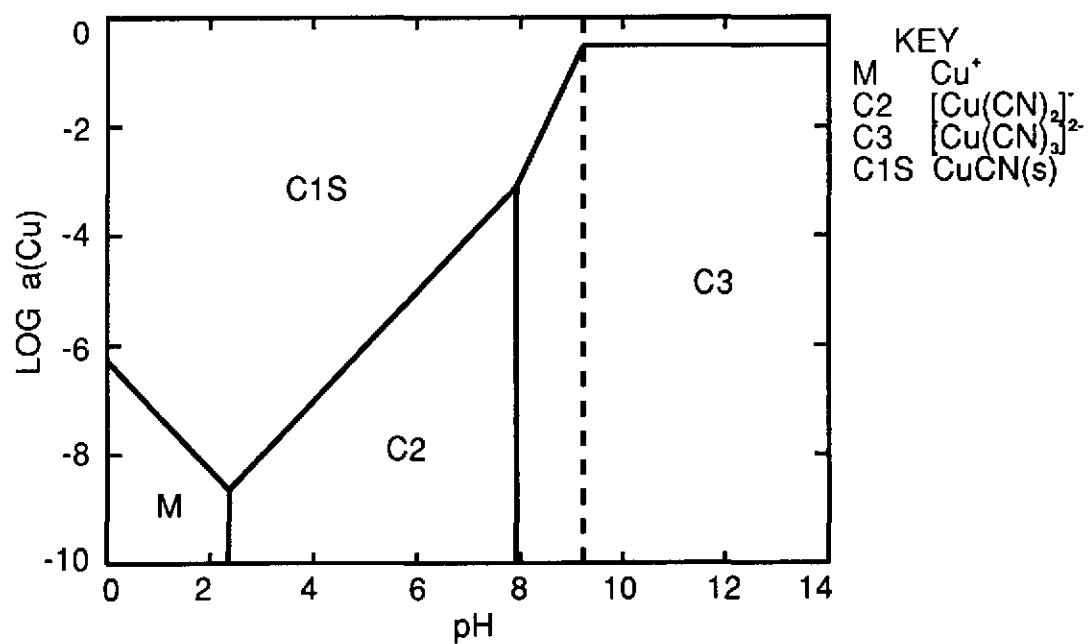
Eh-pH diagram for pHg = 2.0 and pCN = 2.0.

Figure E-75



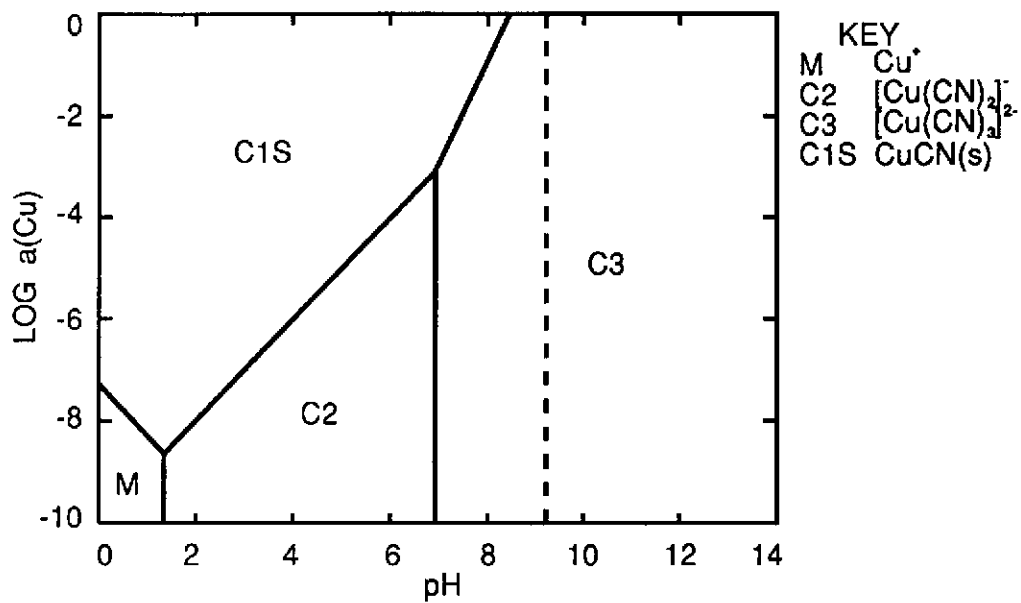
$p\text{Cu(I)}$ - pH diagram for $p\text{CN} = 5.0$.

Figure E-76



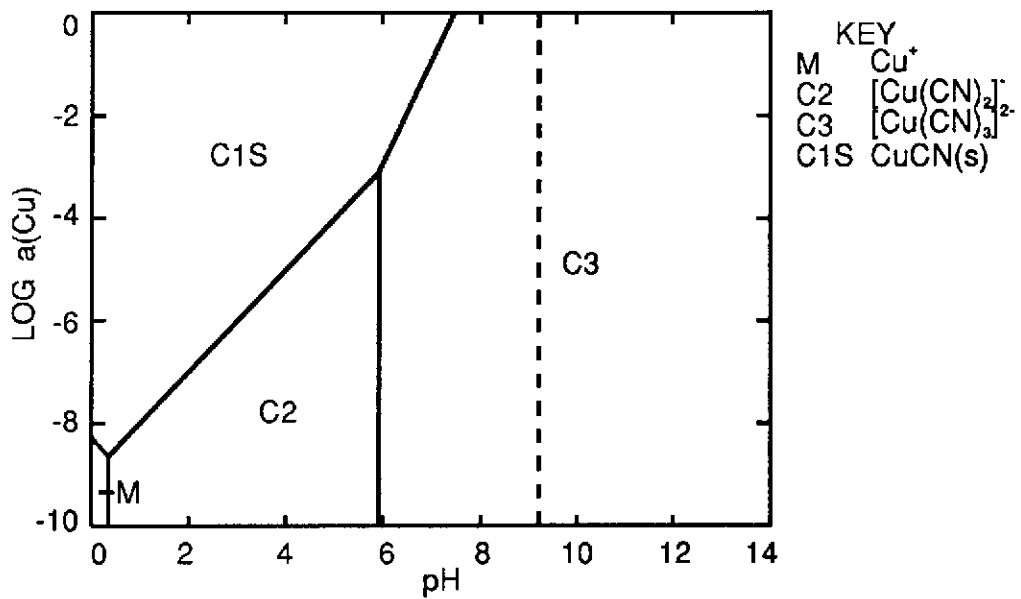
$p\text{Cu(I)}$ - pH diagram for $p\text{CN} = 4.0$.

Figure E-77



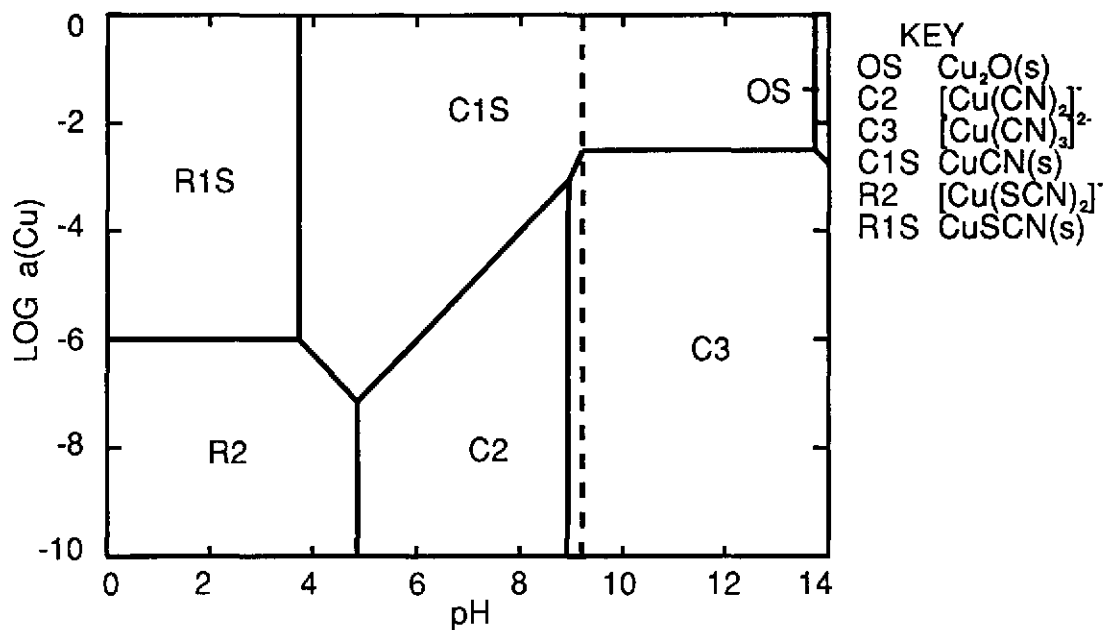
$p\text{Cu(I)}$ - pH diagram for $p\text{CN} = 3.0$.

Figure E-78



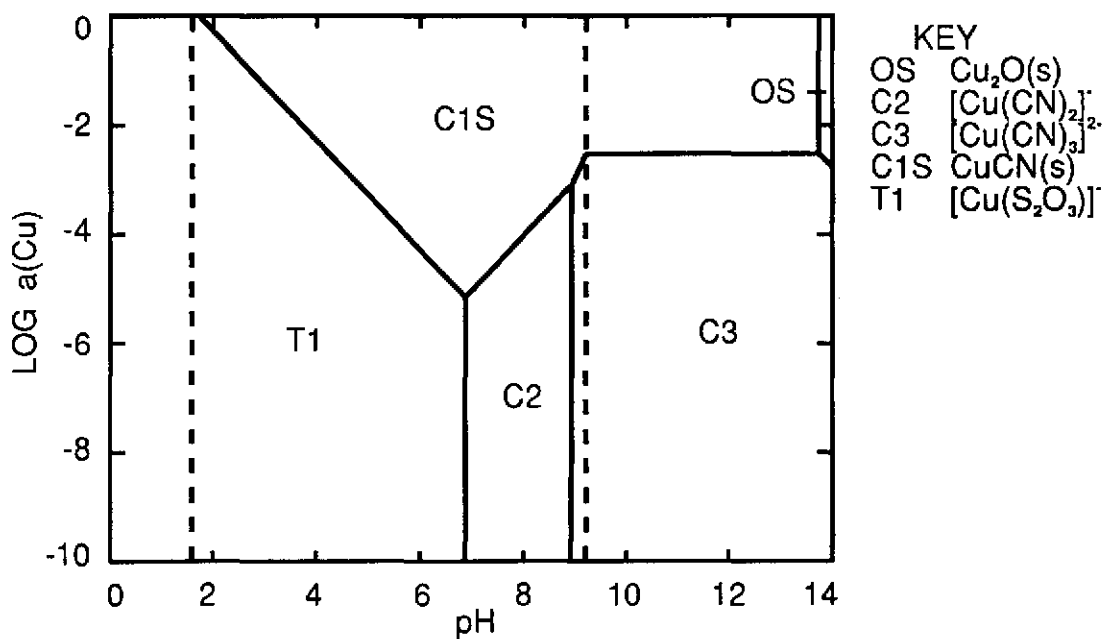
$p\text{Cu(I)}$ - pH diagram for $p\text{CN} = 2.0$.

Figure E-79



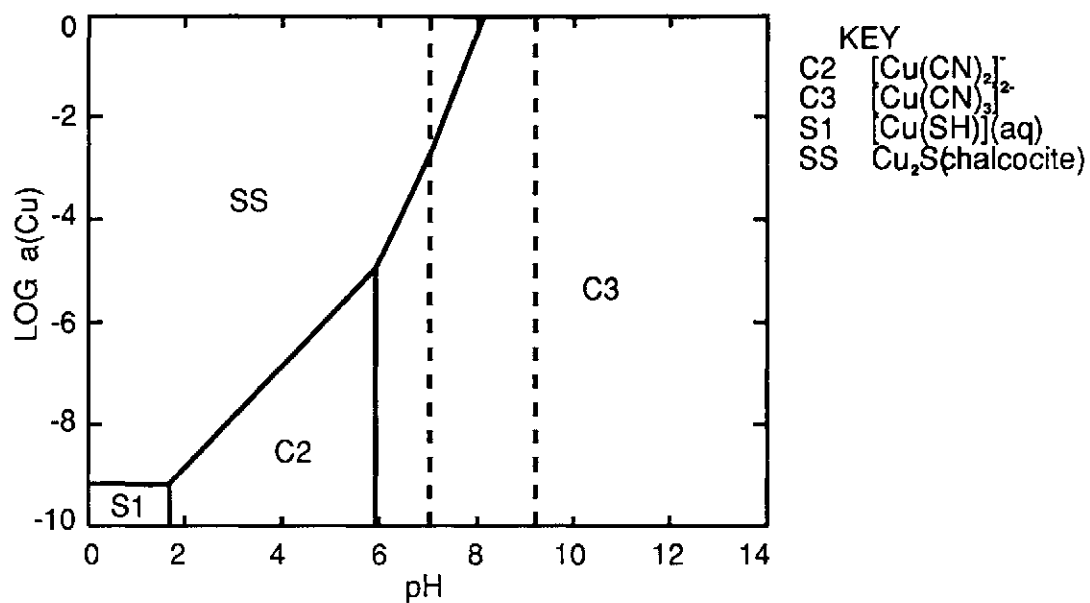
pCu(I)-pH diagram for $p\text{CN} = 5.0$ and $p\text{SCN} = 4.0$.

Figure E-80



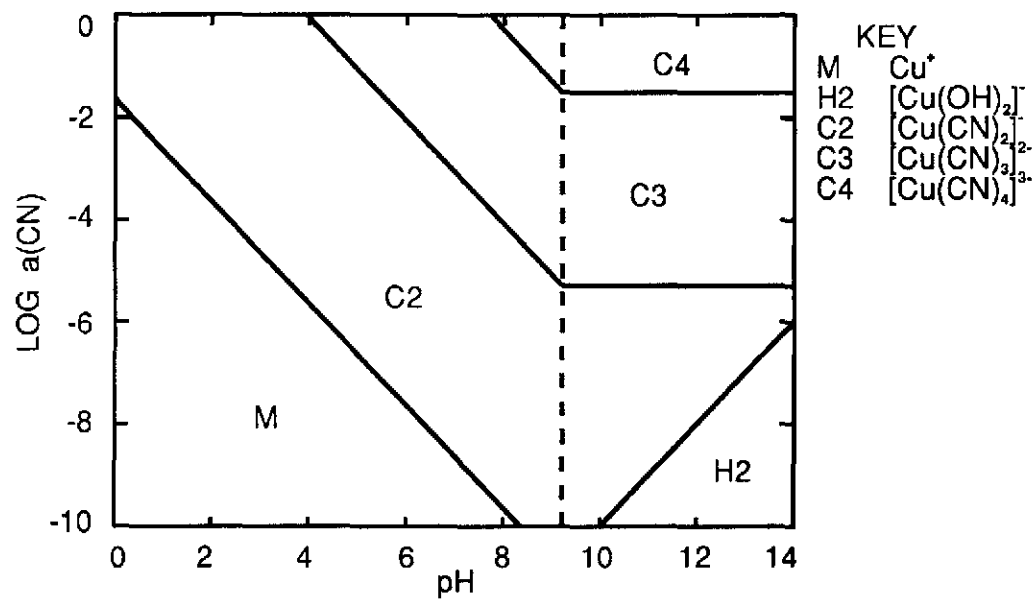
pCu(I)-pH diagram for $p\text{CN} = 5.0$ and $p\text{S}_2\text{O}_3 = 4.0$.

Figure E-81



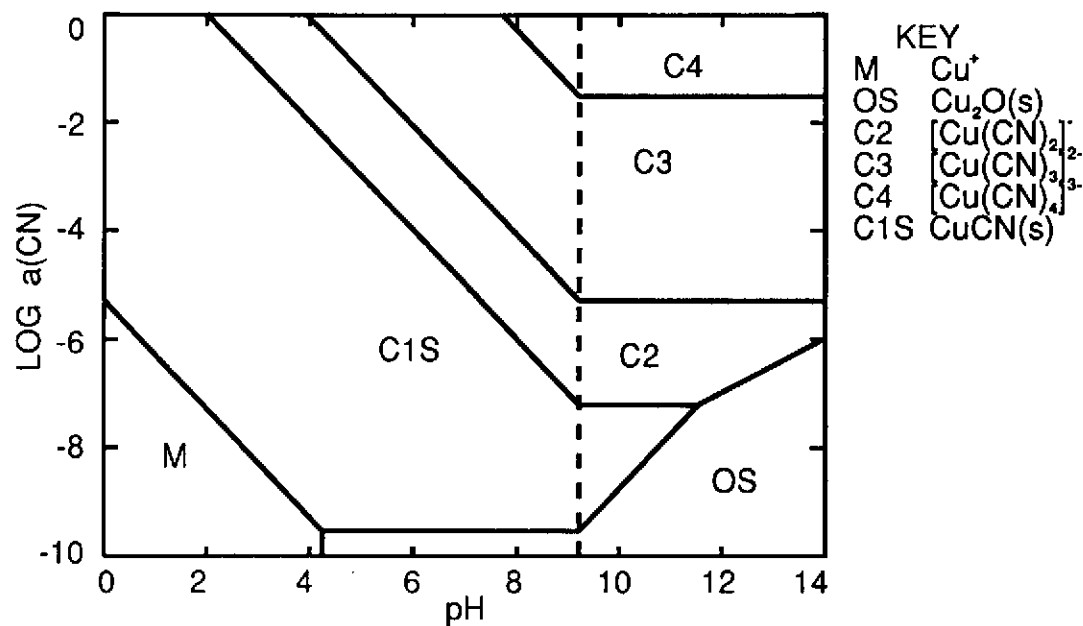
pCu(1)-pH diagram for $p\text{CN} = 2.0$ and $p\text{SH} = 6.0$.

Figure E-82



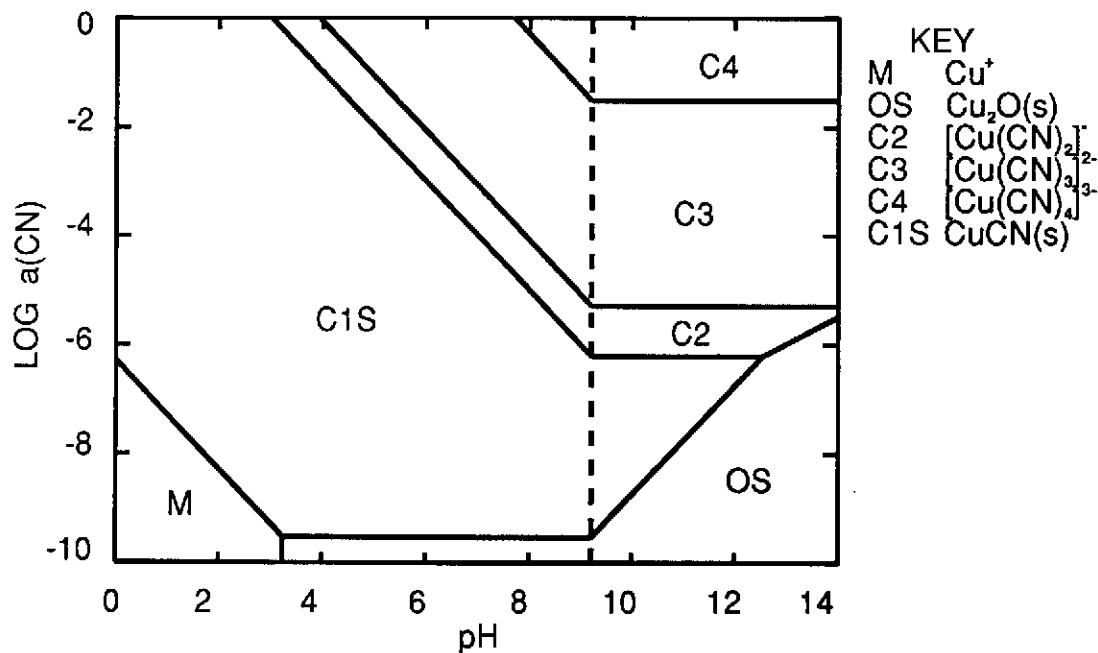
pCN-pH diagram for copper(I) solution species.

Figure E-83



pCN-pH diagram for $p\text{Cu(I)} = 5.0$.

Figure E-84



pCN-pH diagram for $p\text{Cu(I)} = 4.0$.

Figure E-85

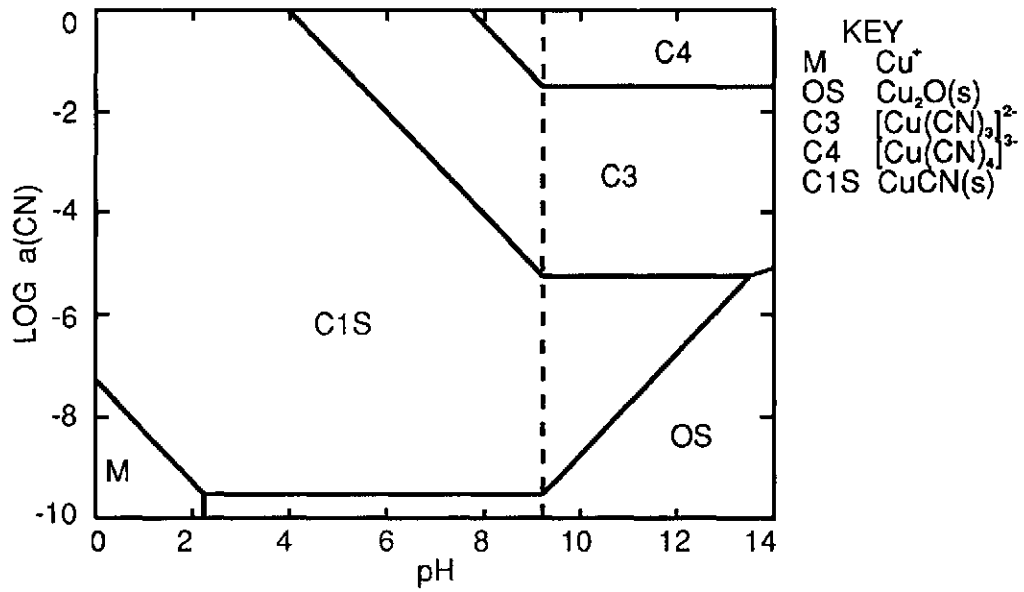


Figure E-86

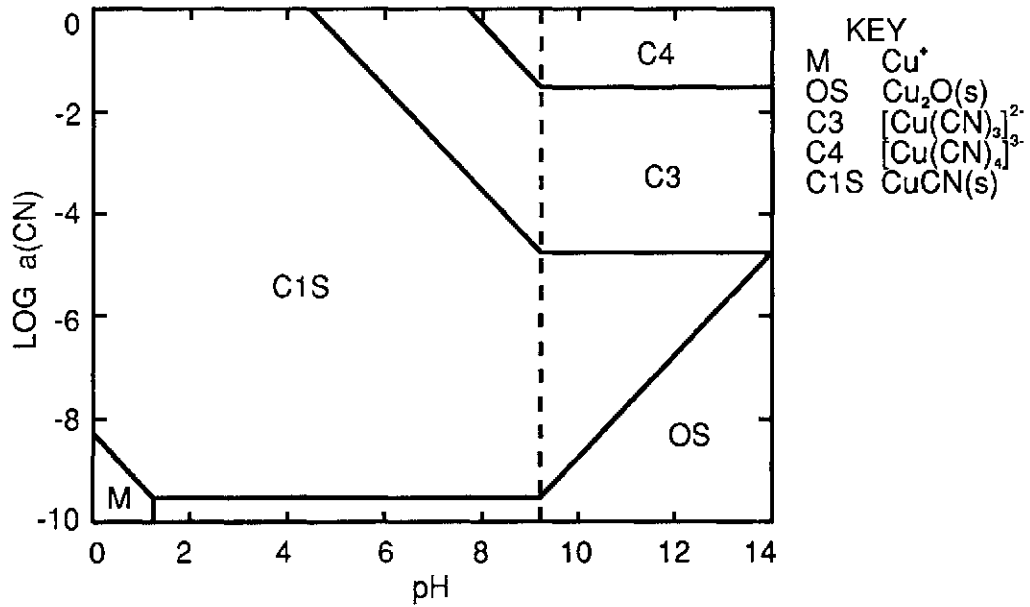
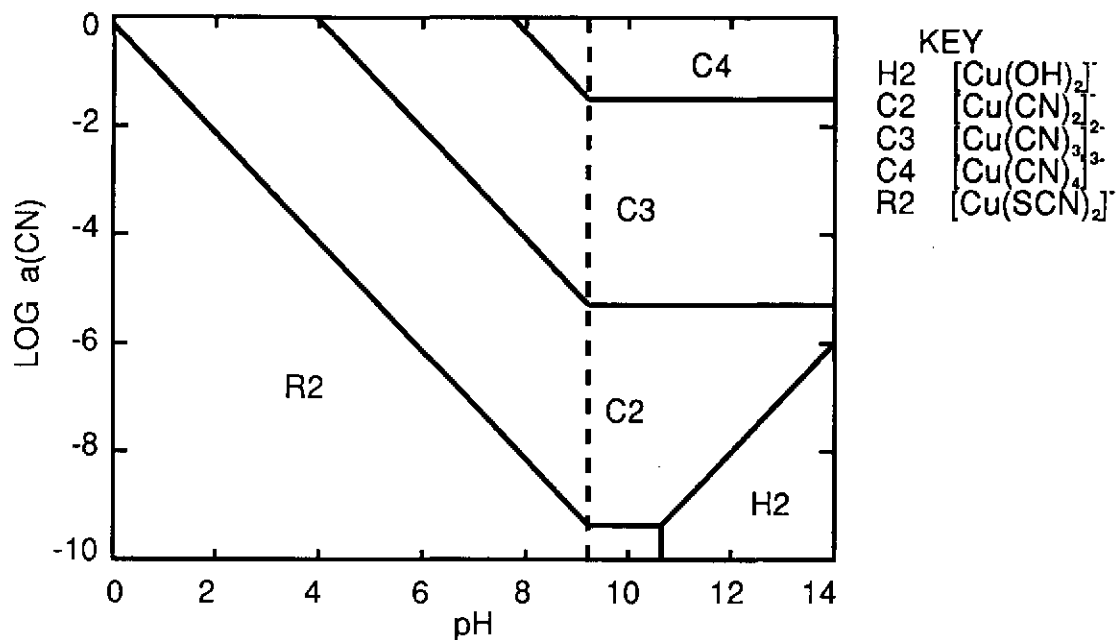
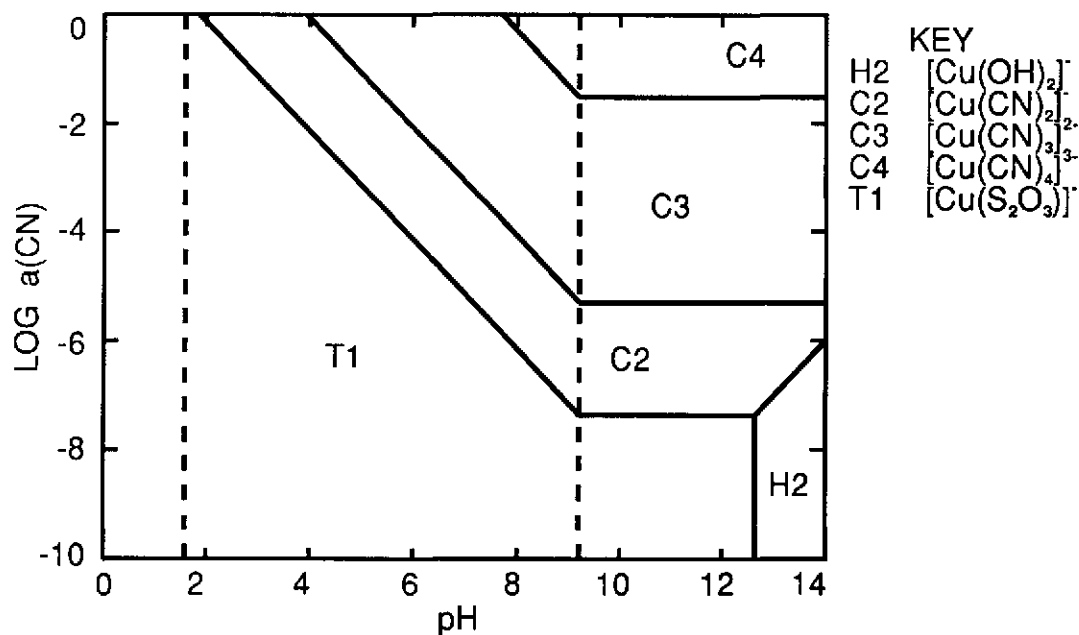


Figure E-87



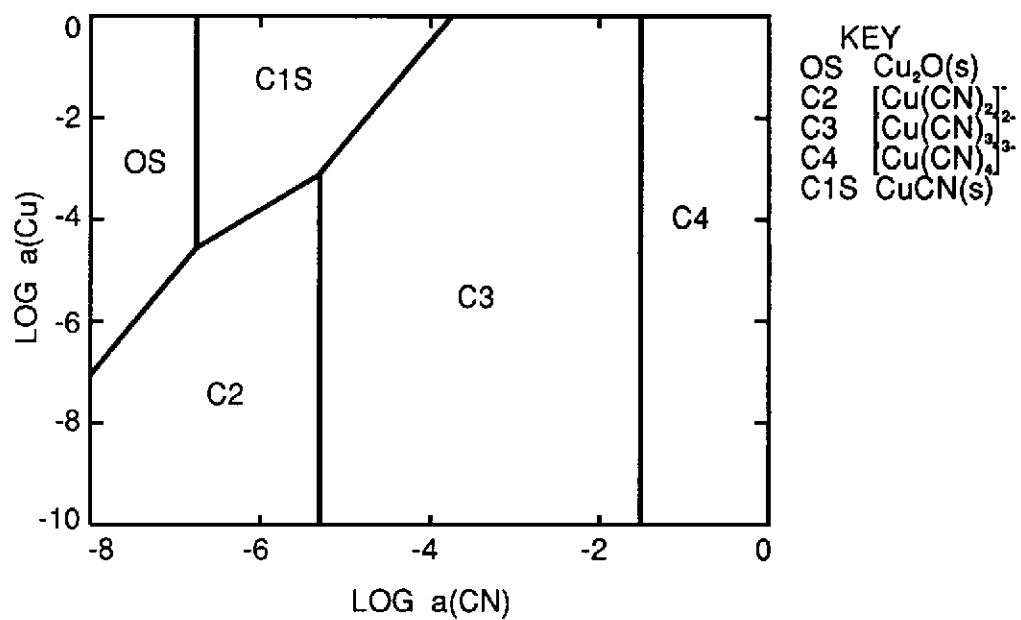
pCN-pH diagram for copper(I) solution species with $p\text{SCN} = 4.0$.

Figure E-88



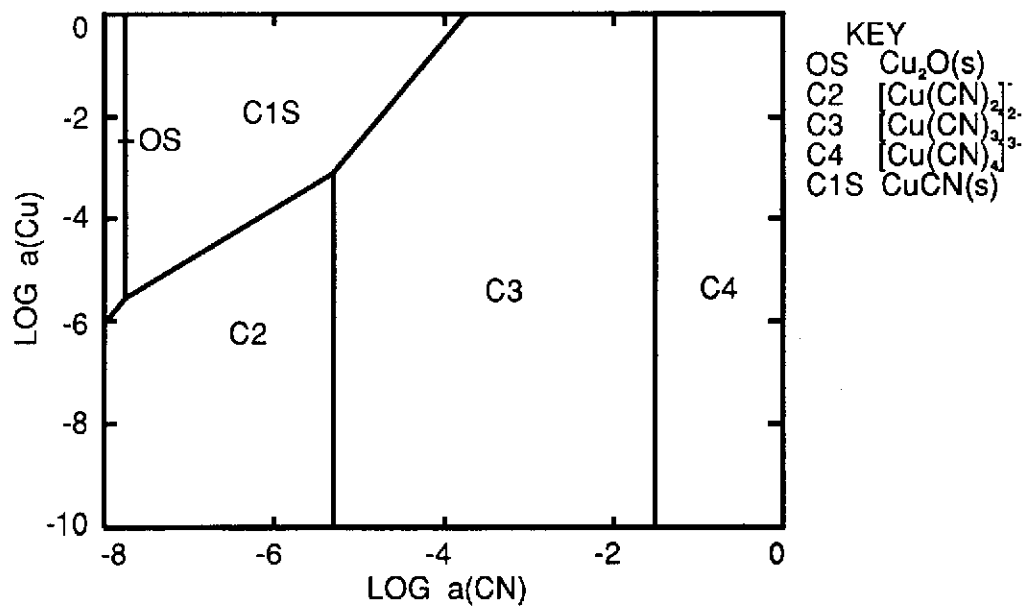
pCN-pH diagram for copper(I) solution species with $p\text{S}_2\text{O}_3 = 4.0$.

Figure E-89



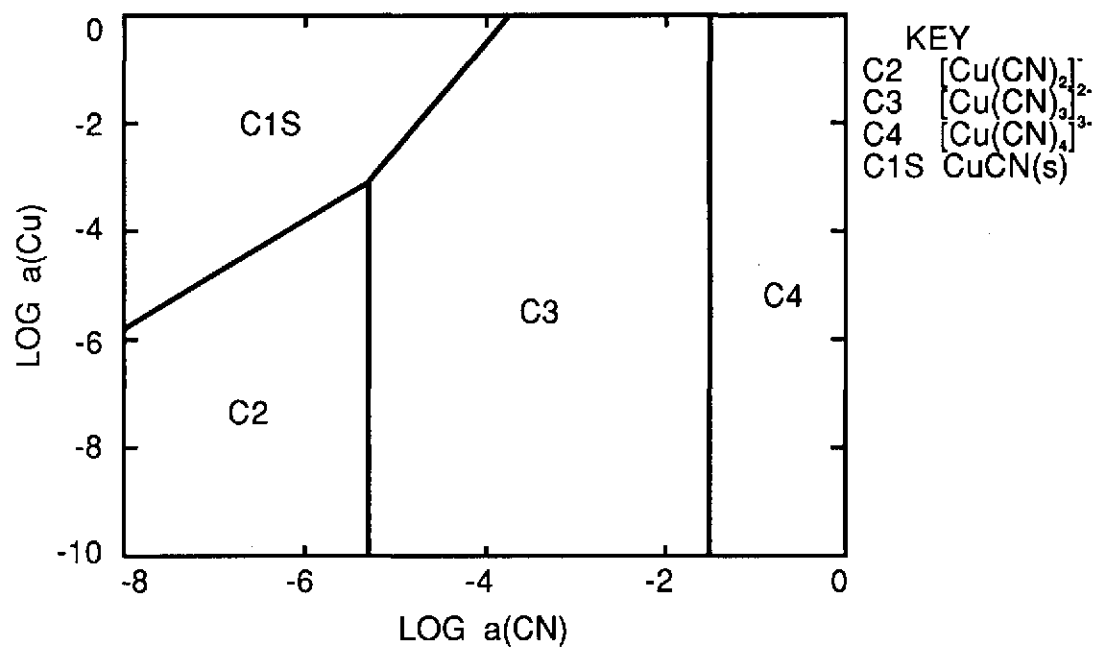
$p\text{Cu(I)}-p\text{CN}$ diagram for $\text{pH} = 12.0$.

Figure E-90



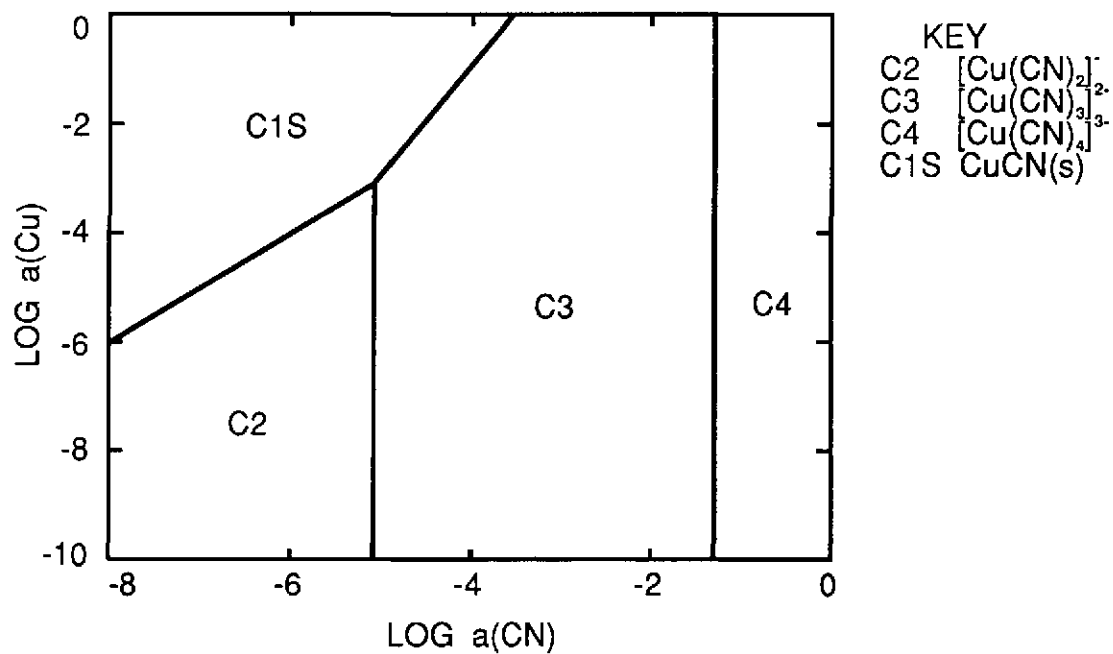
$p\text{Cu(I)}-p\text{CN}$ diagram for $\text{pH} = 11.0$.

Figure E-91



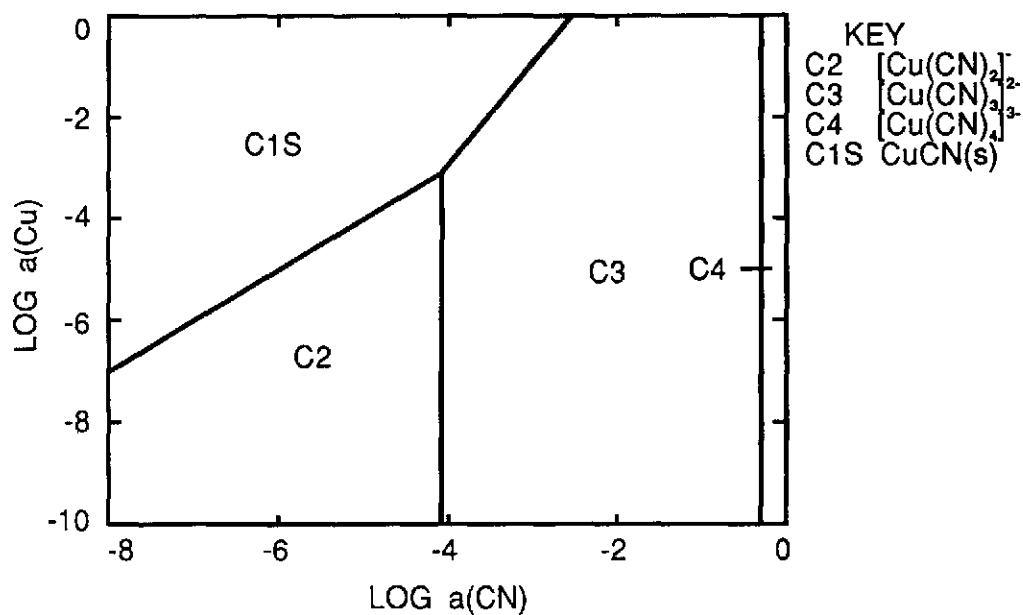
pCu(I)-pCN diagram for pH = 10.0.

Figure E-92



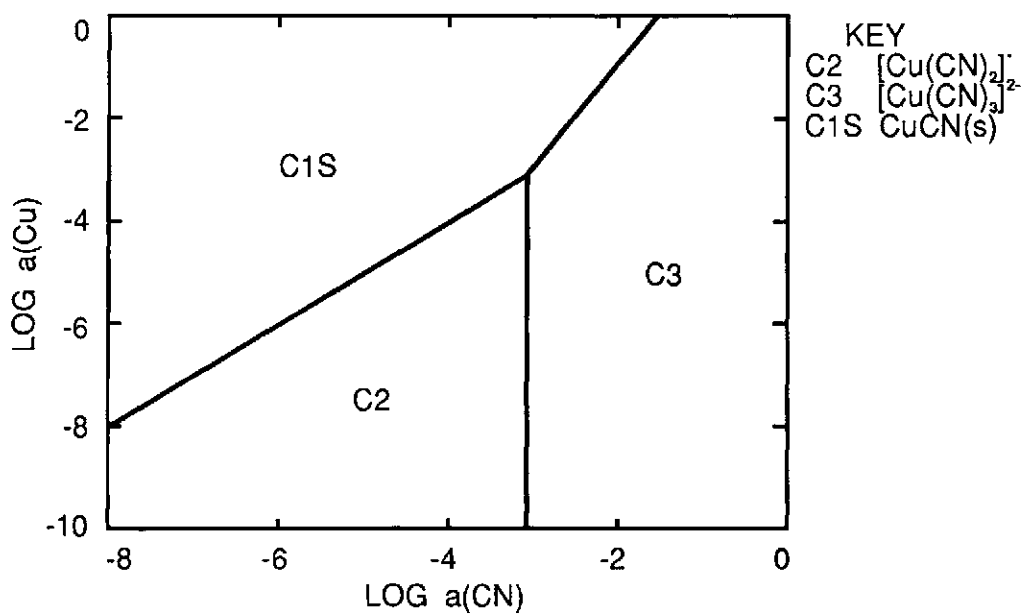
pCu(I)-pCN diagram for pH = 9.0.

Figure E-93



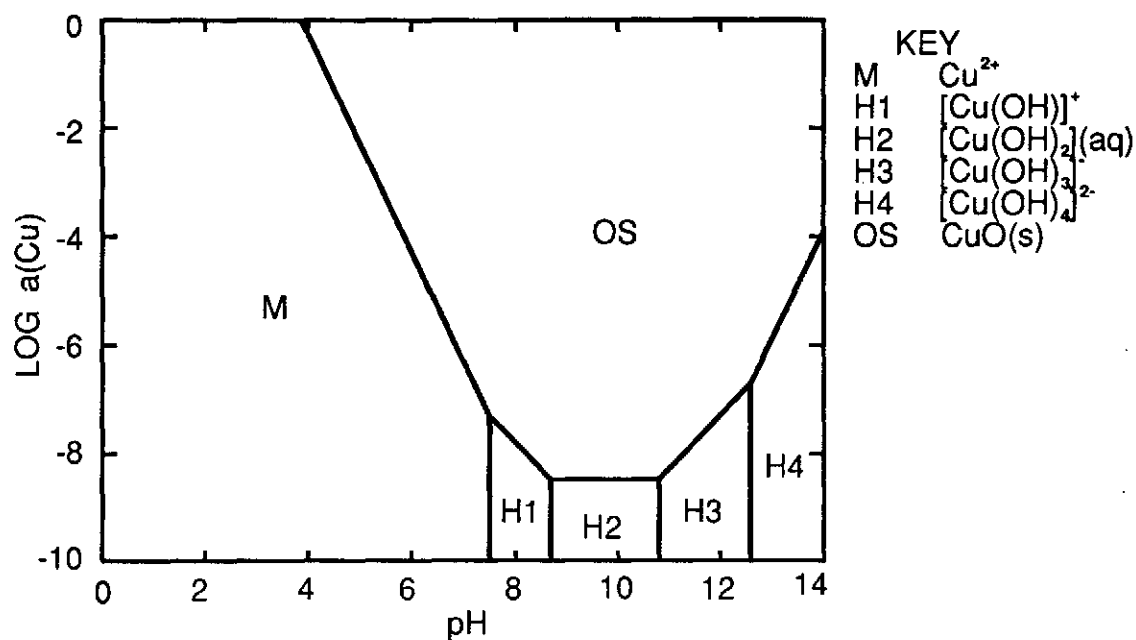
$p\text{Cu(I)}-p\text{CN}$ diagram for $\text{pH} = 8.0$.

Figure E-94



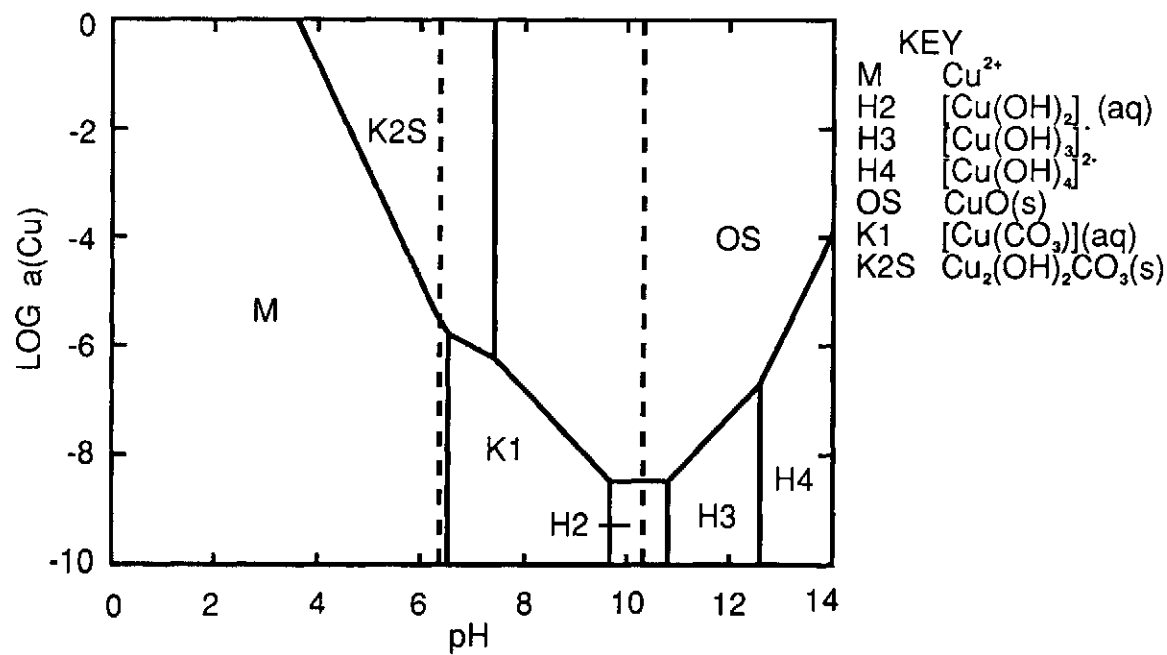
$p\text{Cu(I)}-p\text{CN}$ diagram for $\text{pH} = 7.0$.

Figure E-95



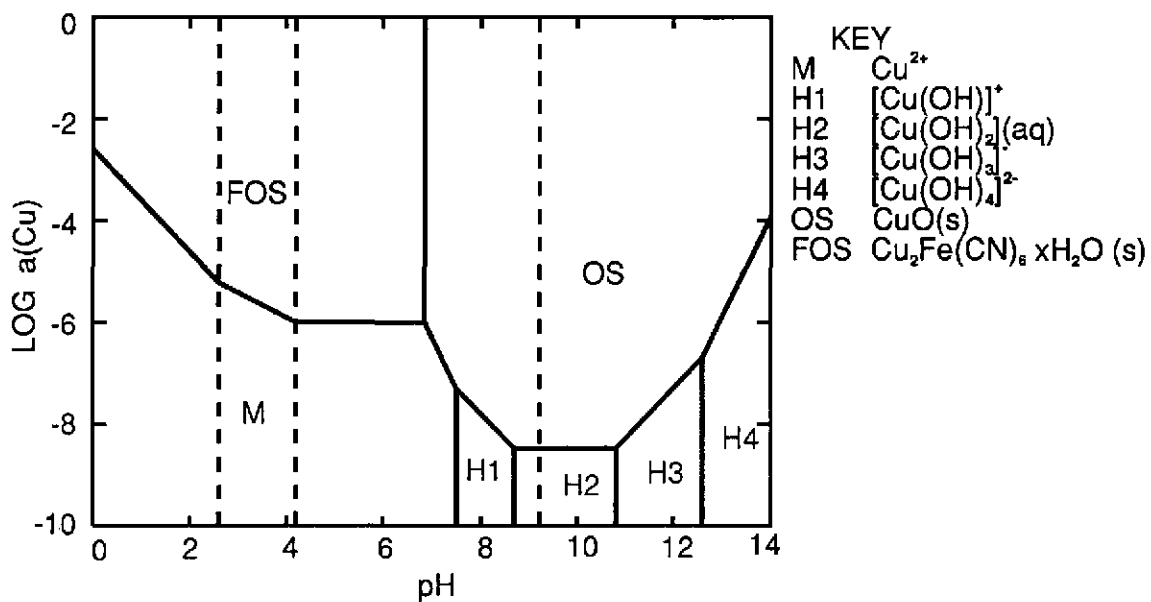
pCu(II)-pH diagram with no ligands.

Figure E-96



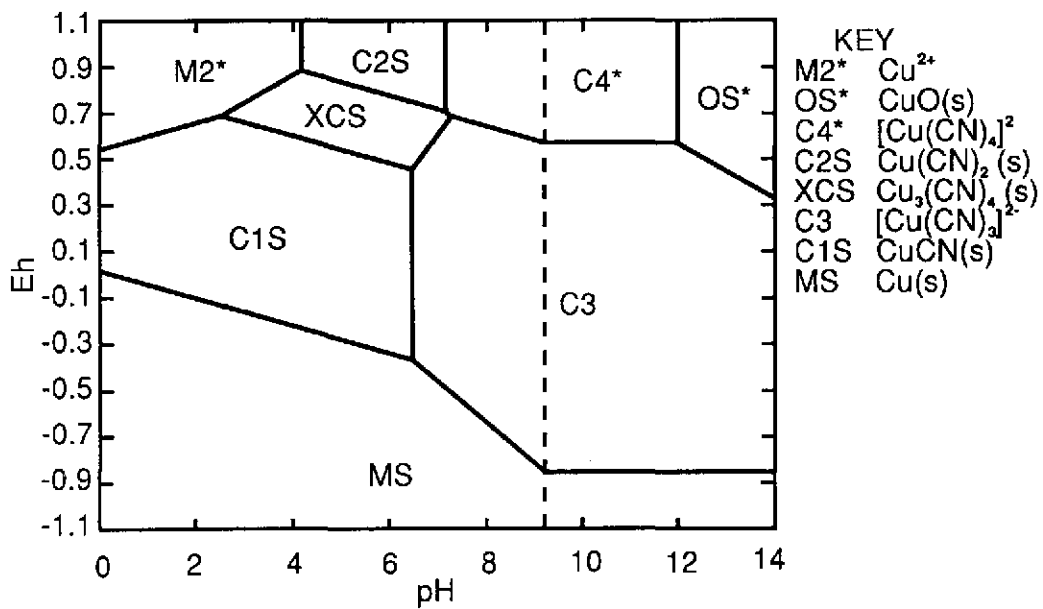
pCu(II)-pH diagram for $p\text{CO}_3 = 3.0$.

Figure E-97



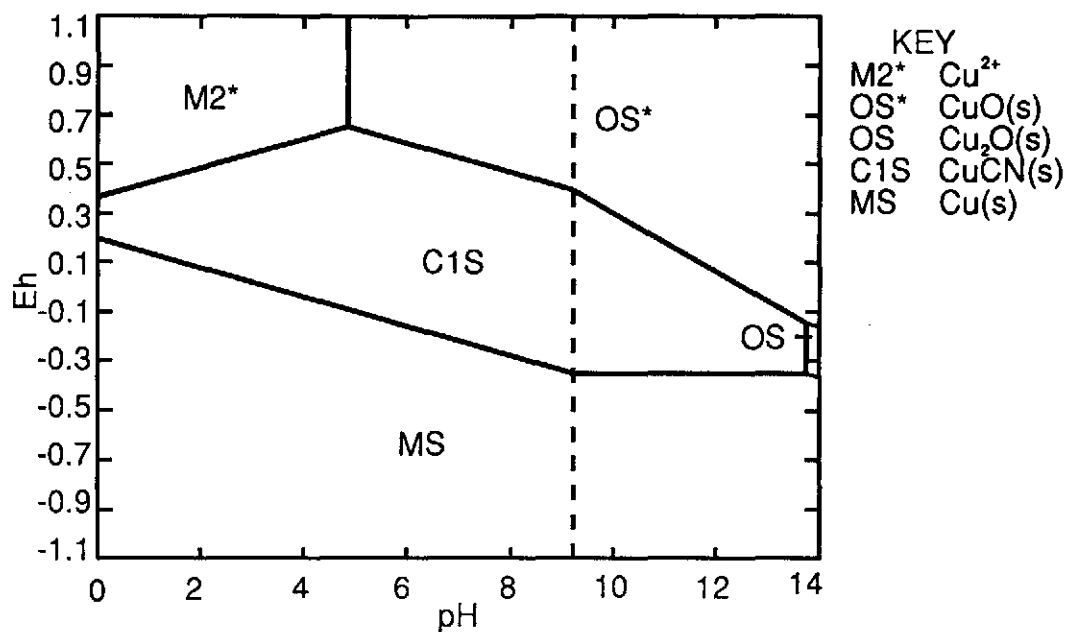
$p\text{Cu}(\text{II})$ - pH diagram for $p\text{CN} = 5.0$ and $p[\text{Fe}(\text{CN})_6^+] = 4.0$.

Figure E-98



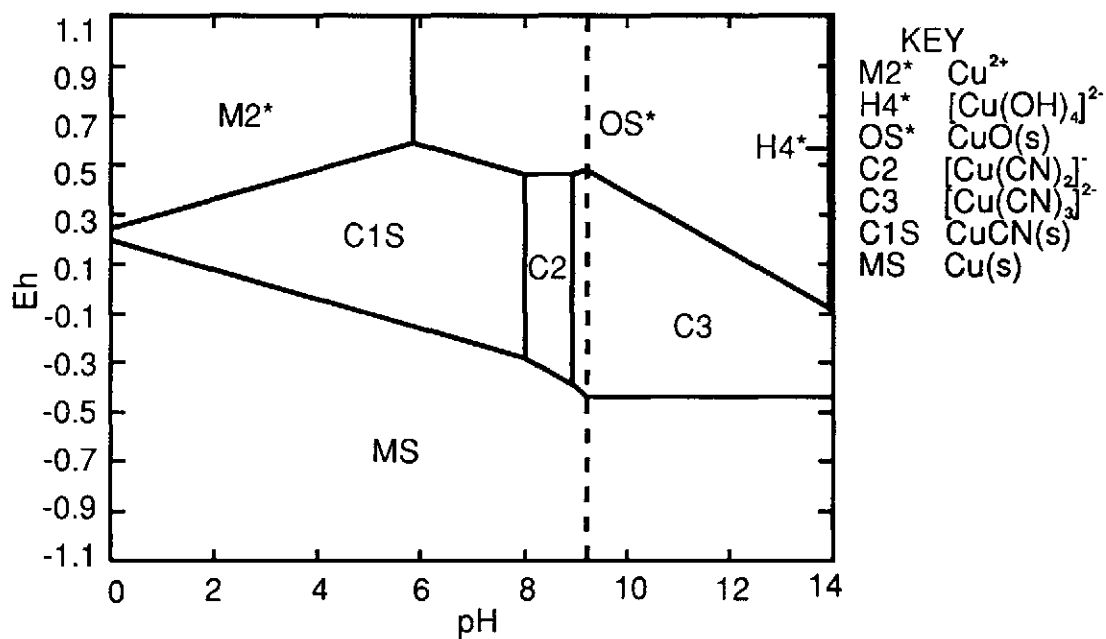
Eh - pH diagram for $p\text{Cu}(\text{II}) = 2.0$ and $p\text{CN} = 2.0$.

Figure E-99



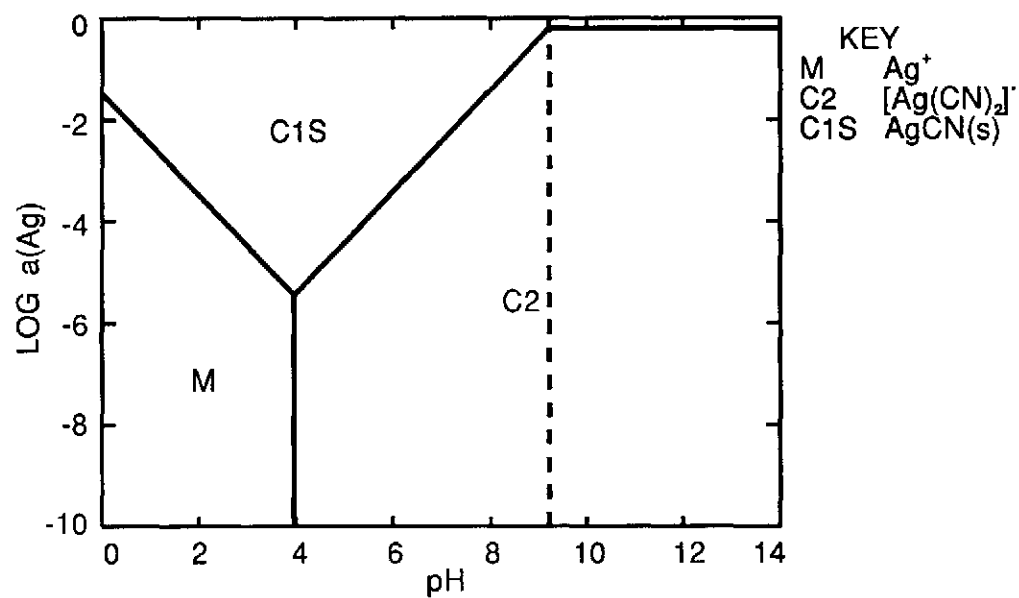
Eh-pH diagram for $p\text{Cu(II)} = 2.0$ and $p\text{CN} = 5.0$.

Figure E-100



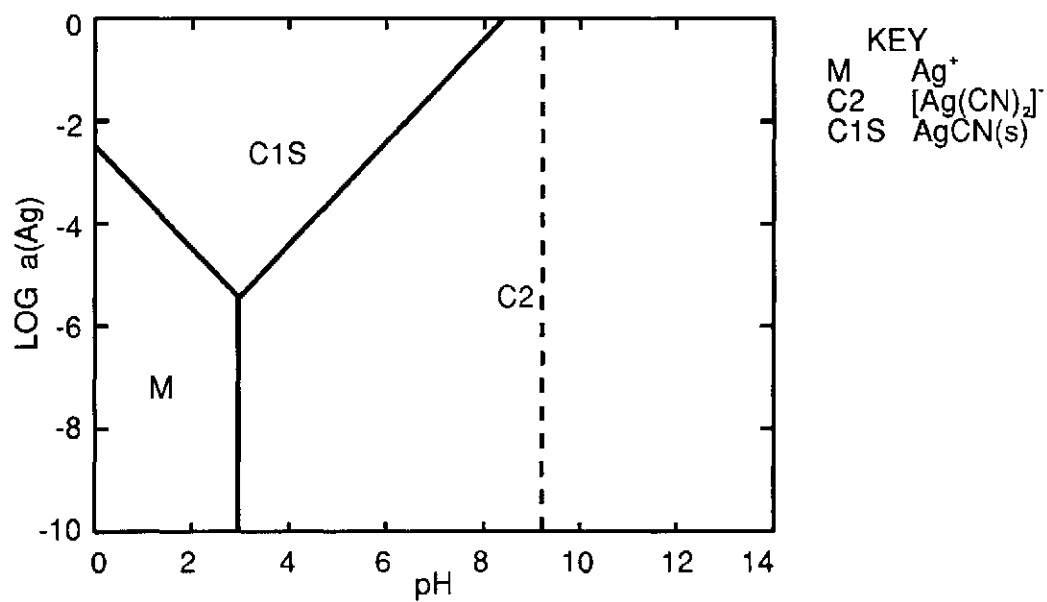
Eh-pH diagram for $p\text{Cu(II)} = 4.0$ and $p\text{CN} = 5.0$.

Figure E-101



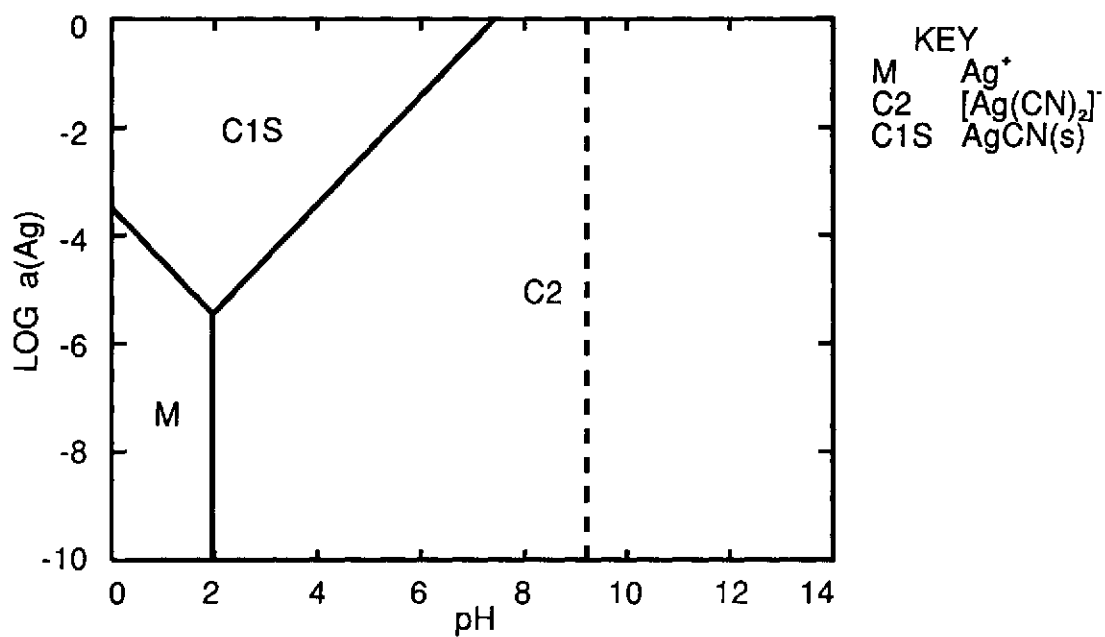
pAg-pH diagram for $pCN = 5.0$.

Figure E-102



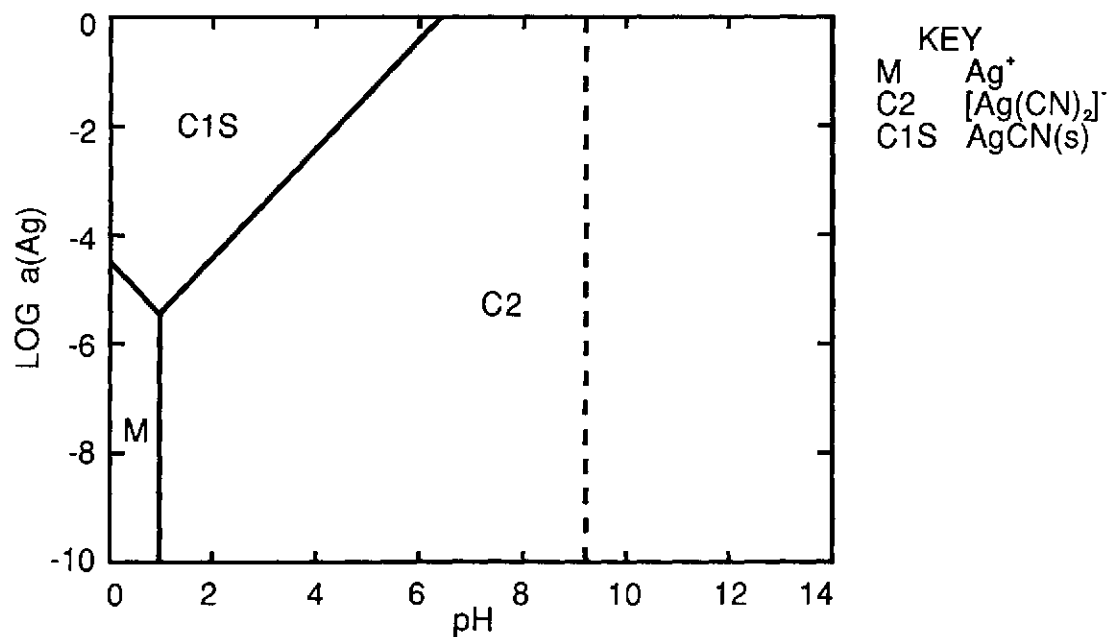
pAg-pH diagram for $pCN = 4.0$.

Figure E-103



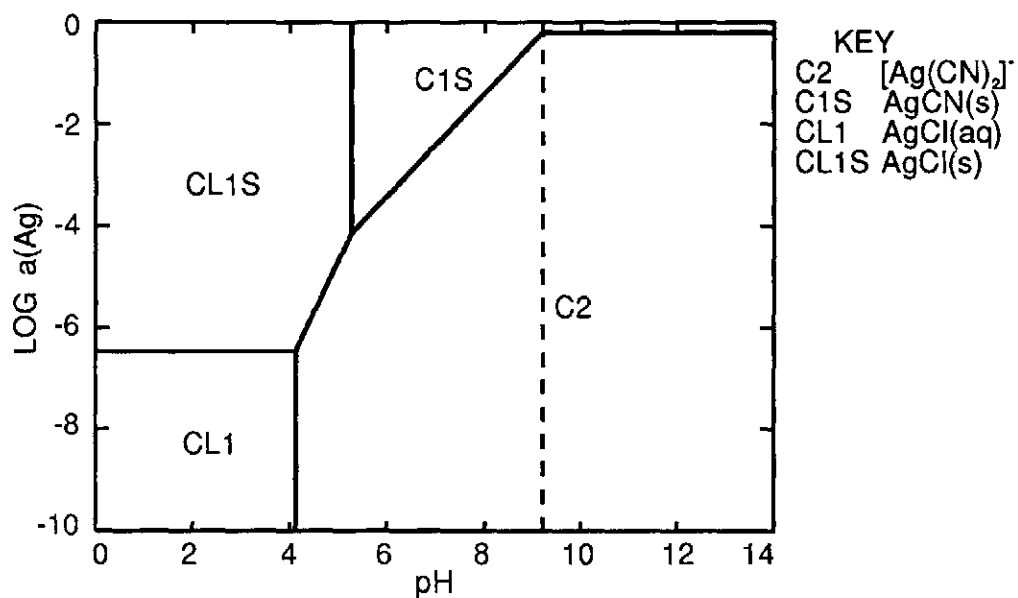
pAg-pH diagram for $p\text{CN} = 3.0$.

Figure E-104



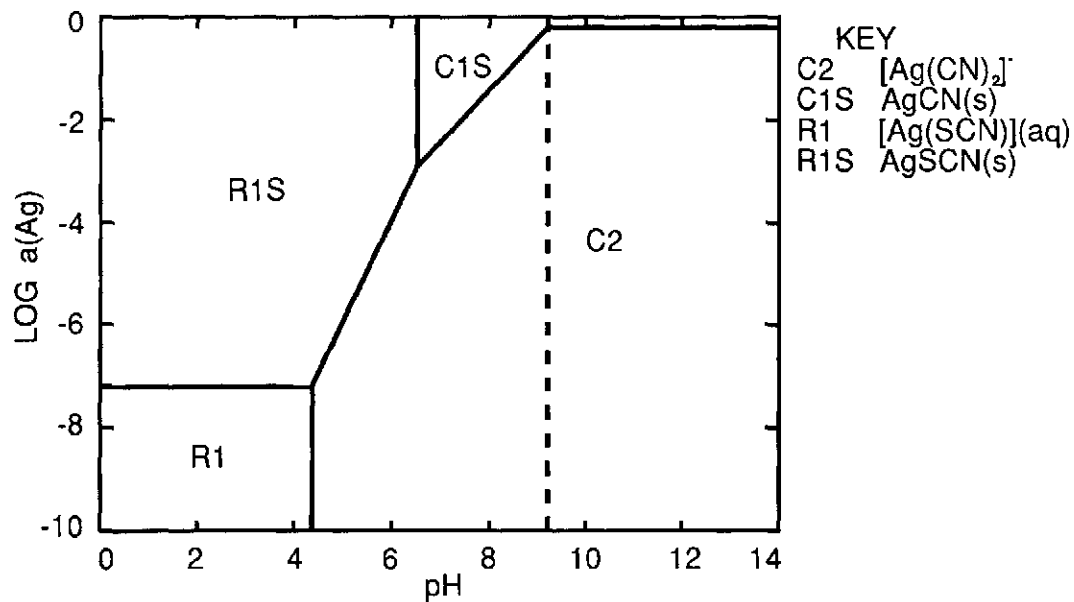
pAg-pH diagram for $p\text{CN} = 2.0$.

Figure E-105



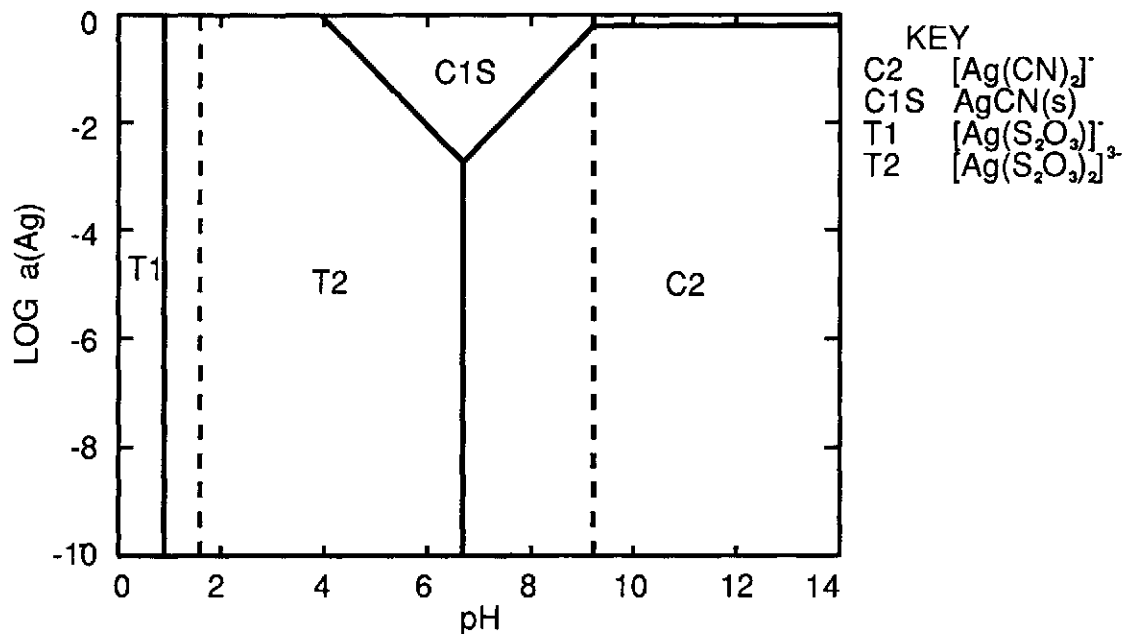
pAg-pH diagram for $p\text{CN} = 5.0$ and $p\text{Cl} = 3.0$.

Figure E-106



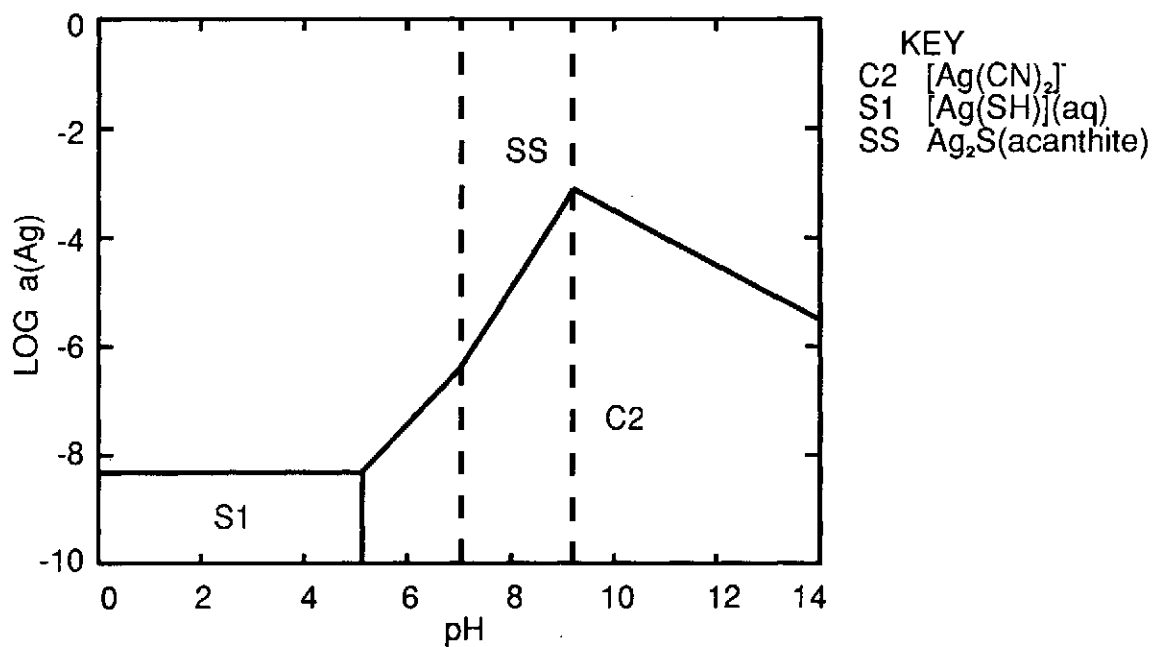
pAg-pH diagram for $p\text{CN} = 5.0$ and $p\text{SCN} = 4.0$.

Figure E-107



pAg-pH diagram for $p\text{CN} = 5.0$ and $p\text{S}_2\text{O}_3 = 4.0$.

Figure E-108



pAg-pH diagram for $p\text{CN} = 2.0$ and $p\text{SH} = 6.0$.

Figure E-109

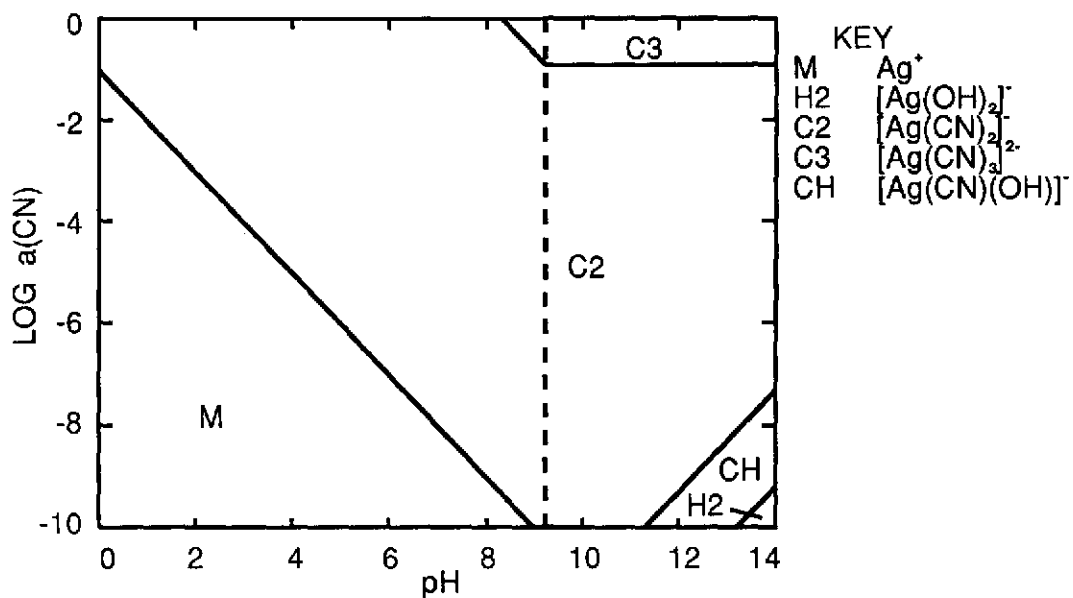
*pCN-pH diagram for silver solution species.*

Figure E-110

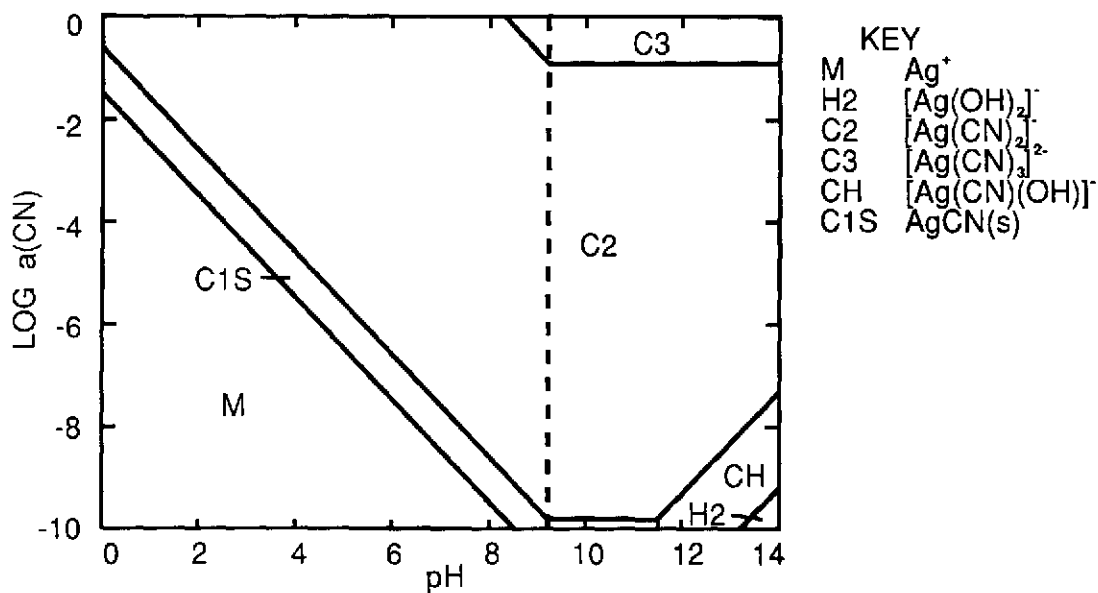
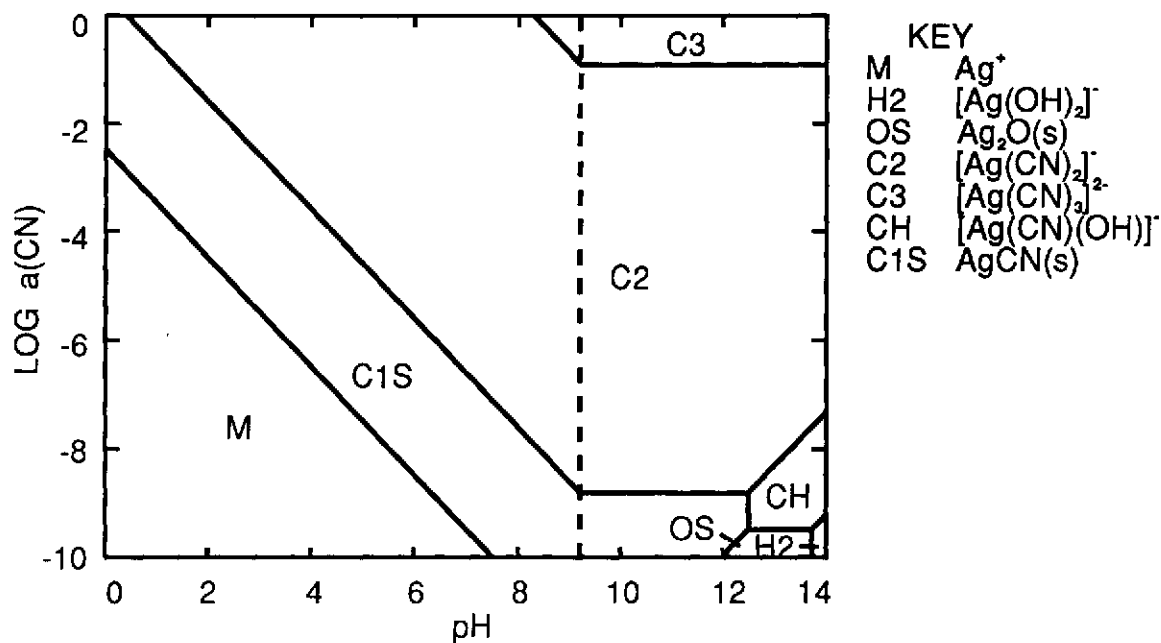
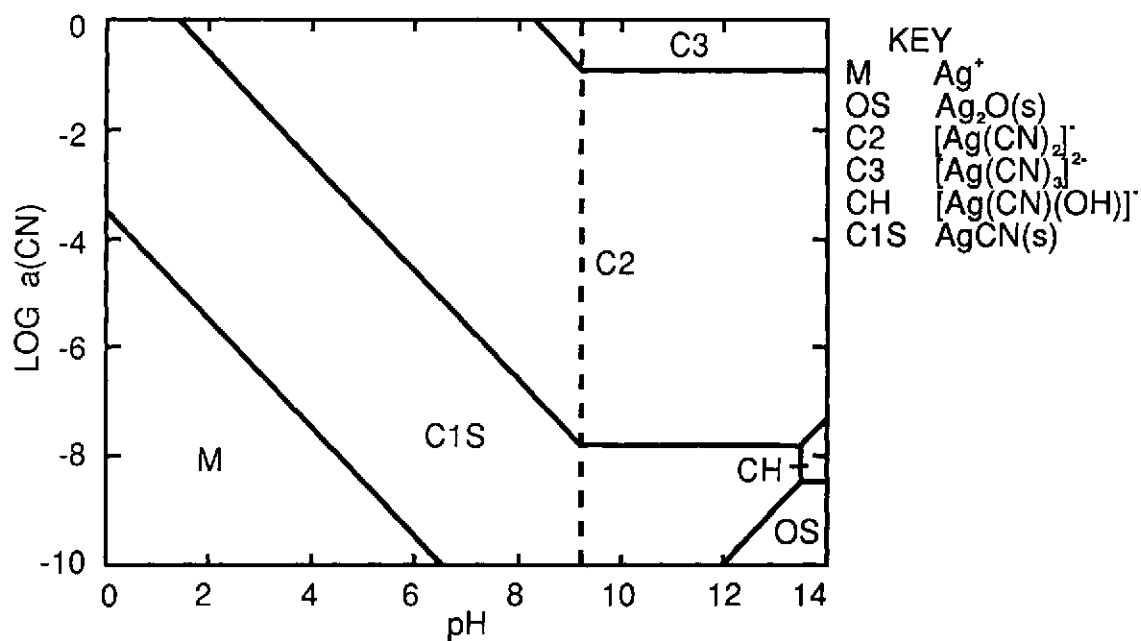
*pCN-pH diagram for $p\text{Ag} = 5.0$.*

Figure E-111



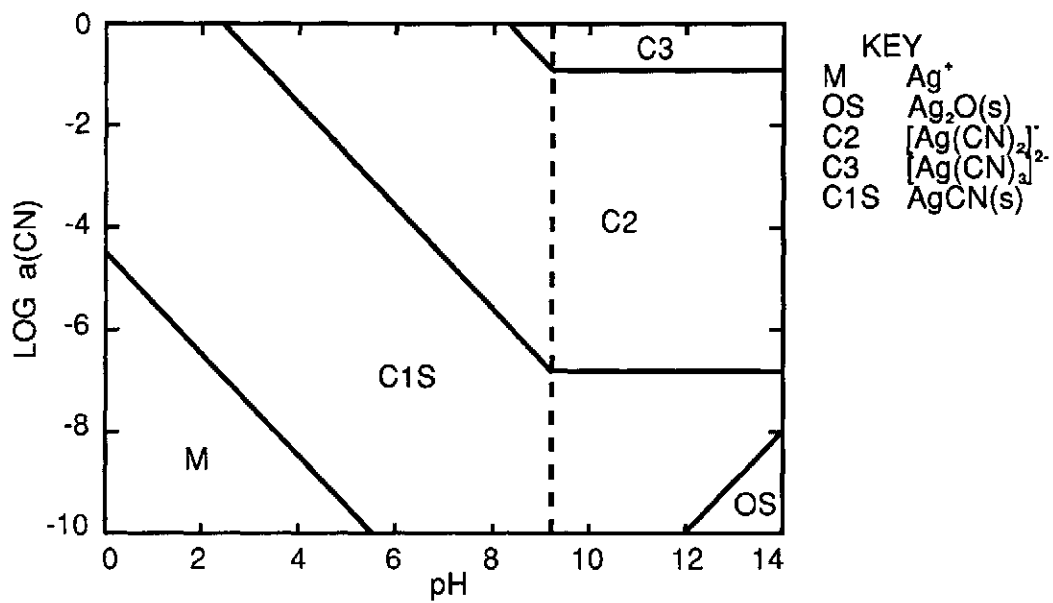
pCN-pH diagram for $p\text{Ag} = 4.0$.

Figure E-112



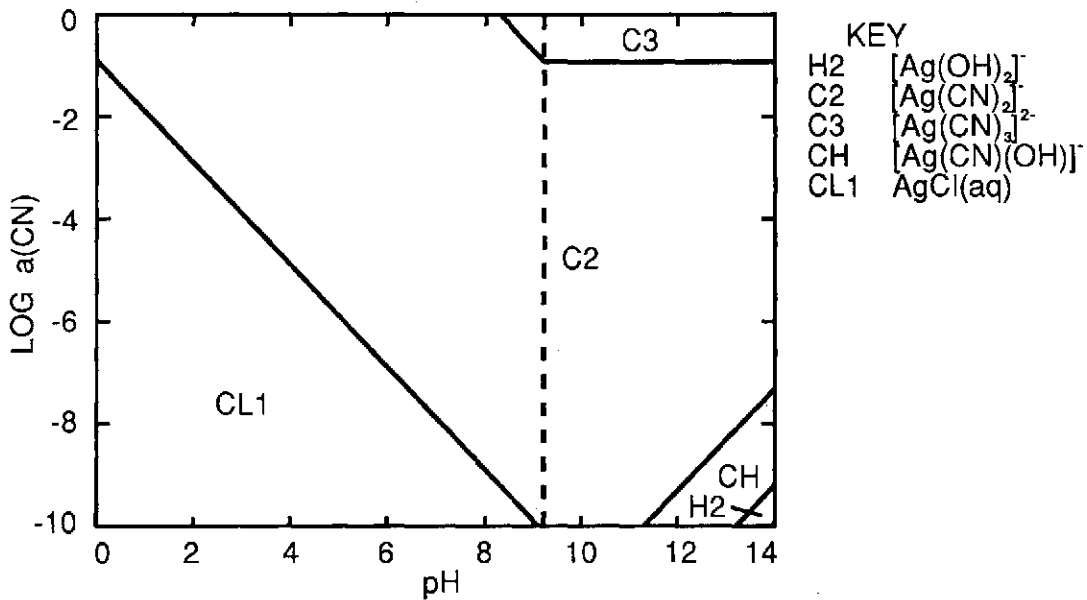
pCN-pH diagram for $p\text{Ag} = 3.0$.

Figure E-113



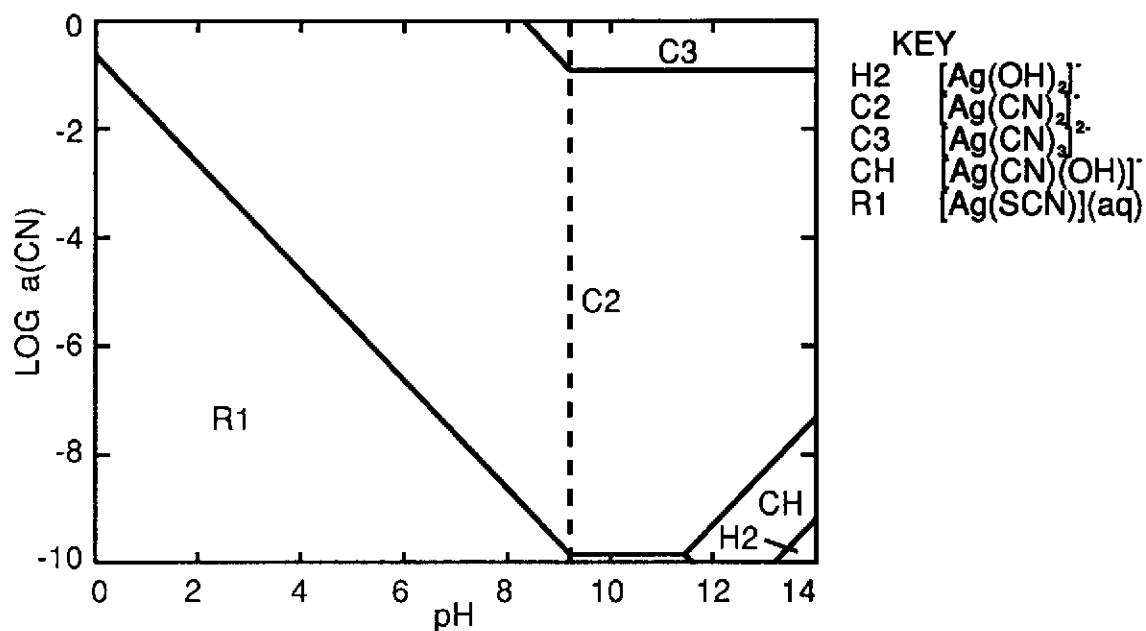
pCN-pH diagram for $p\text{Ag} = 2.0$.

Figure E-114



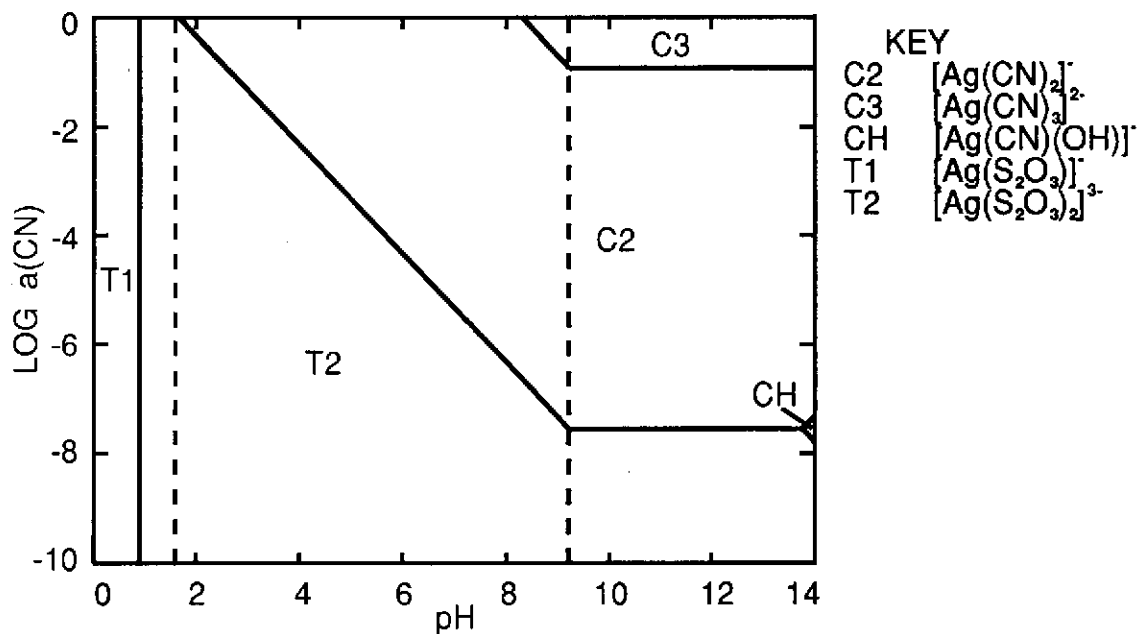
pCN-pH diagram for silver solution species with $p\text{Cl} = 3.0$.

Figure E-115



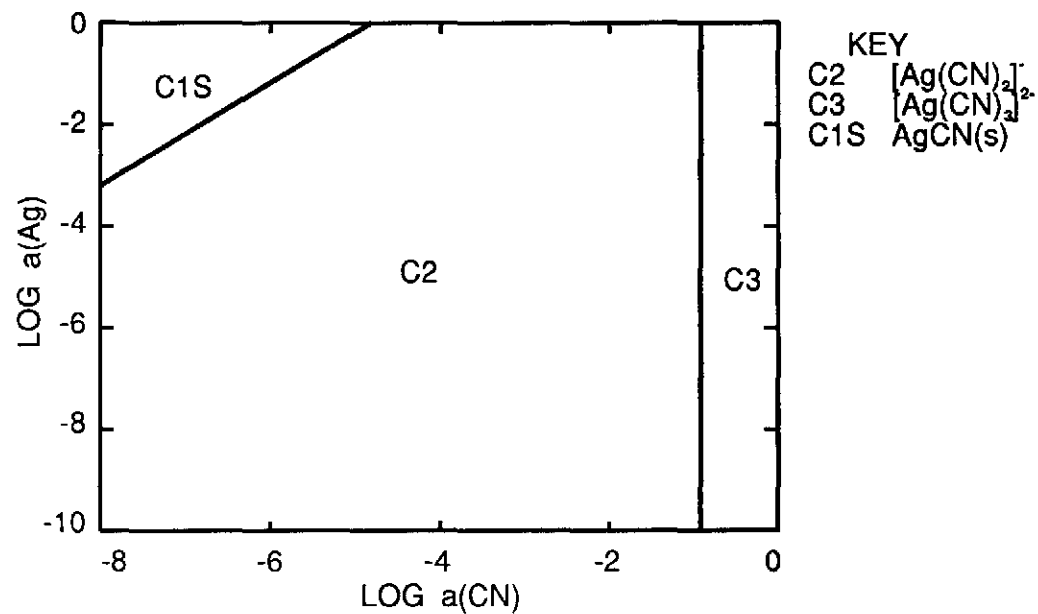
pCN-pH diagram for silver solution species with $pSCN = 4.0$.

Figure E-116



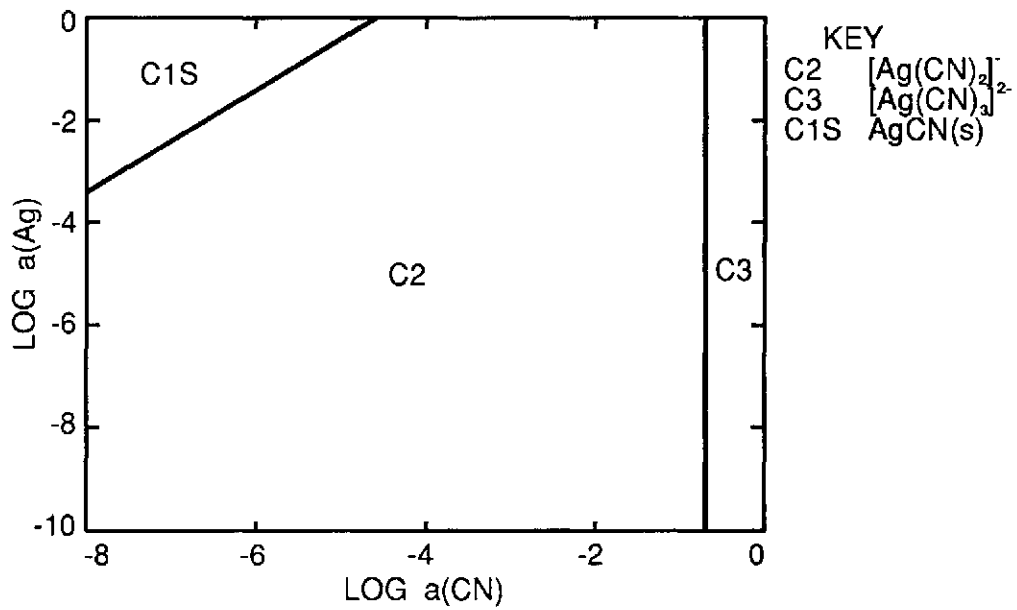
pCN-pH diagram for silver solution species with $pS_2O_3 = 4.0$.

Figure E-117



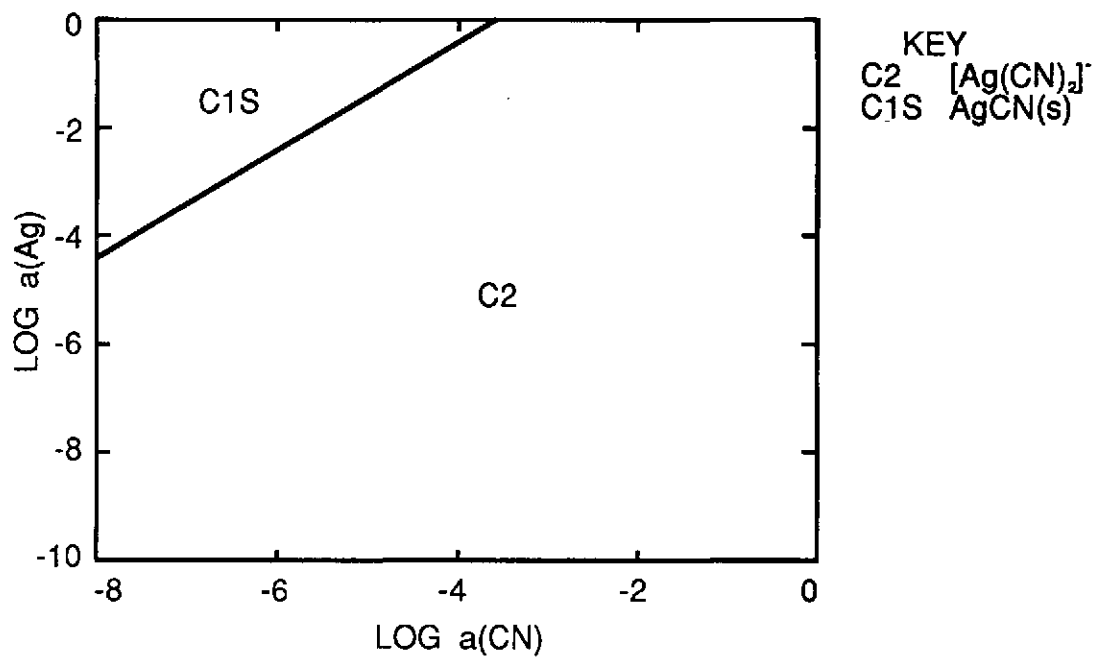
pAg - pCN diagram for $pH = 11.0$.

Figure E-118



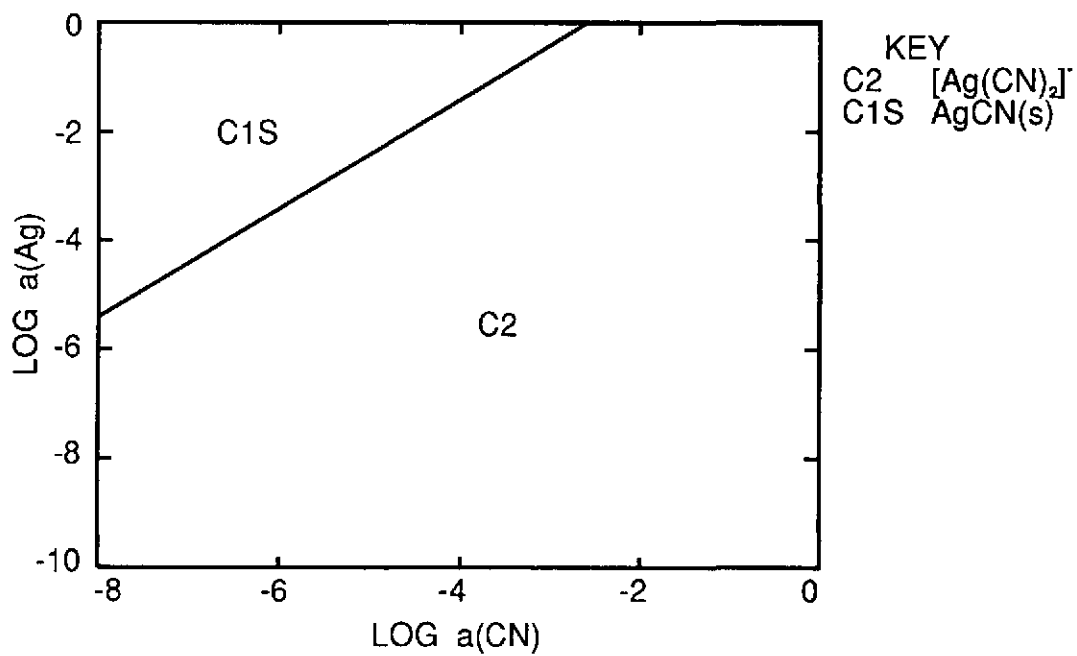
pAg - pCN diagram for $pH = 9.0$.

Figure E-119



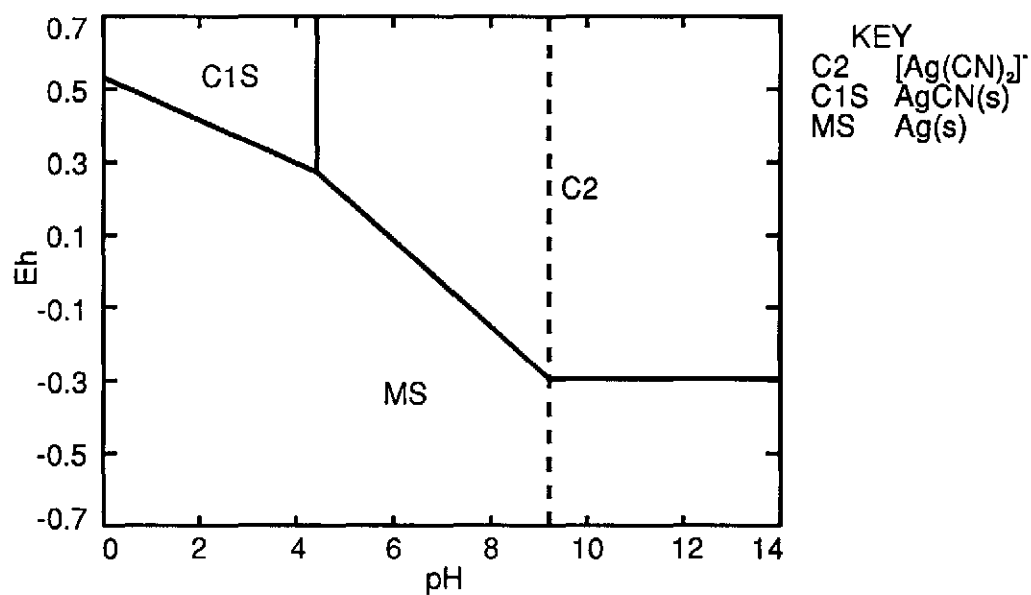
pAg-pCN diagram for pH = 8.0.

Figure E-120



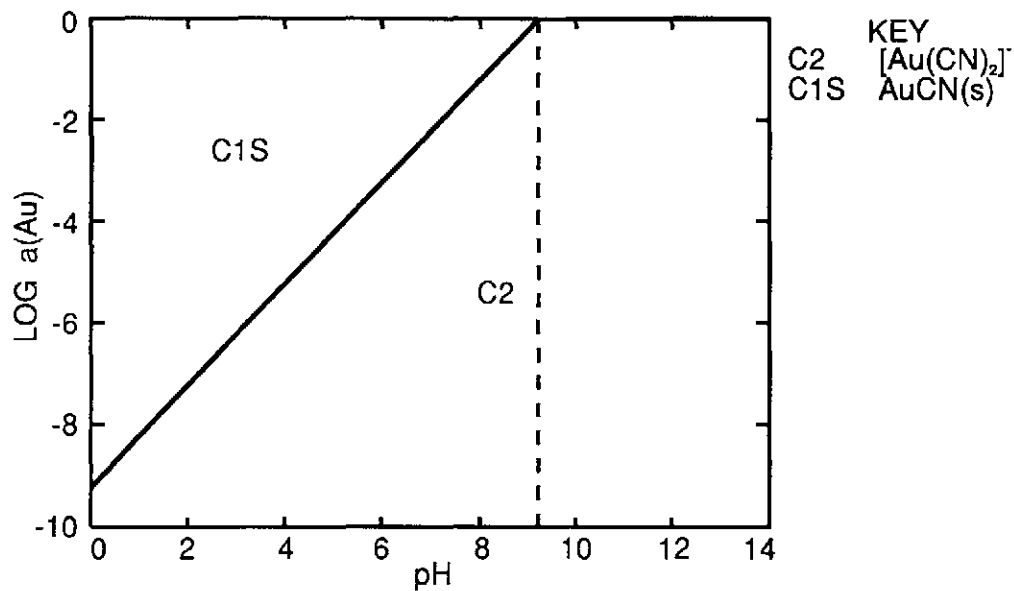
pAg-pCN diagram for pH = 7.0.

Figure E-121



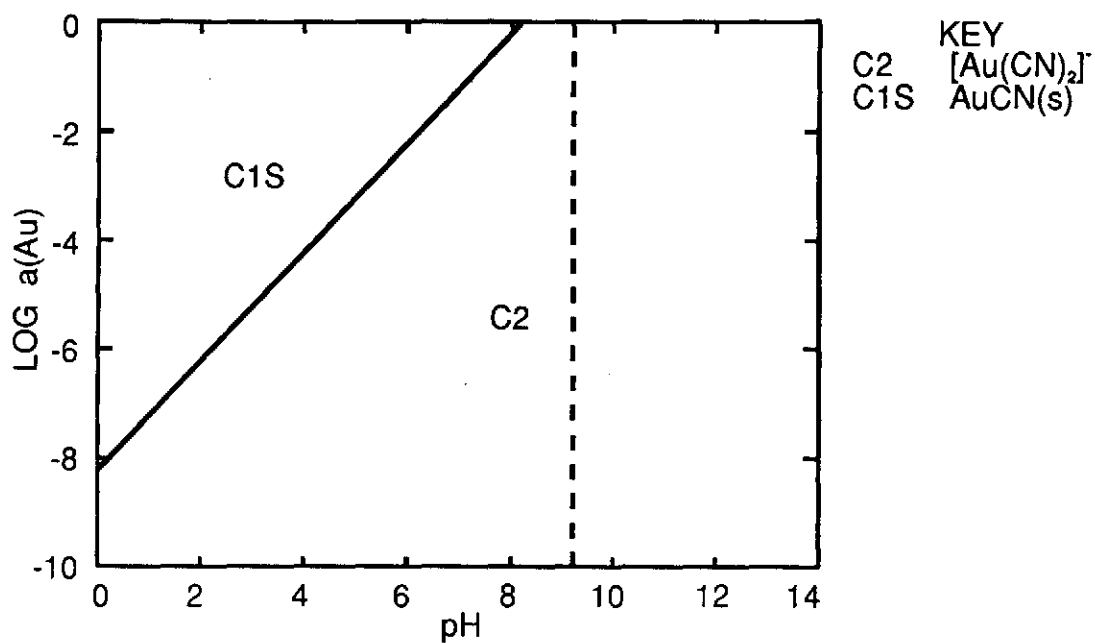
Eh-pH diagram for $p\text{Ag} = 2.0$ and $p\text{CN} = 2.0$.

Figure E-122



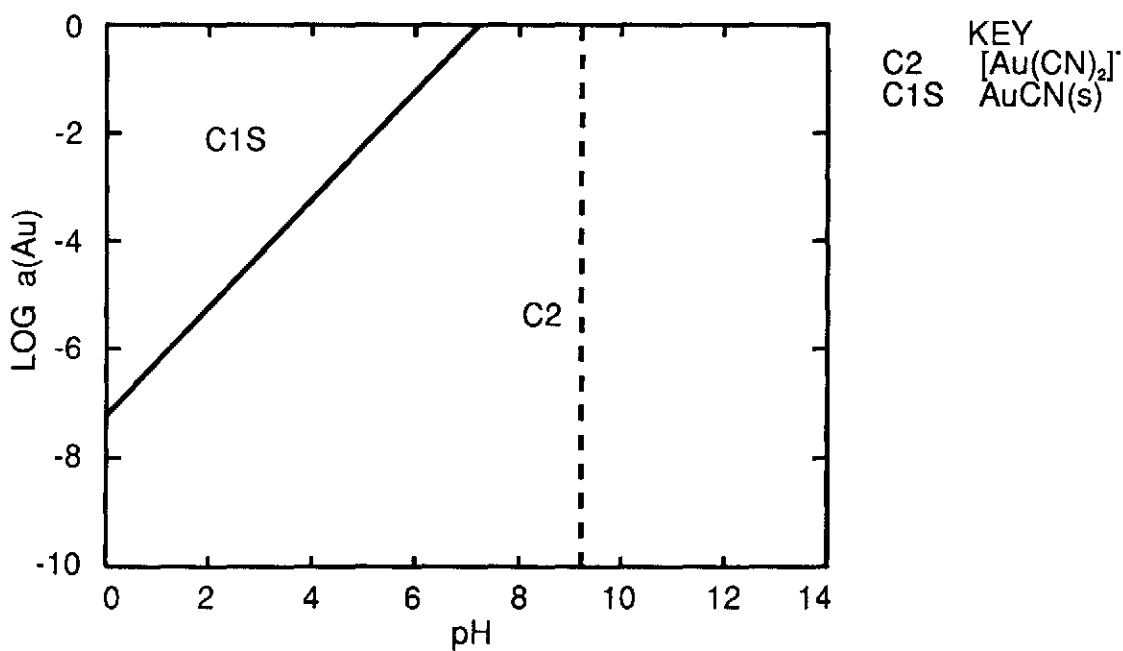
pAu(I)-pH diagram for $p\text{CN} = 5.0$.

Figure E-123



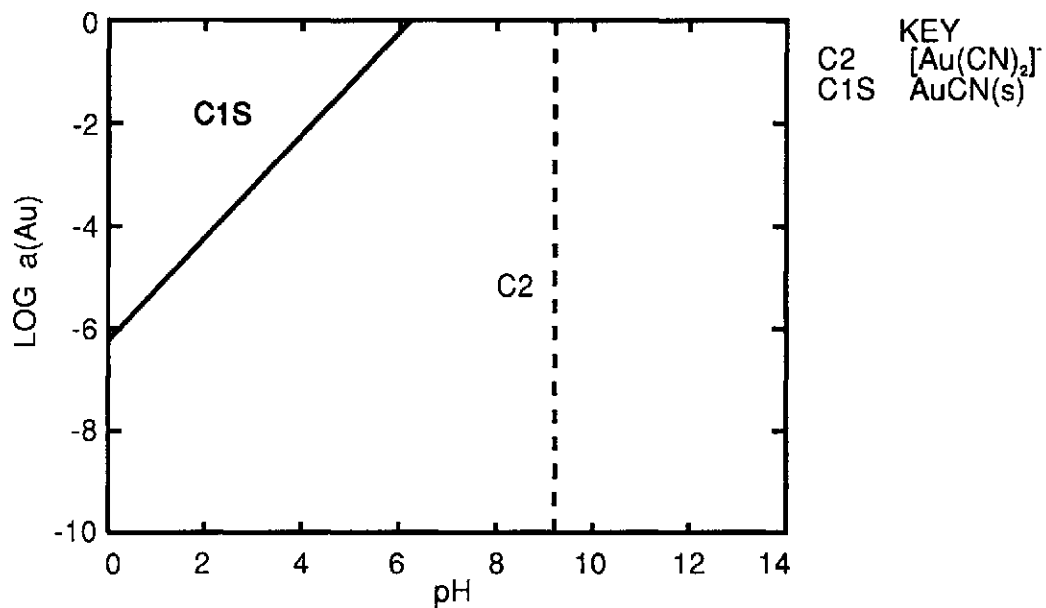
$p\text{Au(I)}$ - pH diagram for $p\text{CN} = 4.0$.

Figure E-124



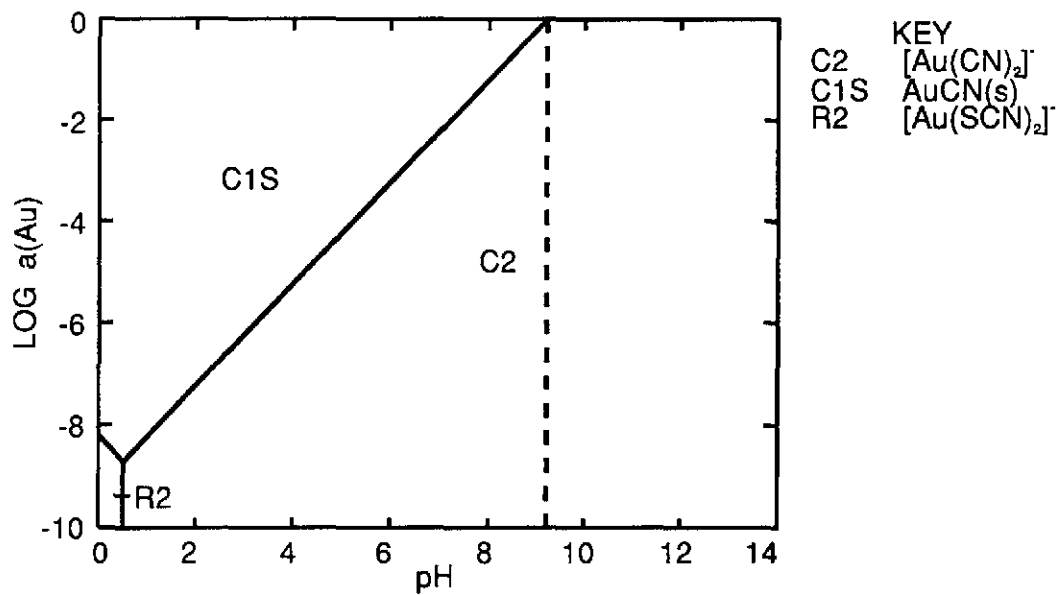
$p\text{Au(I)}$ - pH diagram for $p\text{CN} = 3.0$.

Figure E-125



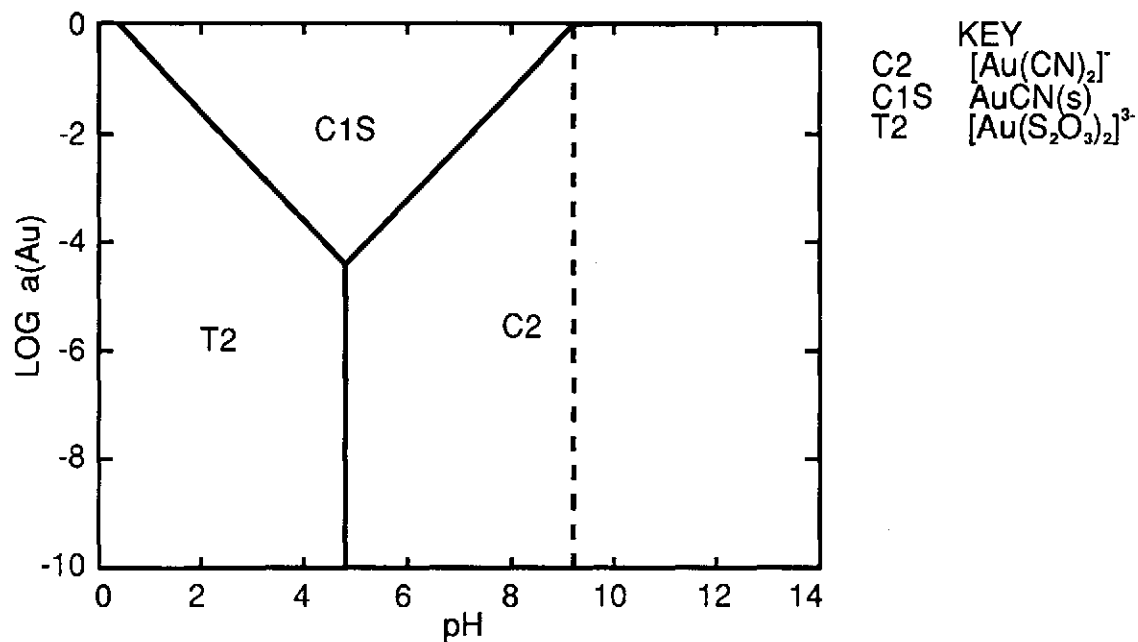
$p\text{Au(I)}$ - pH diagram for $p\text{CN} = 2.0$.

Figure E-126



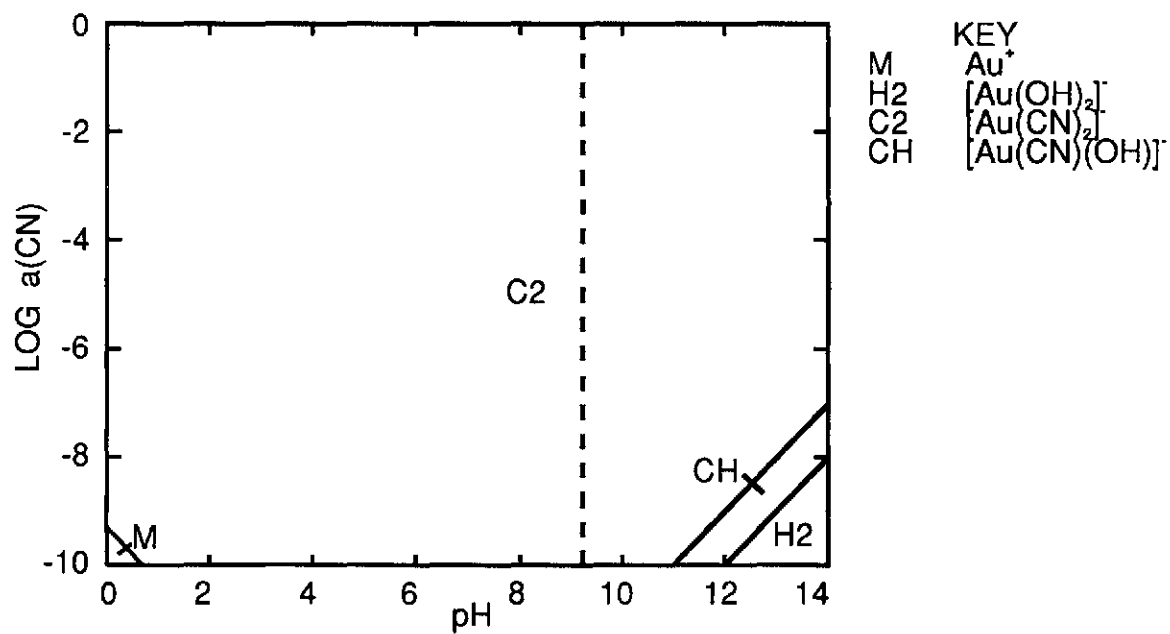
$p\text{Au(I)}$ - pH diagram for $p\text{CN} = 5.0$ and $p\text{SCN} = 4.0$.

Figure E-127



pAu(I)-pH diagram for $p\text{CN} = 5.0$ and $p\text{S}_2\text{O}_3 = 4.0$.

Figure E-128



pCN-pH diagram for gold(I) solution species.

Figure E-129

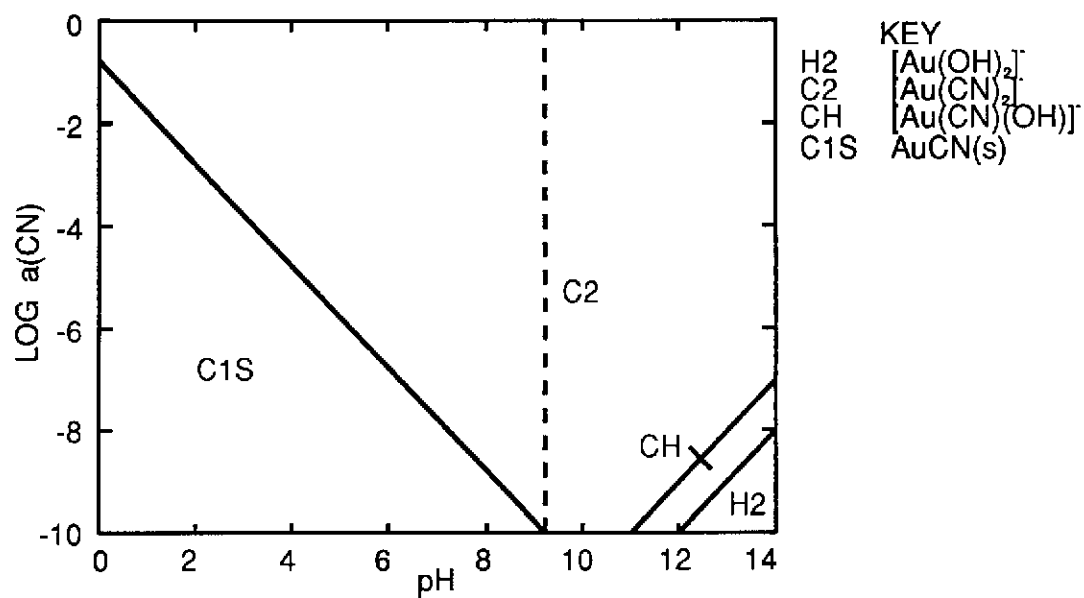
*pCN-pH diagram for $pAu(I) = 5.0$.*

Figure E-130

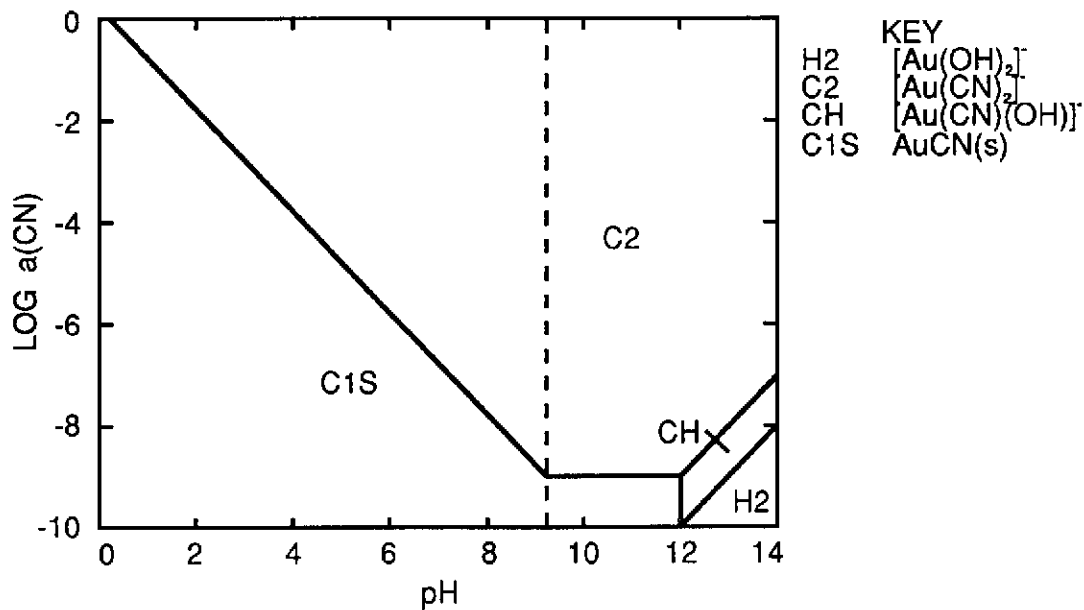
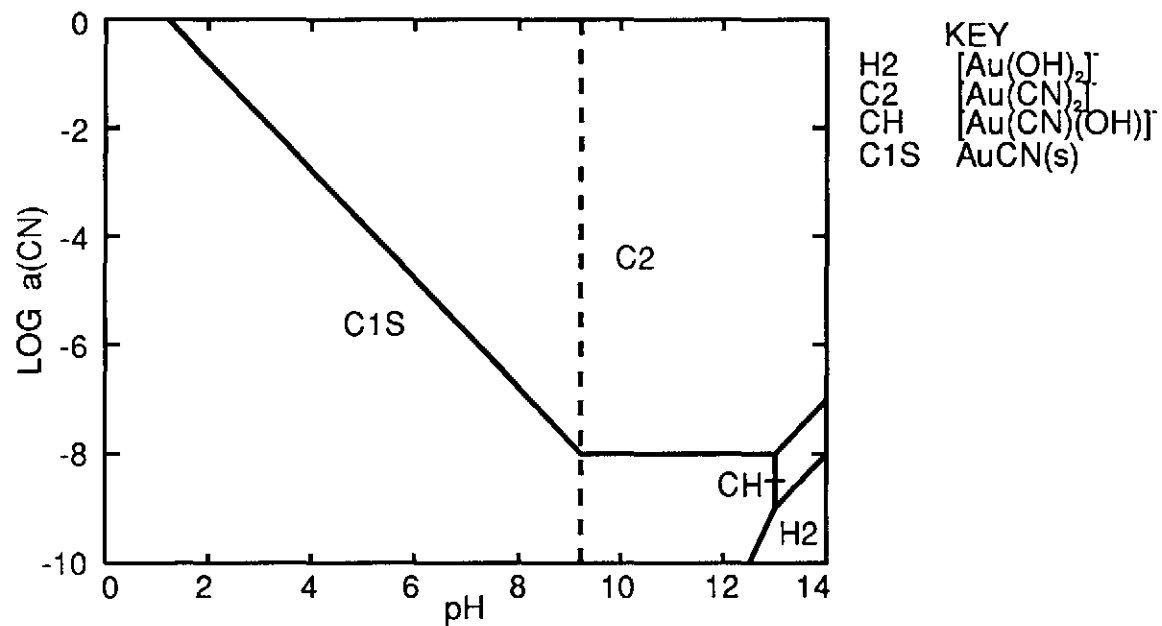
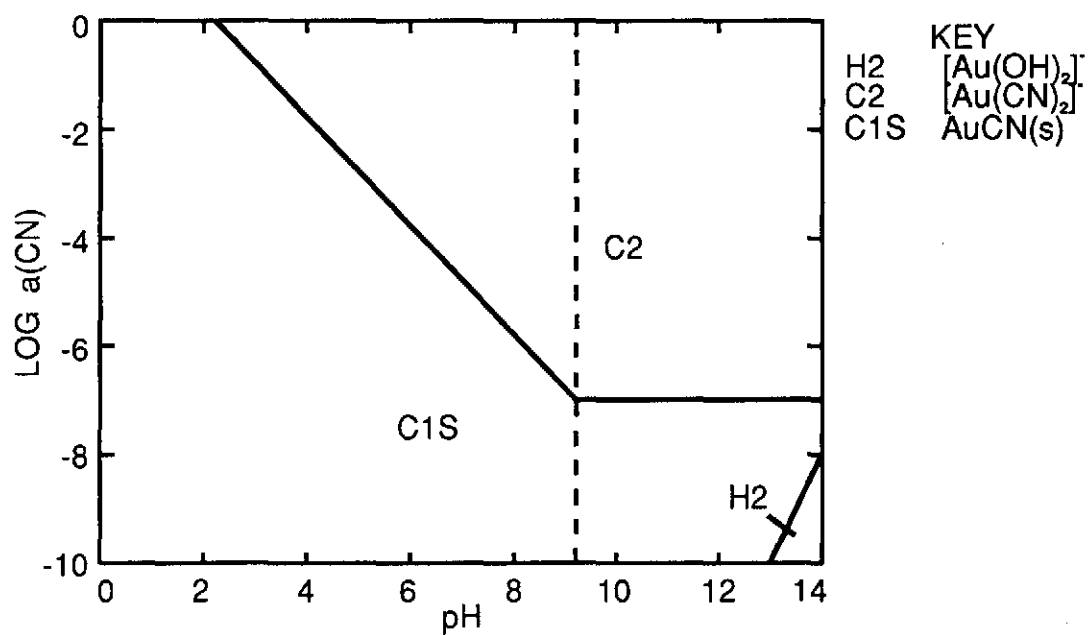
*pCN-pH diagram for $pAu(I) = 4.0$.*

Figure E-131



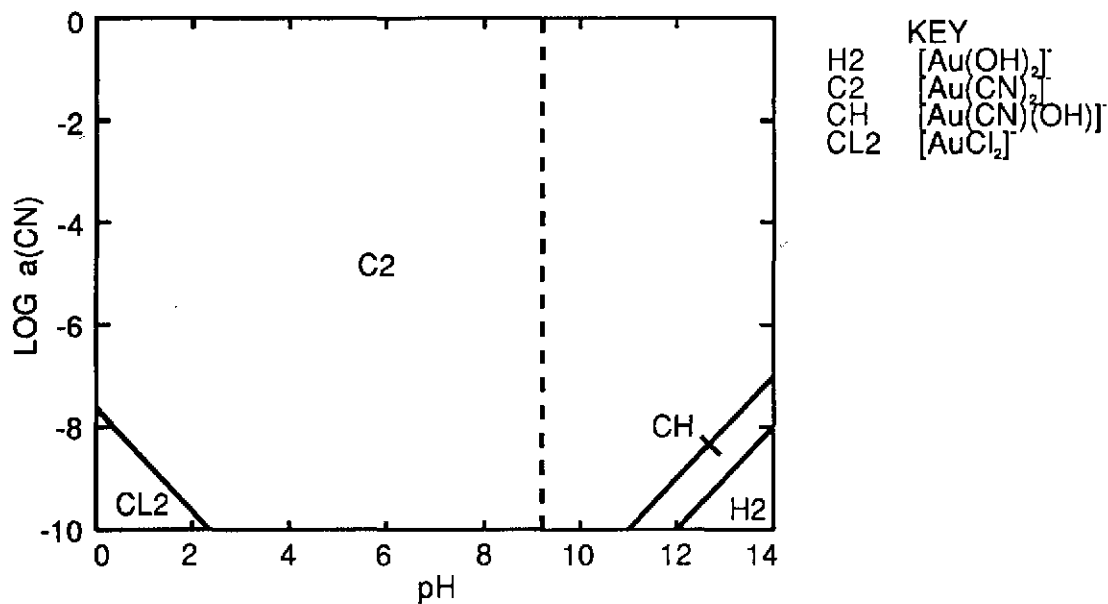
pCN-pH diagram for $pAu(I) = 3.0$.

Figure E-132



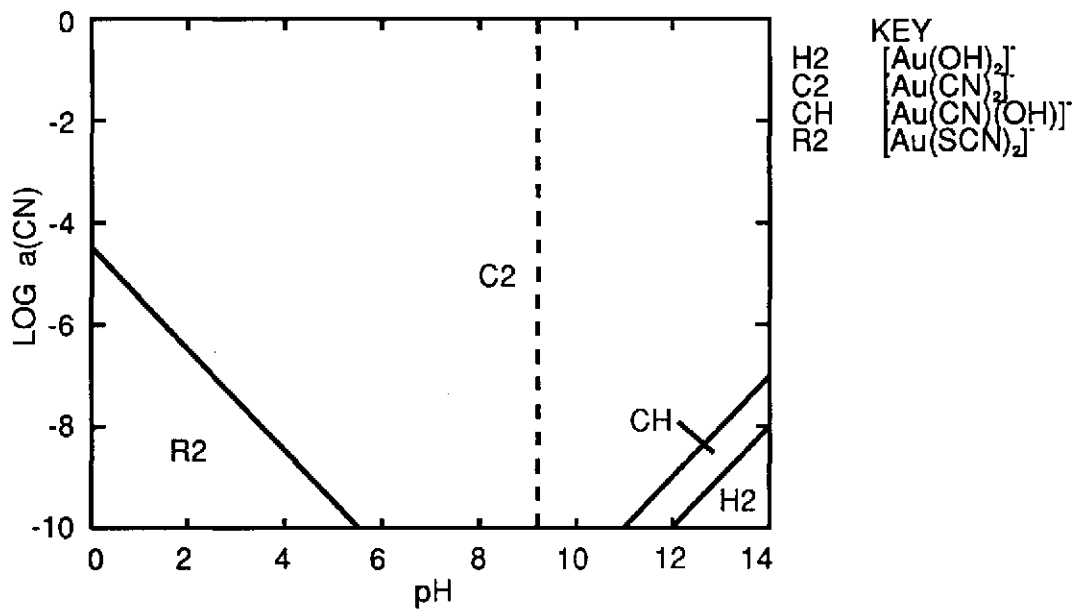
pCN-pH diagram for $pAu(I) = 2.0$.

Figure E-133



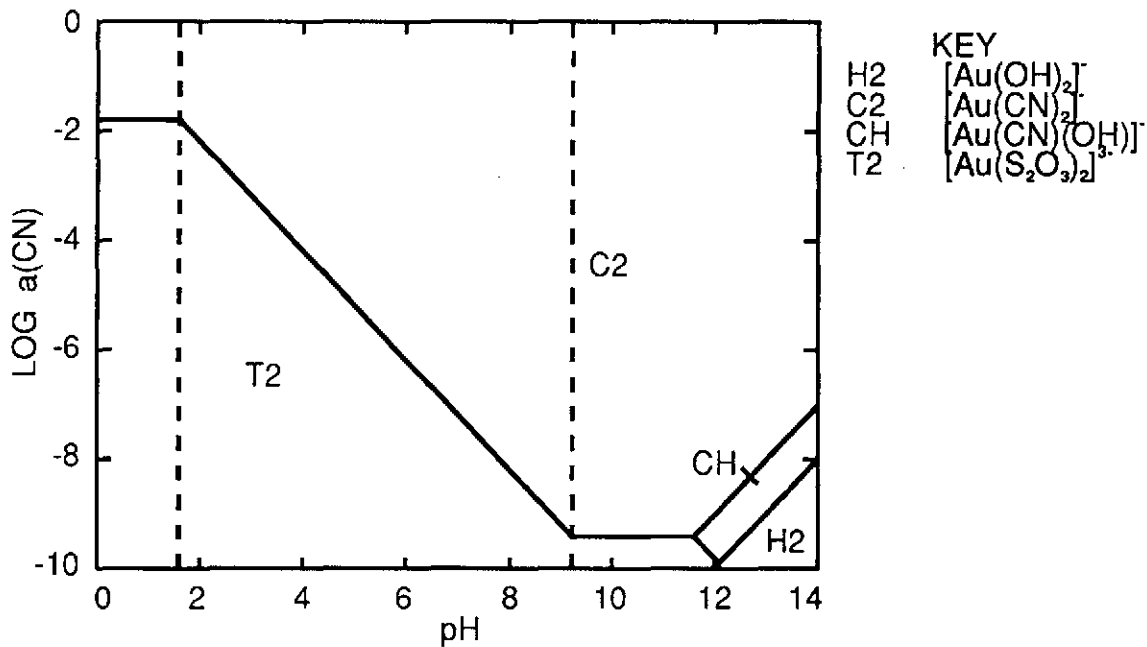
pCN-pH diagram for gold(I) solution species with $p\text{Cl} = 3.0$.

Figure E-134



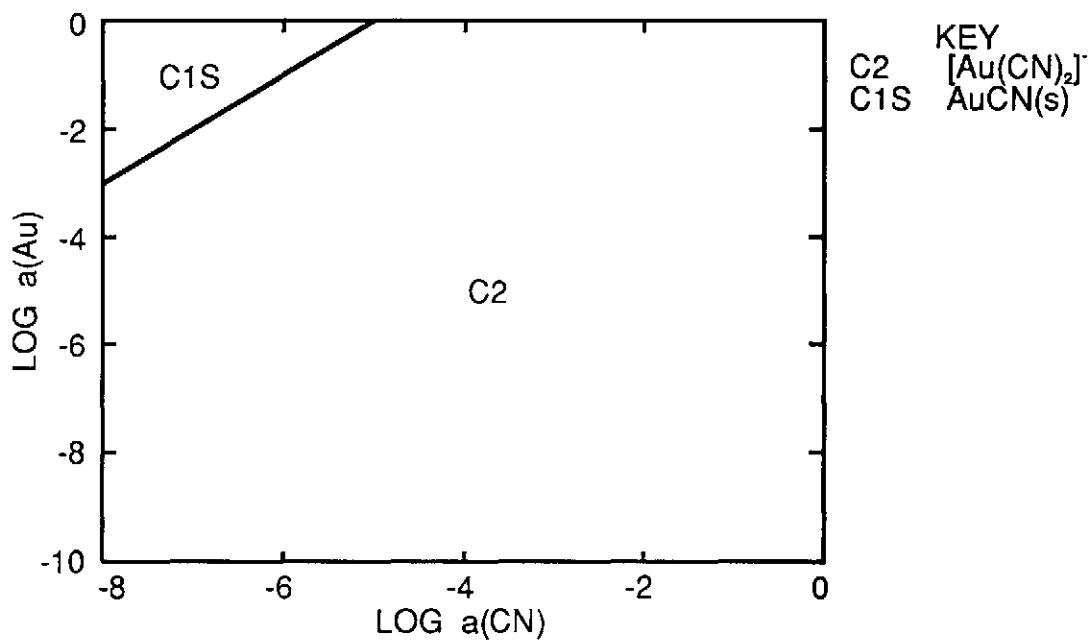
pCN-pH diagram for gold(I) solution species with $p\text{SCN} = 4.0$.

Figure E-135



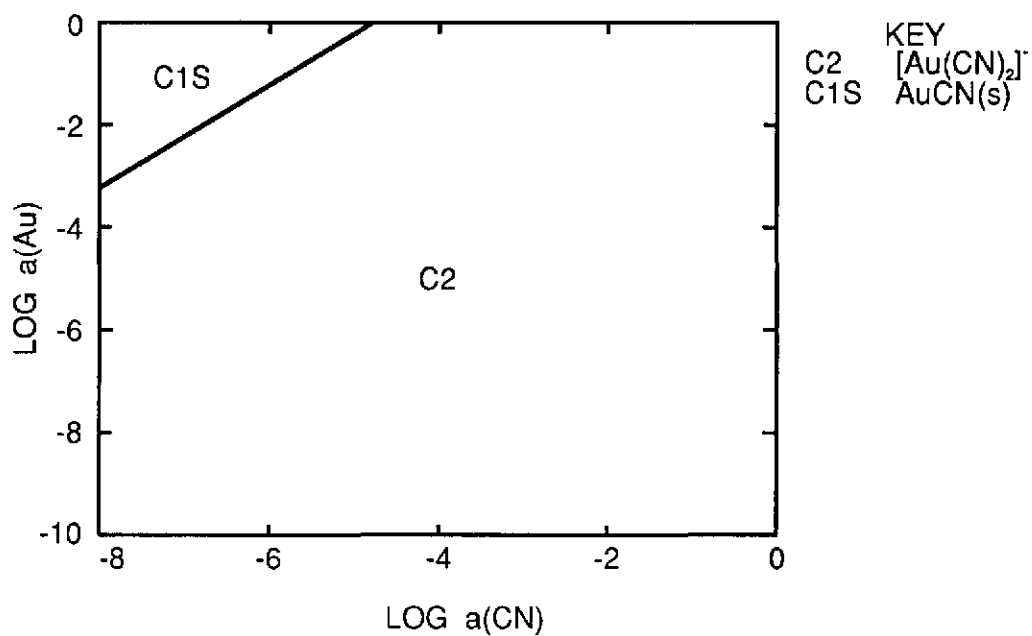
pCN-pH diagram for gold(I) solution species with $pS_2O_3 = 4.0$.

Figure E-136



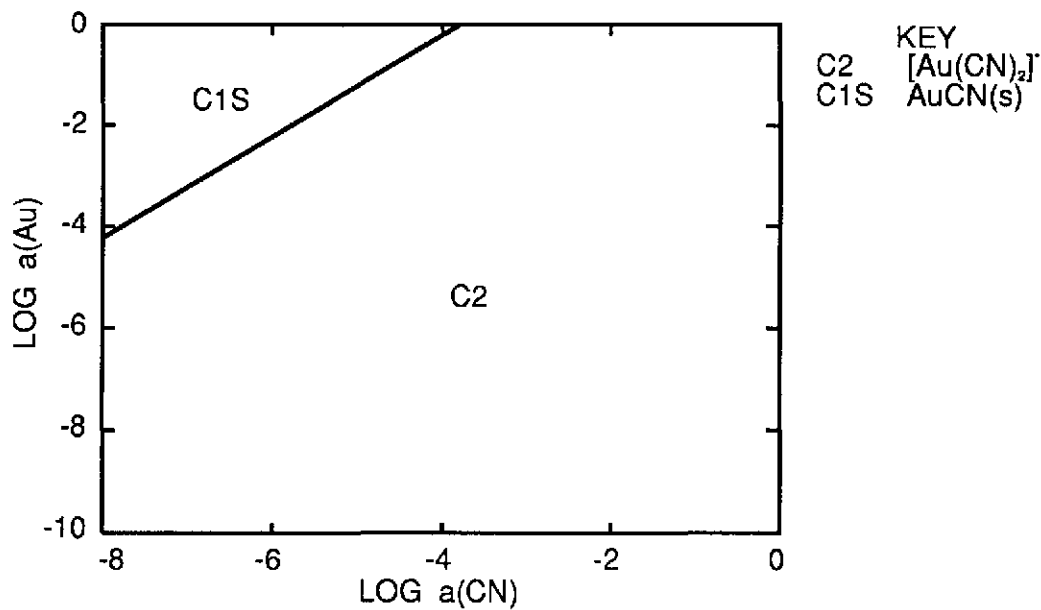
pAu(I)-pCN diagram for $\text{pH} = 11.0$.

Figure E-137



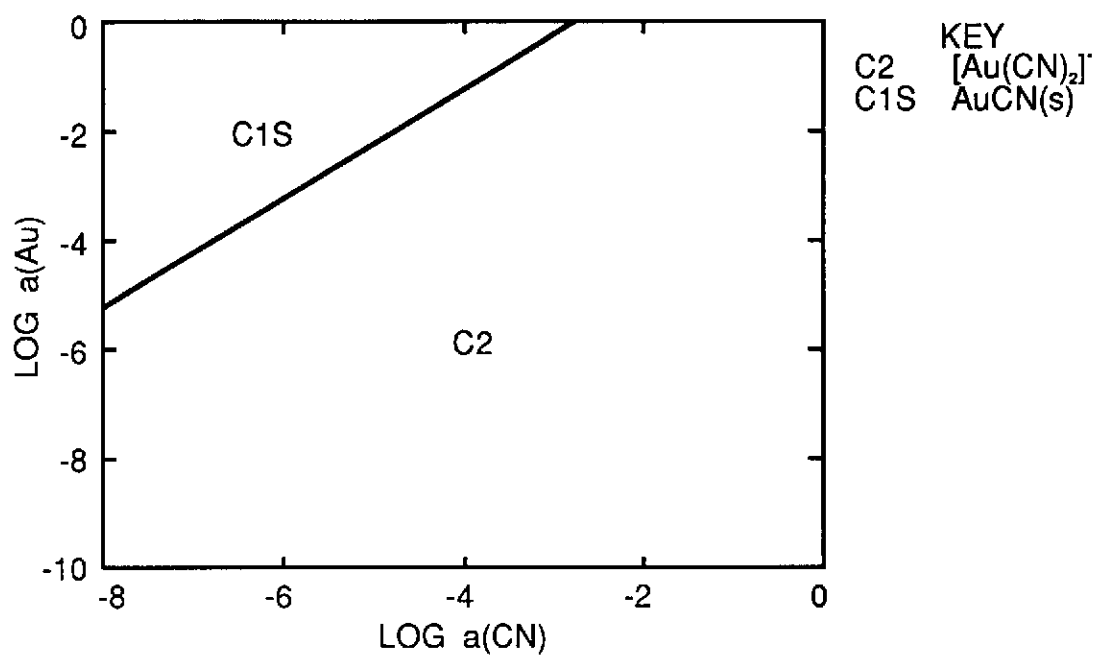
$p\text{Au(I)}-p\text{CN}$ diagram for $\text{pH} = 9.0$.

Figure E-138



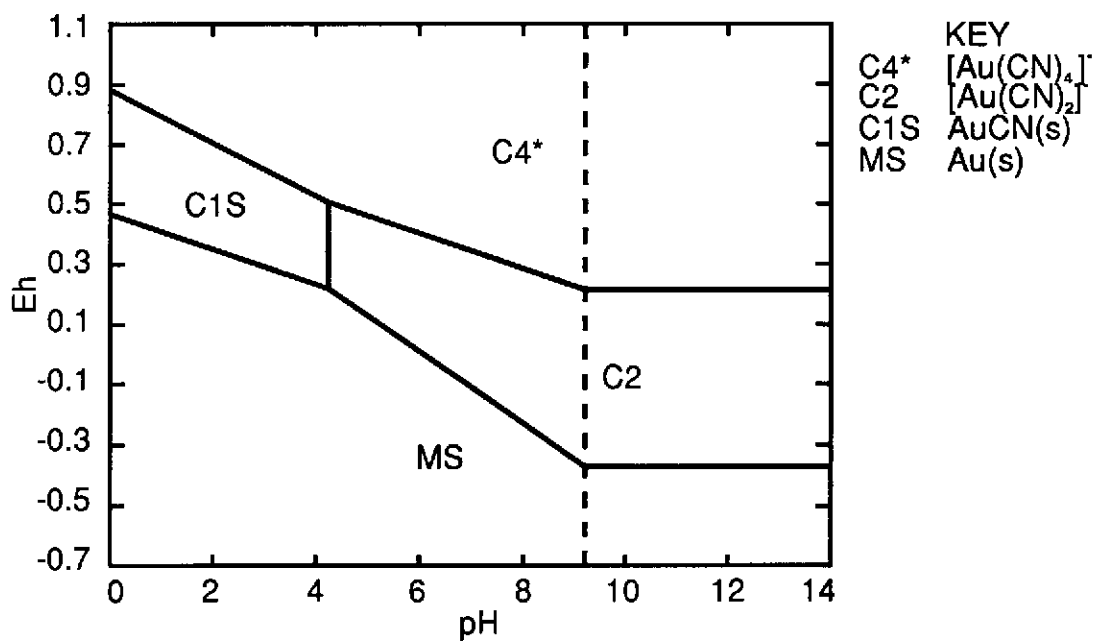
$p\text{Au(I)}-p\text{CN}$ diagram for $\text{pH} = 8.0$.

Figure E-139



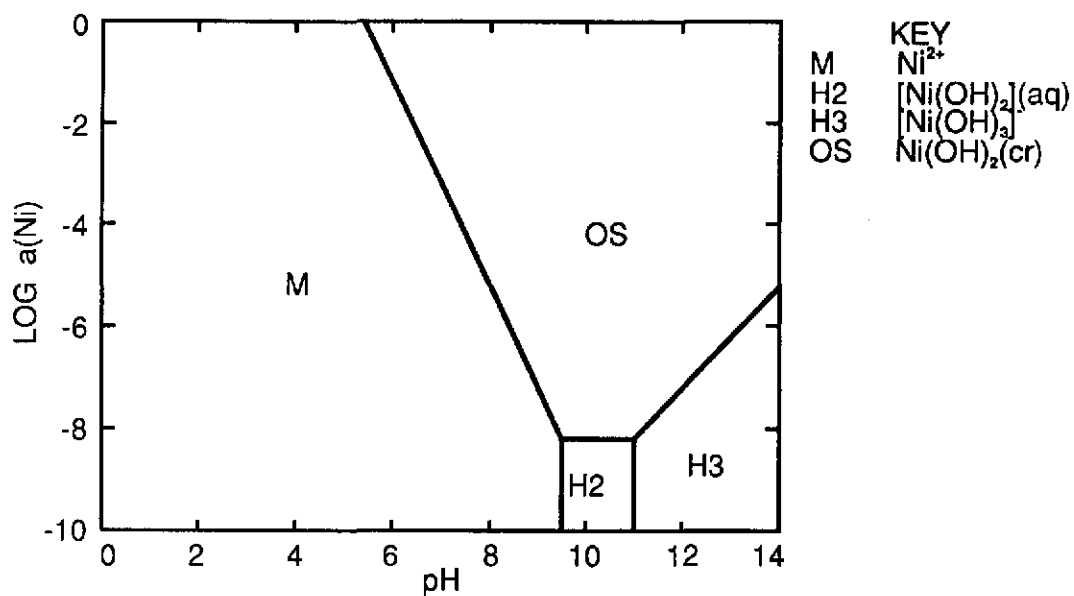
pAu(I)-pCN diagram for pH = 7.0.

Figure E-140



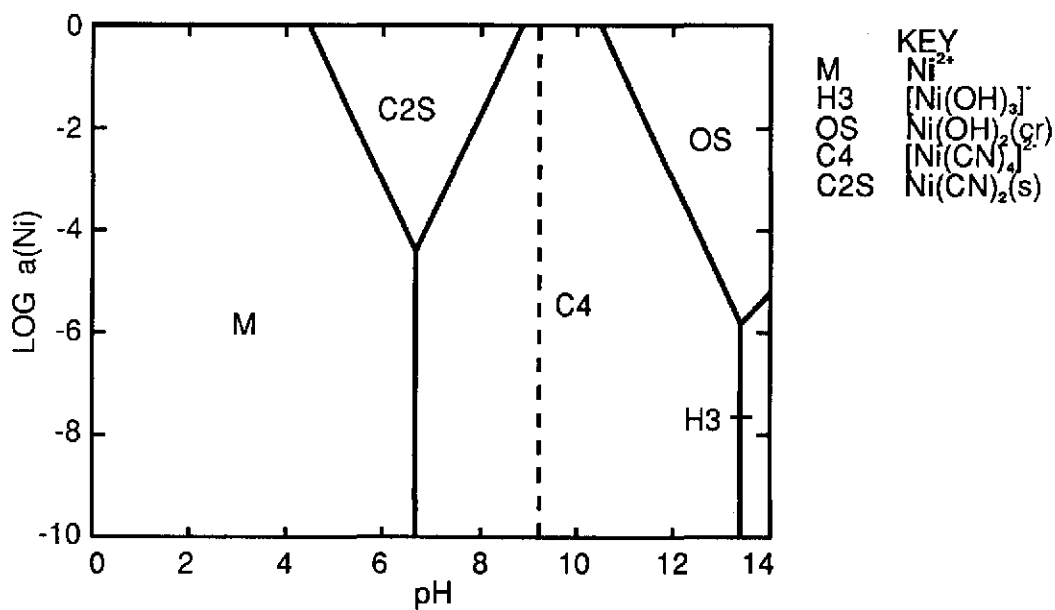
Eh-pH diagram for pAu = 2.0 and pCN = 2.0.

Figure E-141



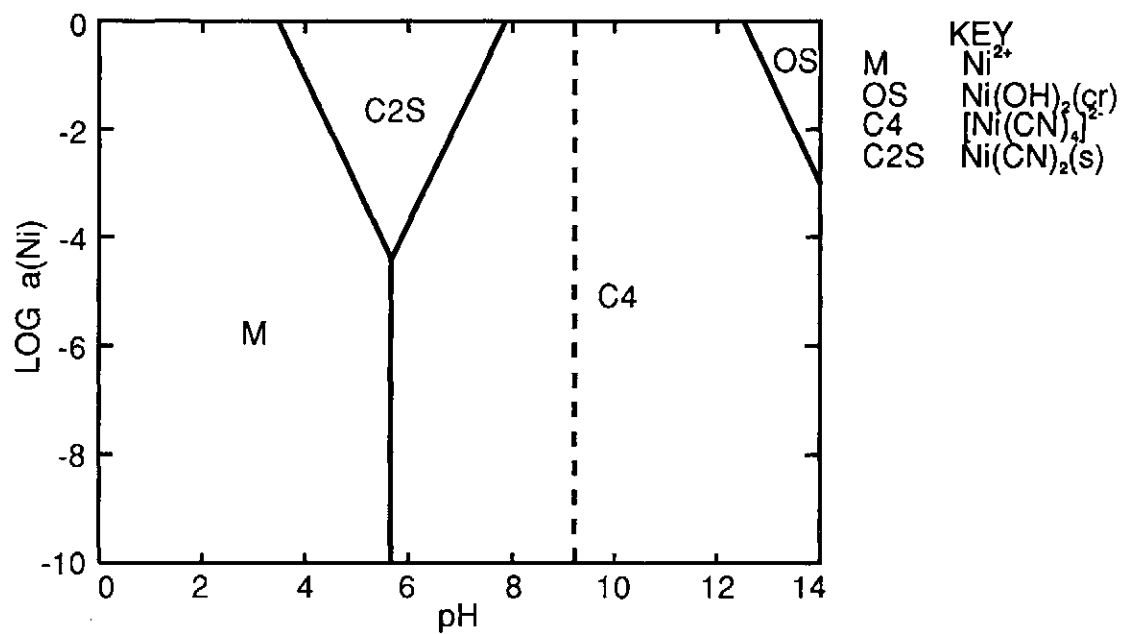
pNi-pH diagram with no ligands.

Figure E-142



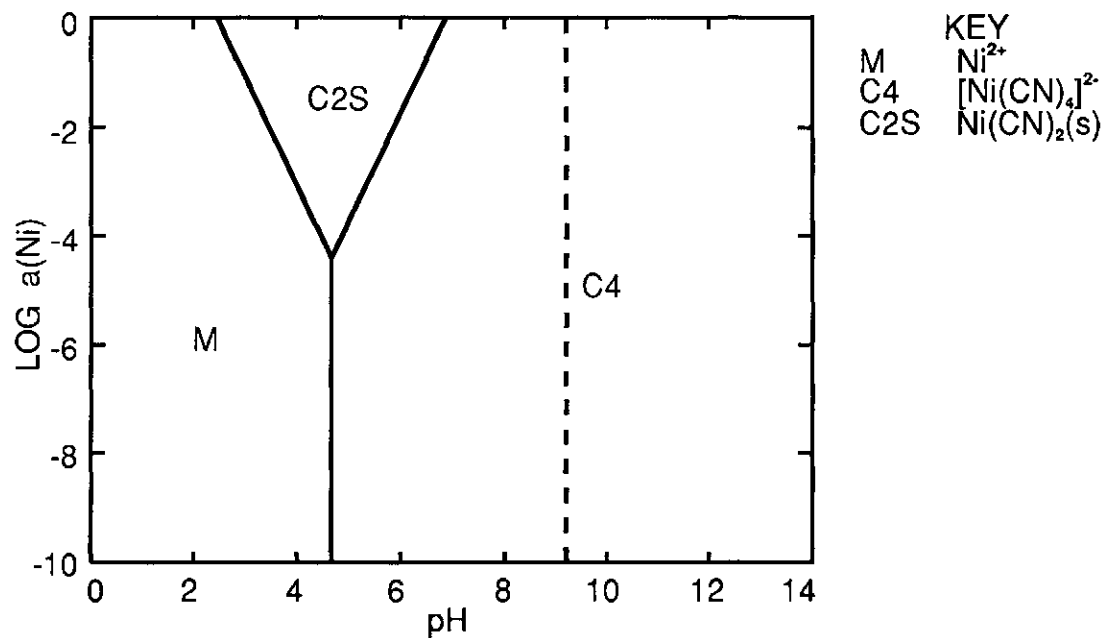
pNi-pH diagram for pCN = 5.0.

Figure E-143



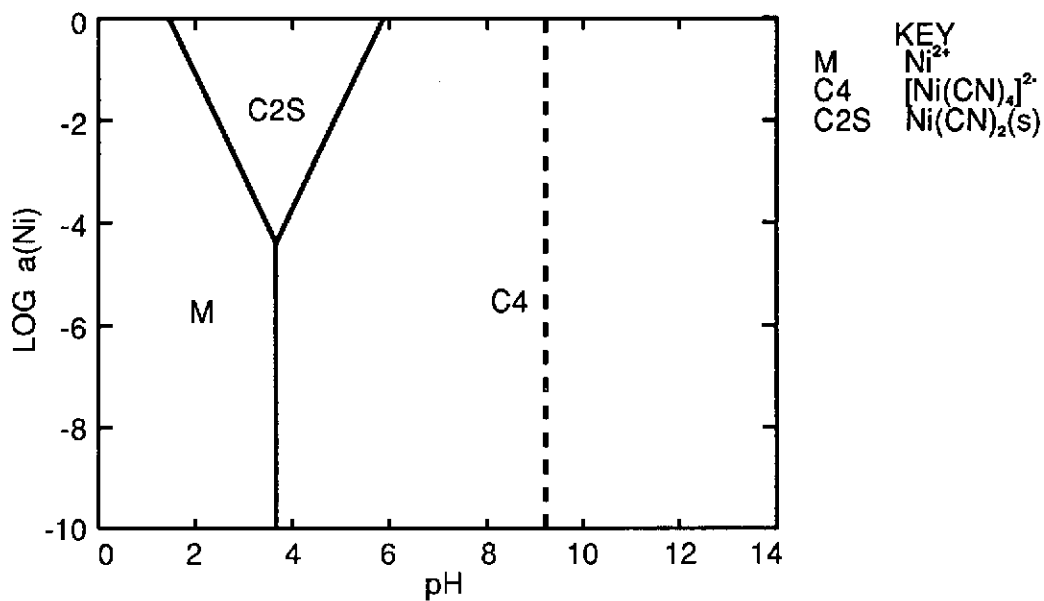
pNi-pH diagram for $p\text{CN} = 4.0$.

Figure E-144



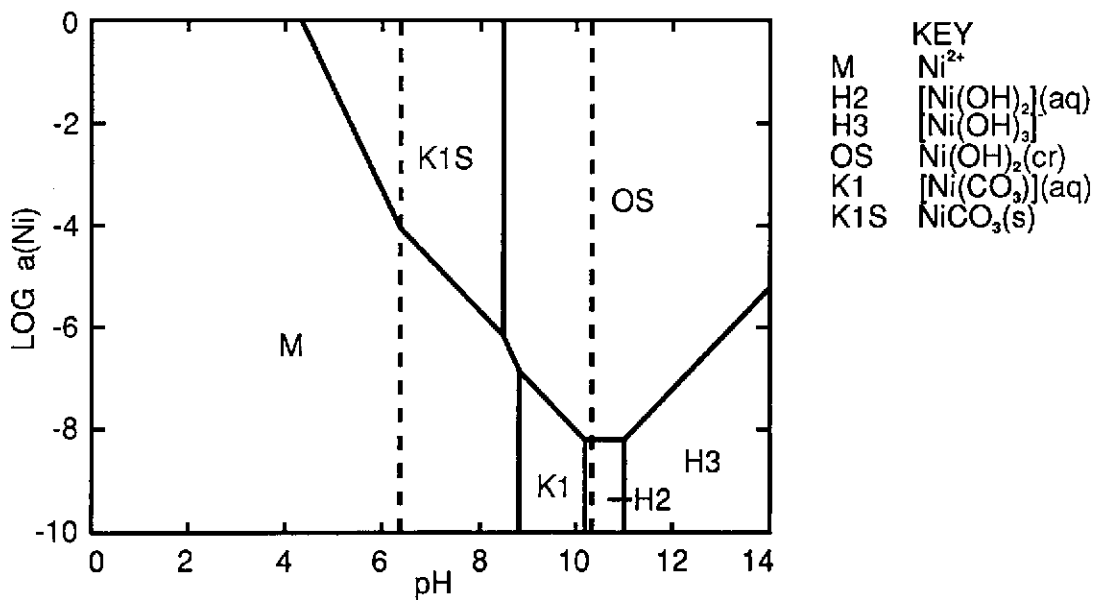
pNi-pH diagram for $p\text{CN} = 3.0$.

Figure E-145



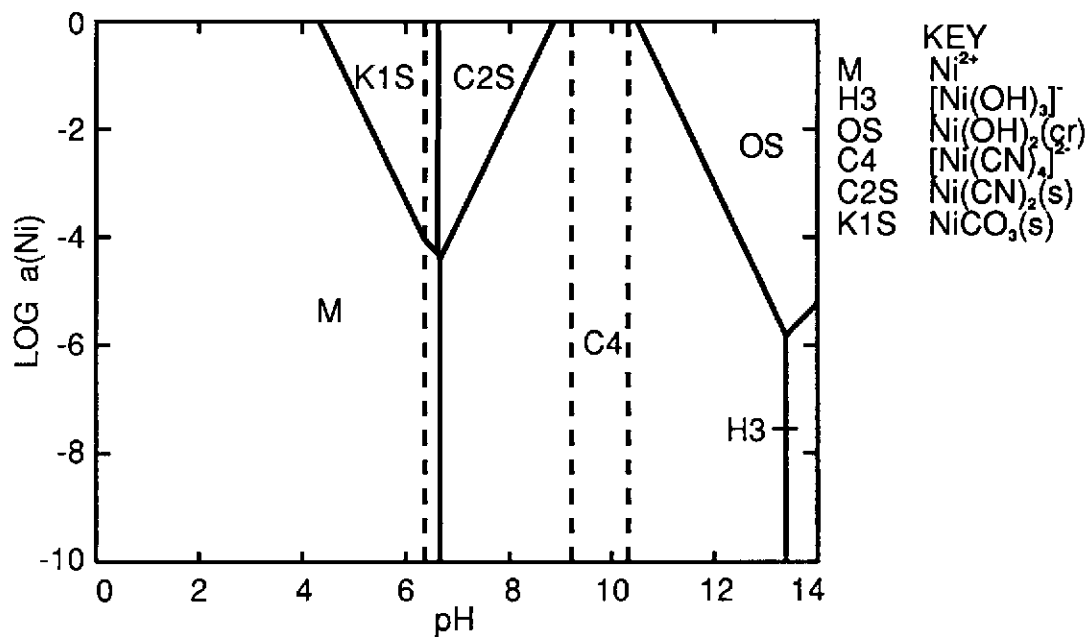
pNi -pH diagram for $pCN = 2.0$.

Figure E-146



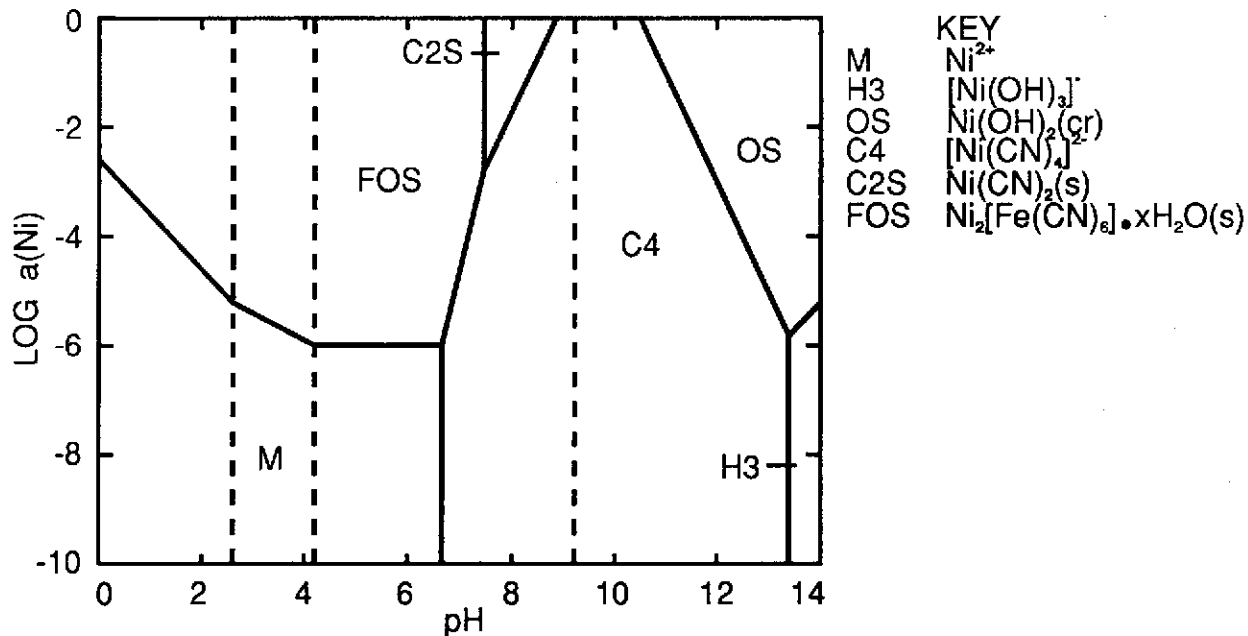
pNi -pH diagram for $pCO_3 = 3.0$.

Figure E-147



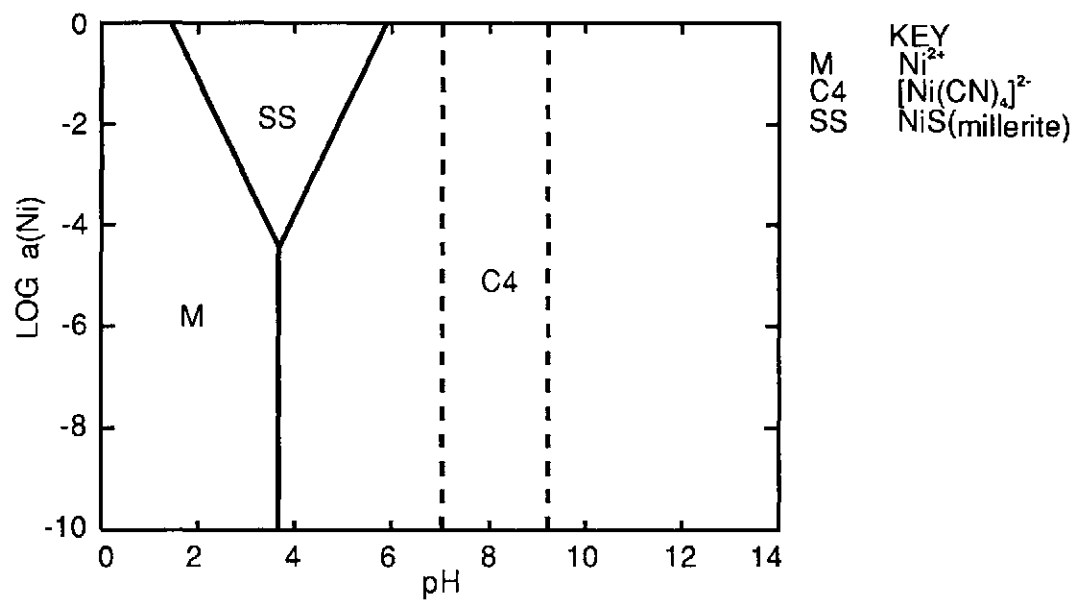
pNi-pH diagram for $p\text{CN} = 5.0$ and $p\text{CO}_3 = 3.0$.

Figure E-148



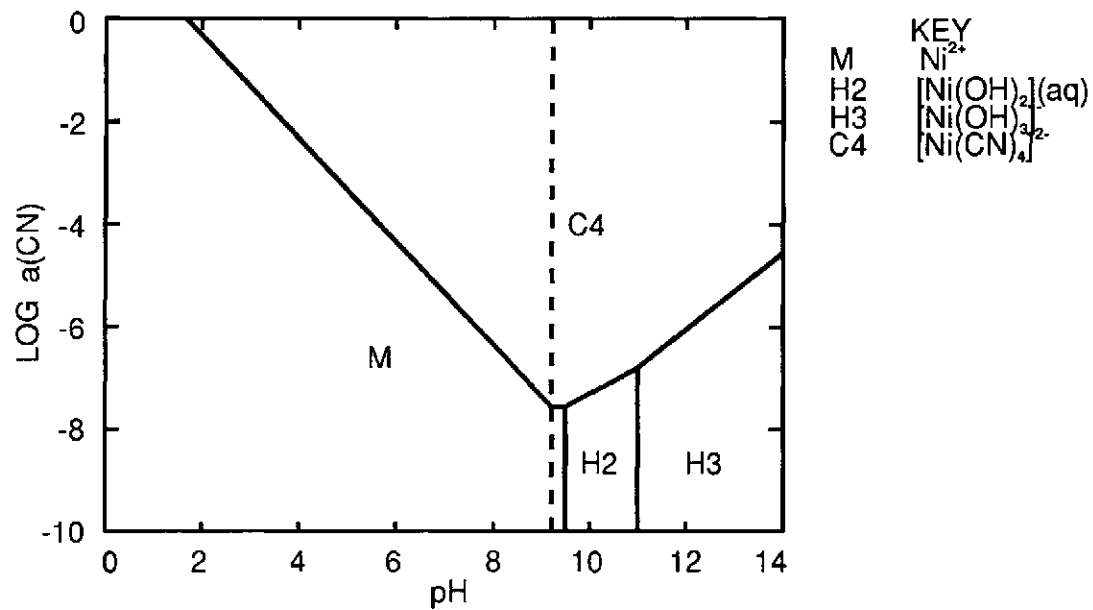
pNi-pH diagram for $p\text{CN} = 5.0$ and $p[\text{Fe}(\text{CN})_6]^{4-} = 4.0$.

Figure E-149



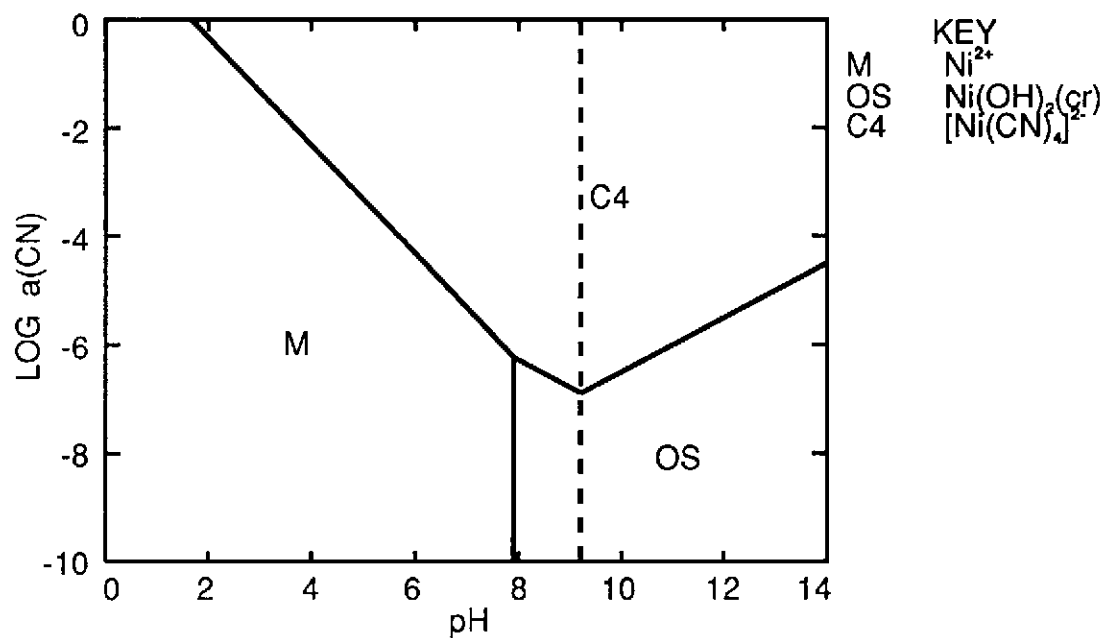
pNi-pH diagram for $p\text{CN} = 2.0$ and $p\text{S} = 6.0$.

Figure E-150



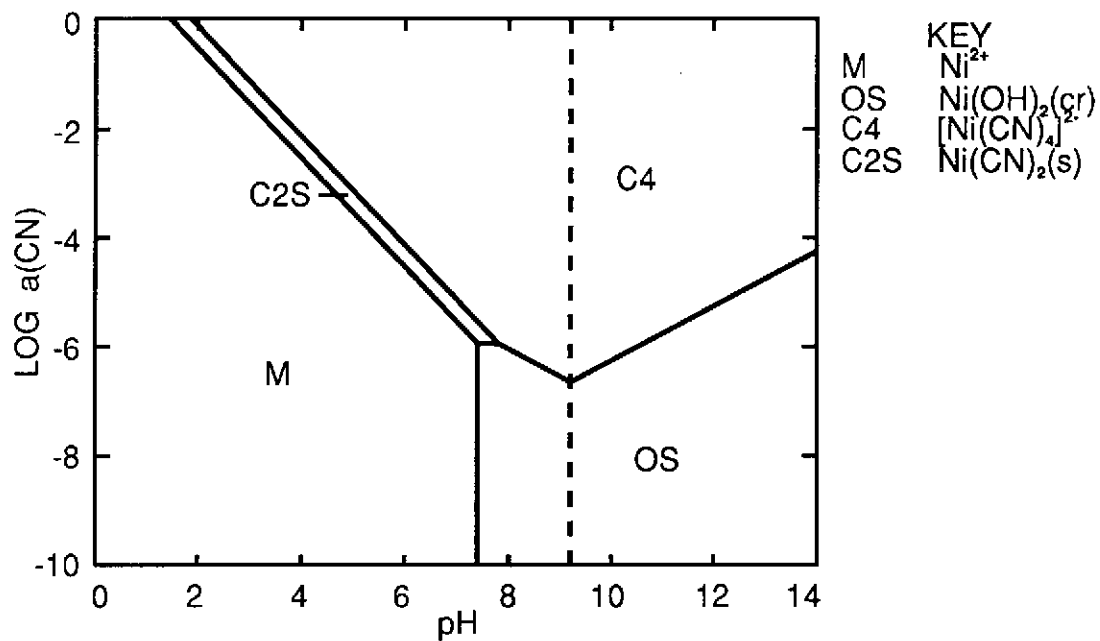
pCN-pH diagram for nickel solution species.

Figure E-151



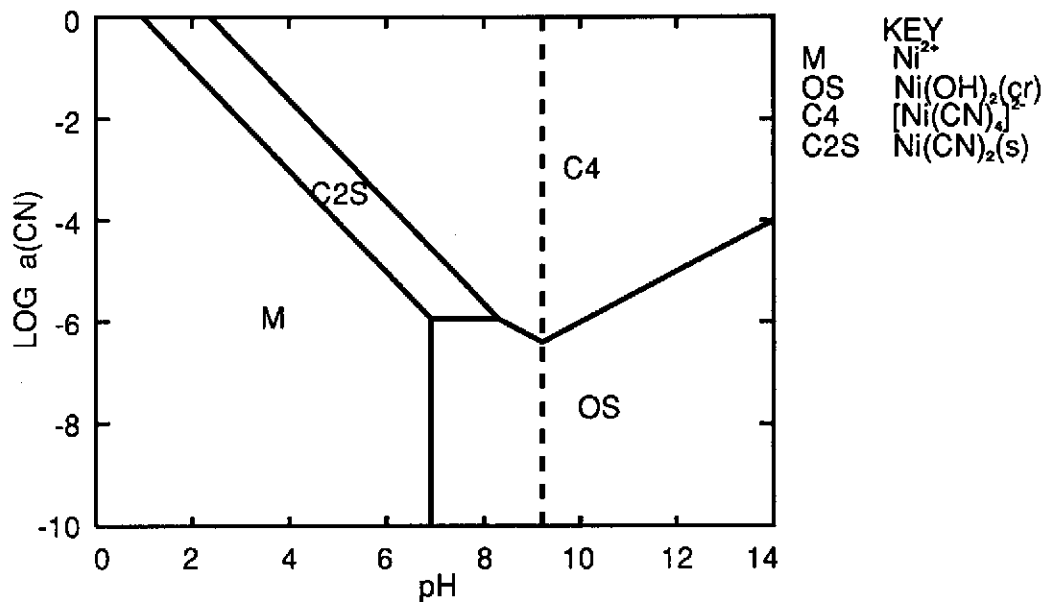
pCN-pH diagram for $p\text{Ni} = 5.0$.

Figure E-152



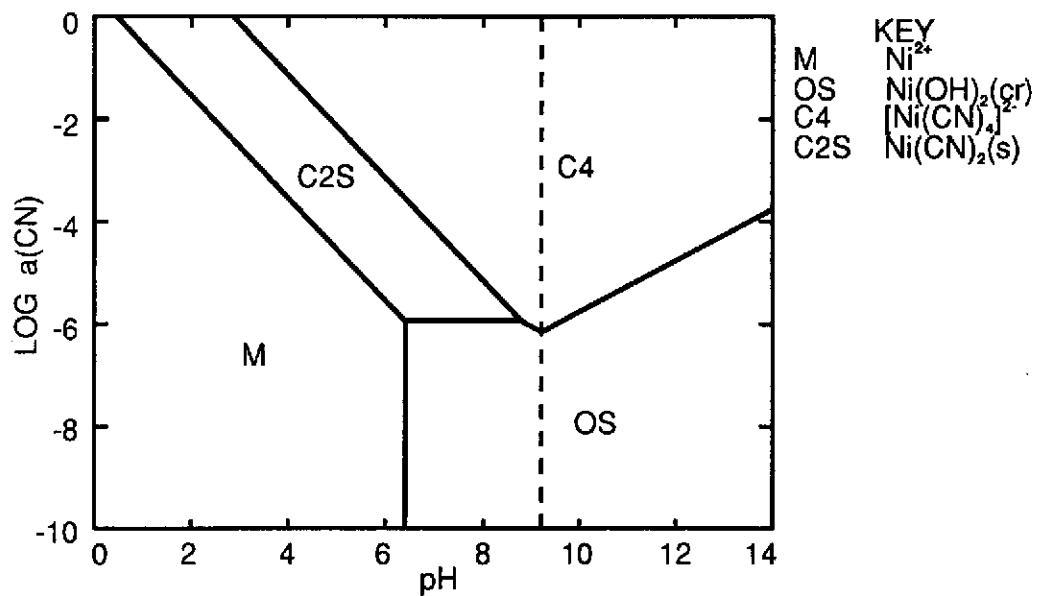
pCN-pH diagram for $p\text{Ni} = 4.0$.

Figure E-153



pCN-pH diagram for $p\text{Ni} = 3.0$.

Figure E-154



pCN-pH diagram for $p\text{Ni} = 2.0$.

Figure E-155

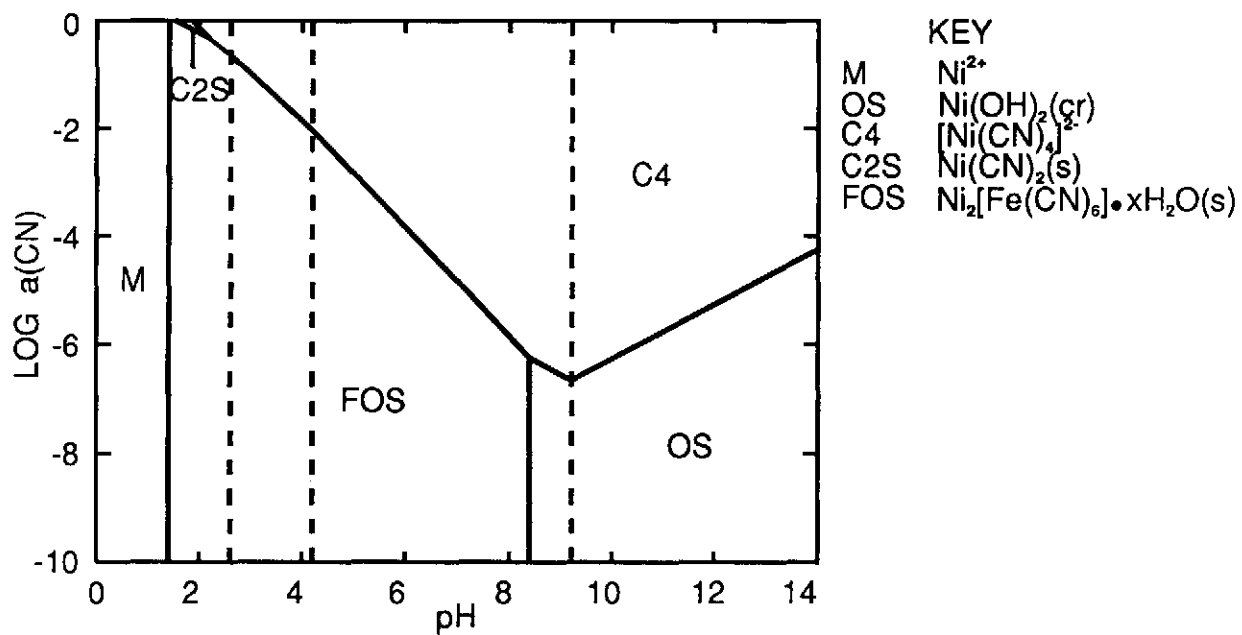


Figure E-156

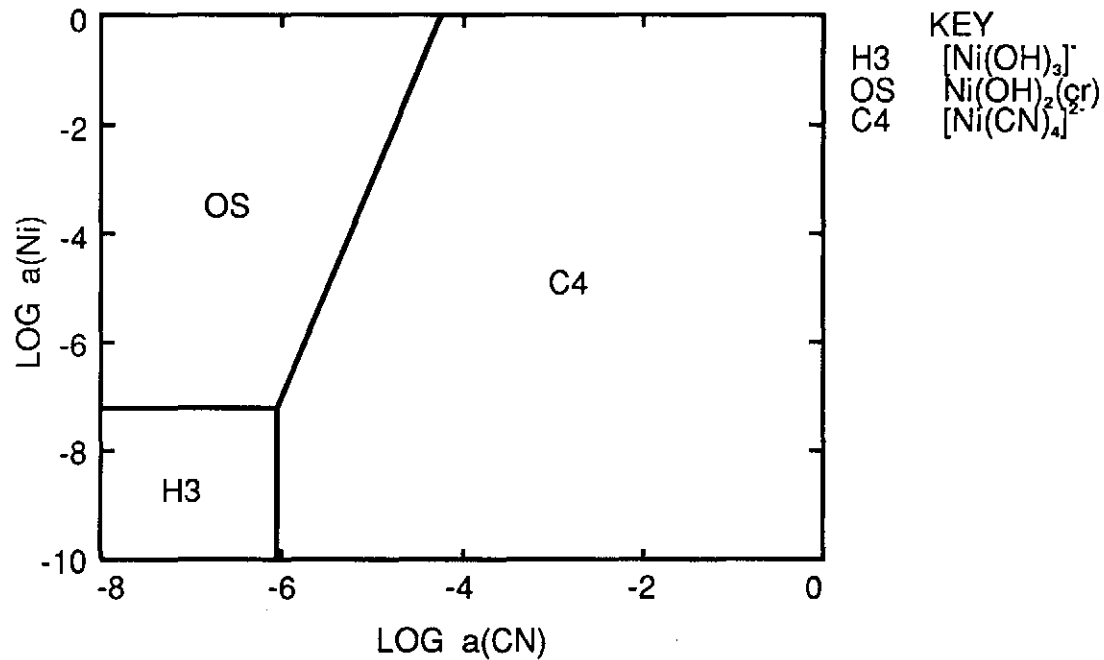
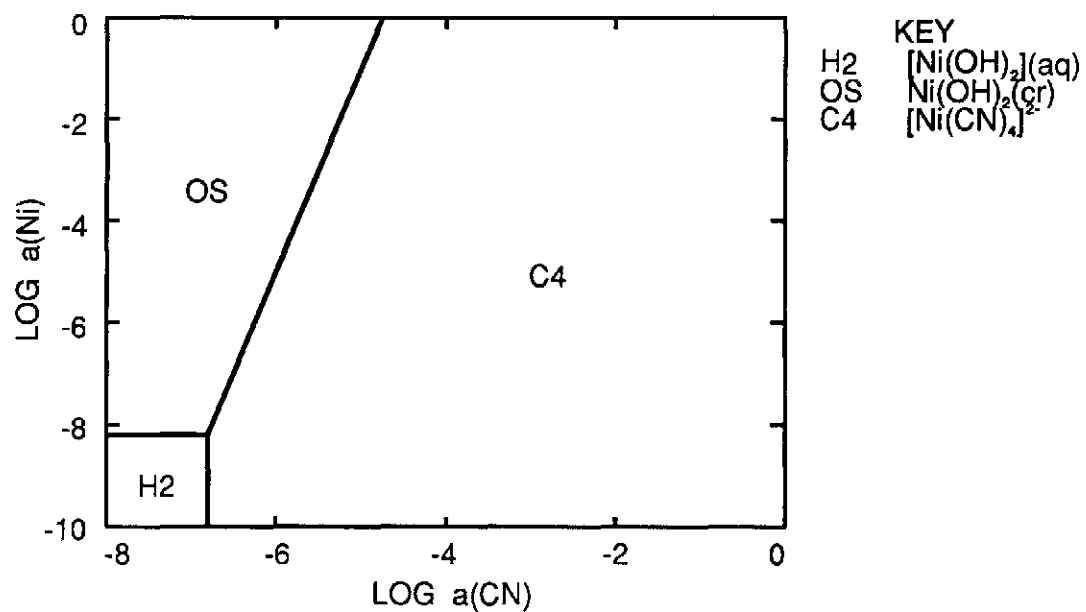
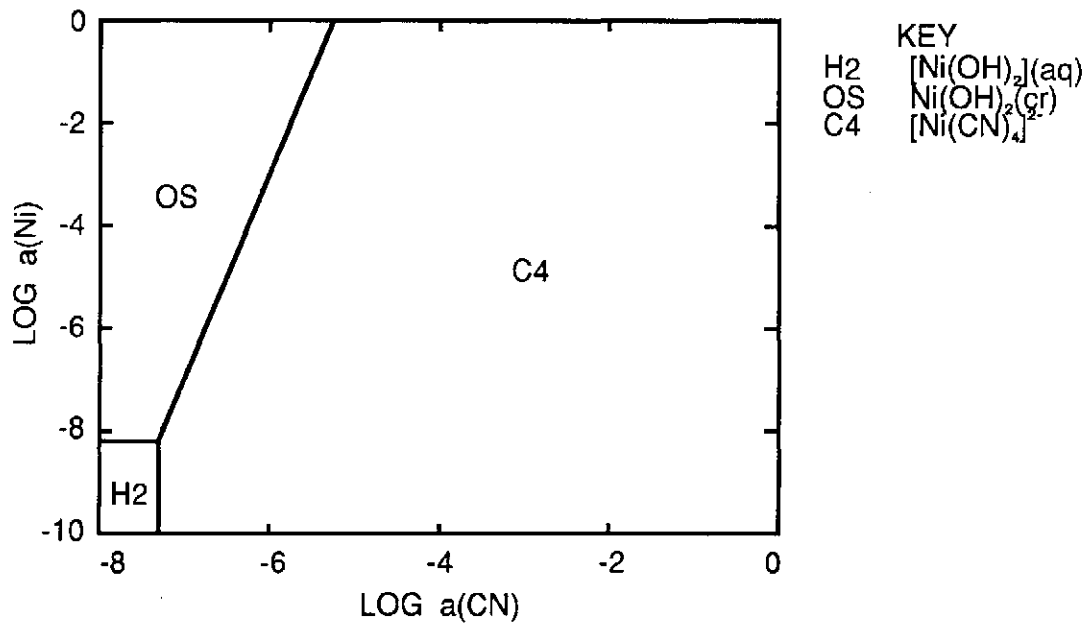


Figure E-157



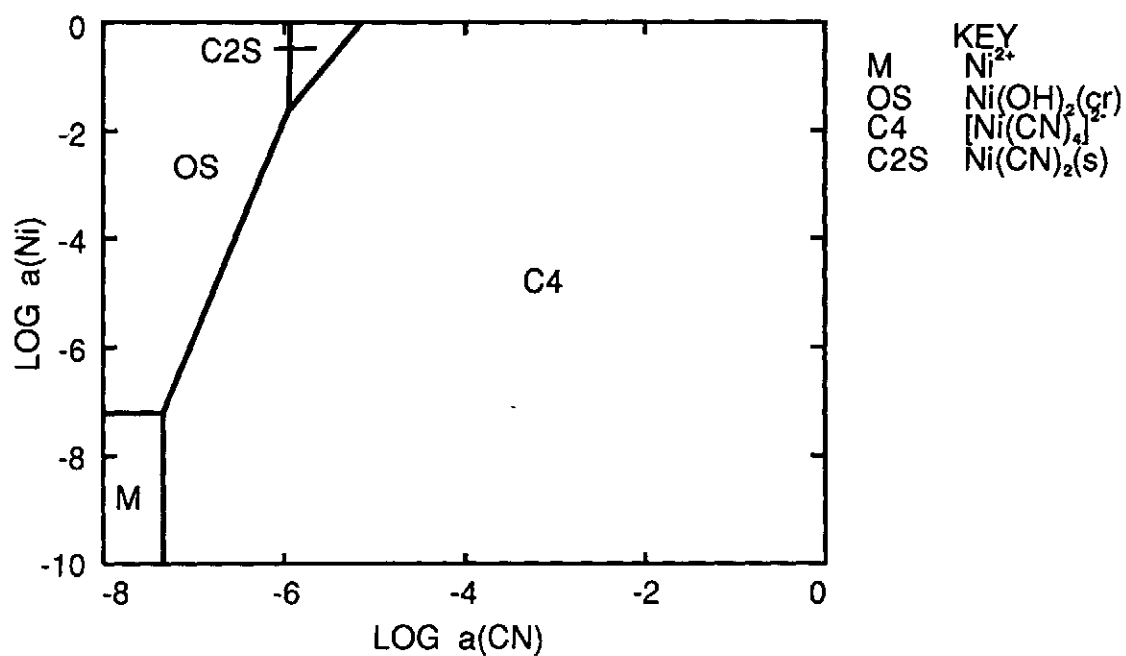
$p\text{Ni}$ - $p\text{CN}$ diagram for $\text{pH} = 11.0$.

Figure E-158



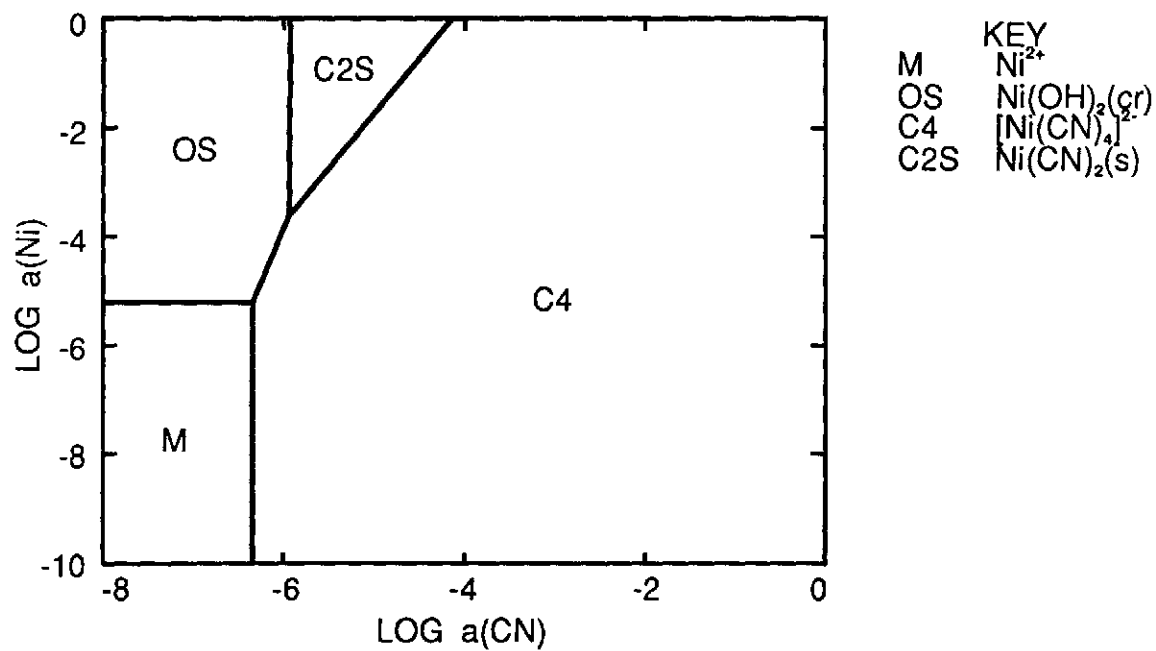
$p\text{Ni}$ - $p\text{CN}$ diagram for $\text{pH} = 10.0$.

Figure E-159



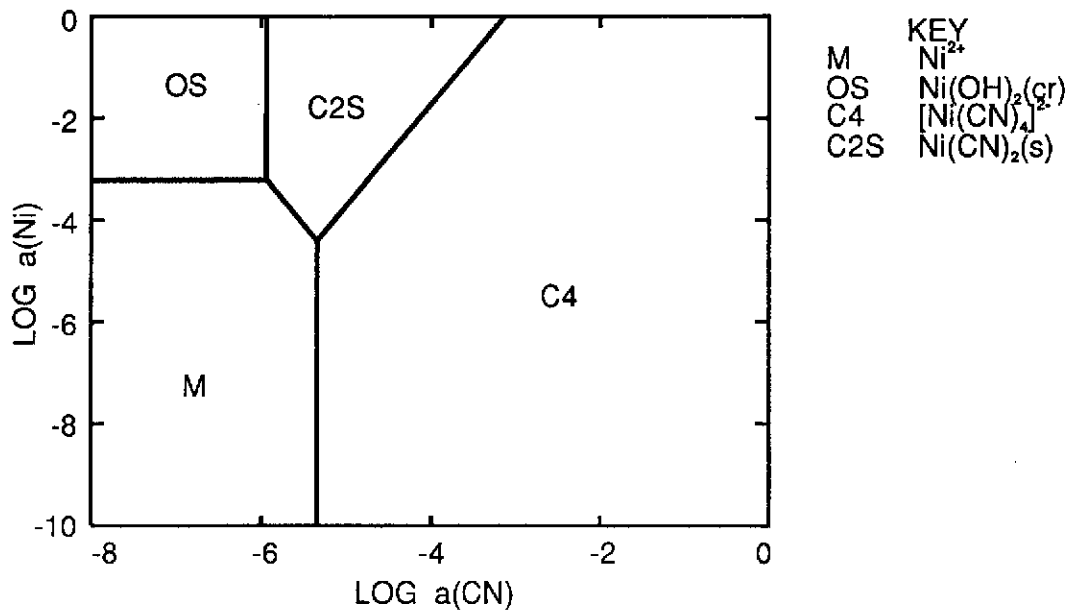
pNi-pCN diagram for pH = 9.0.

Figure E-160



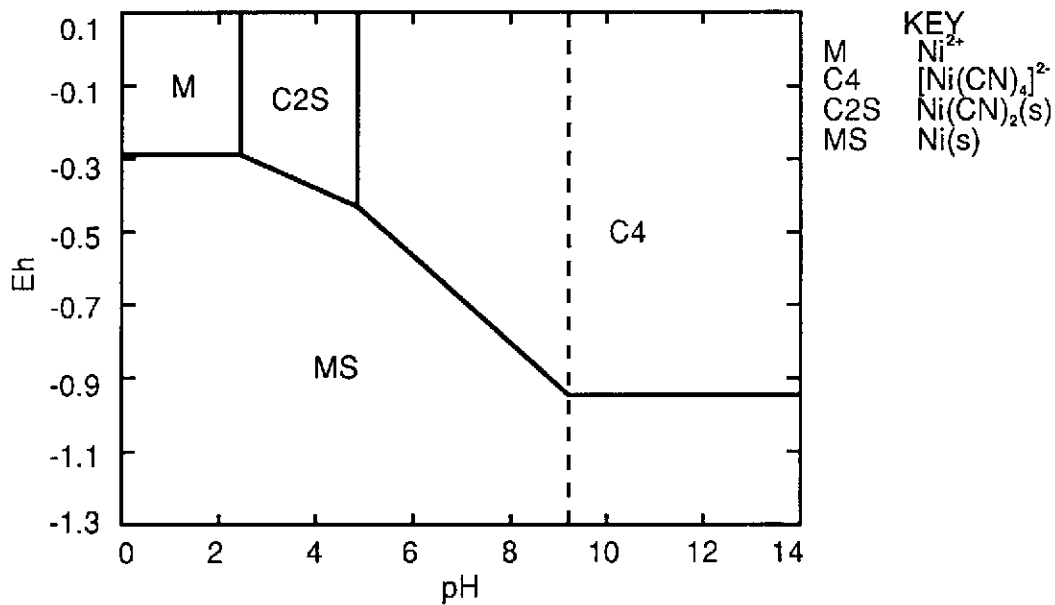
pNi-pCN diagram for pH = 8.0.

Figure E-161



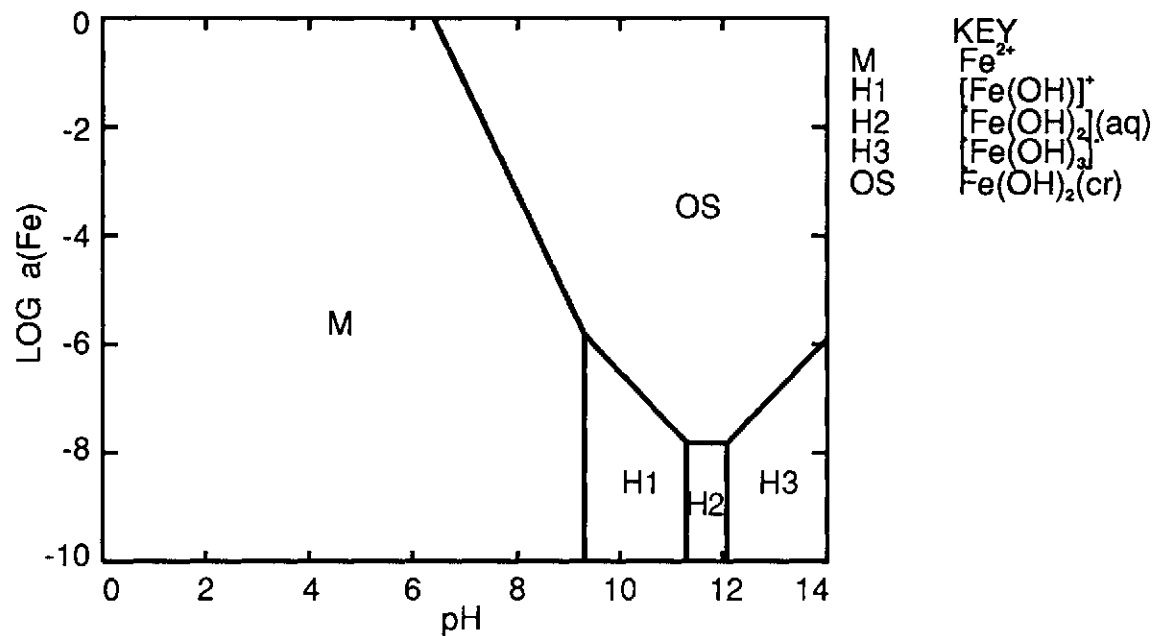
pNi-pCN diagram for pH = 7.0.

Figure E-162



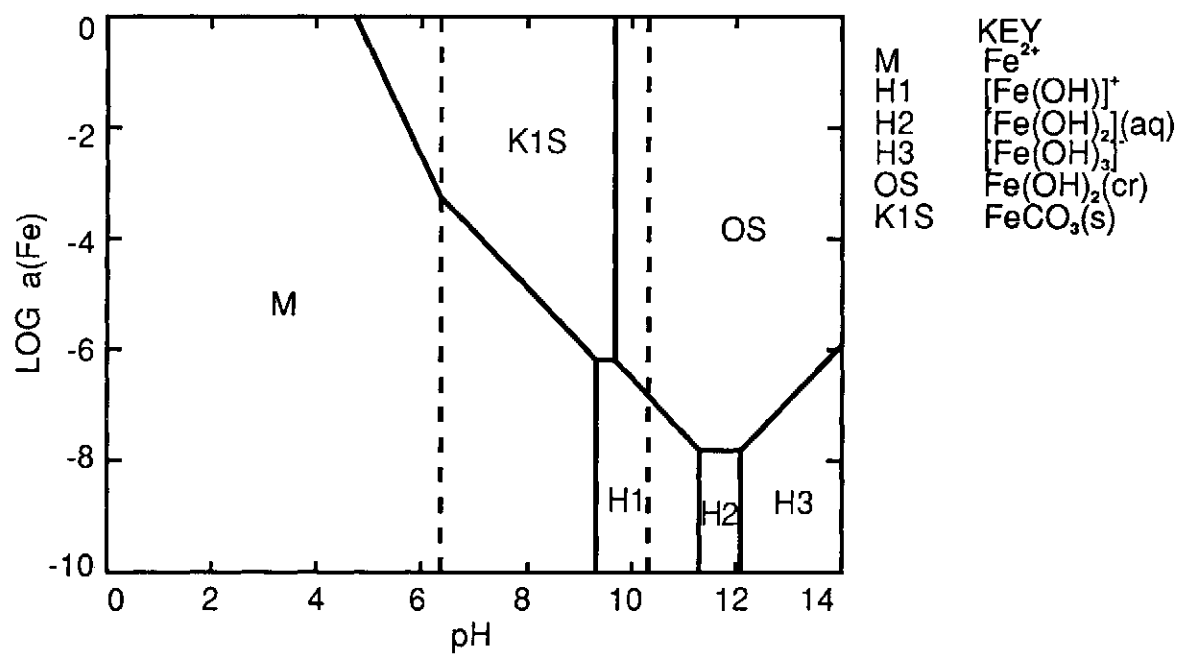
Eh-pH diagram for pNi = 2.0 and pCN = 2.0.

Figure E-163



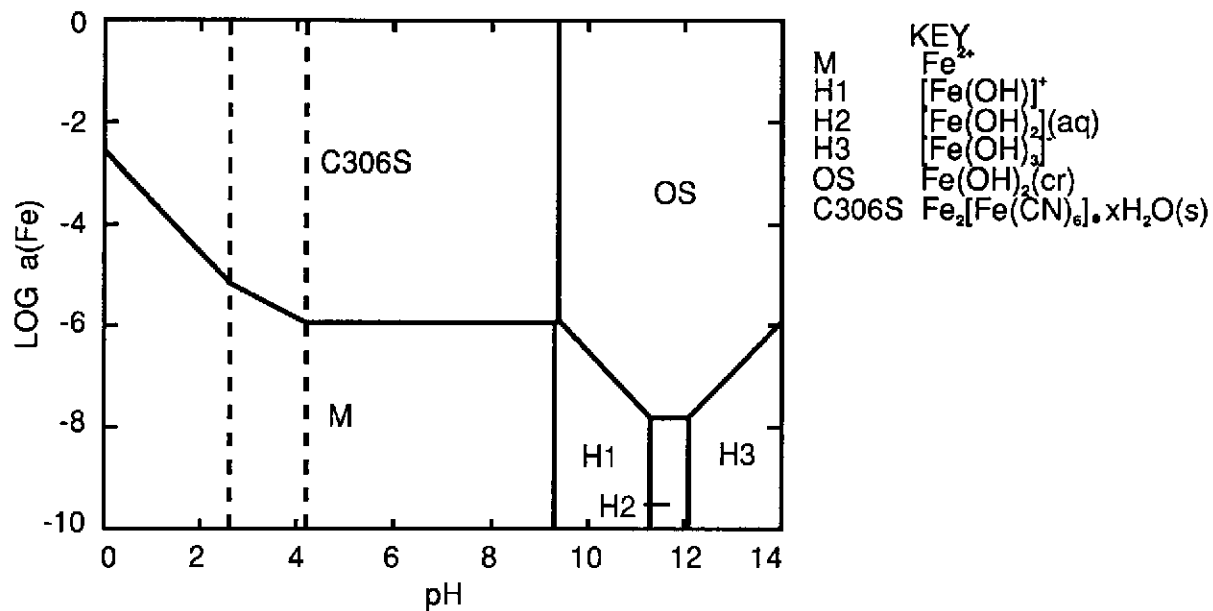
$p\text{Fe(II)}$ - pH diagram with no ligands.

Figure E-164



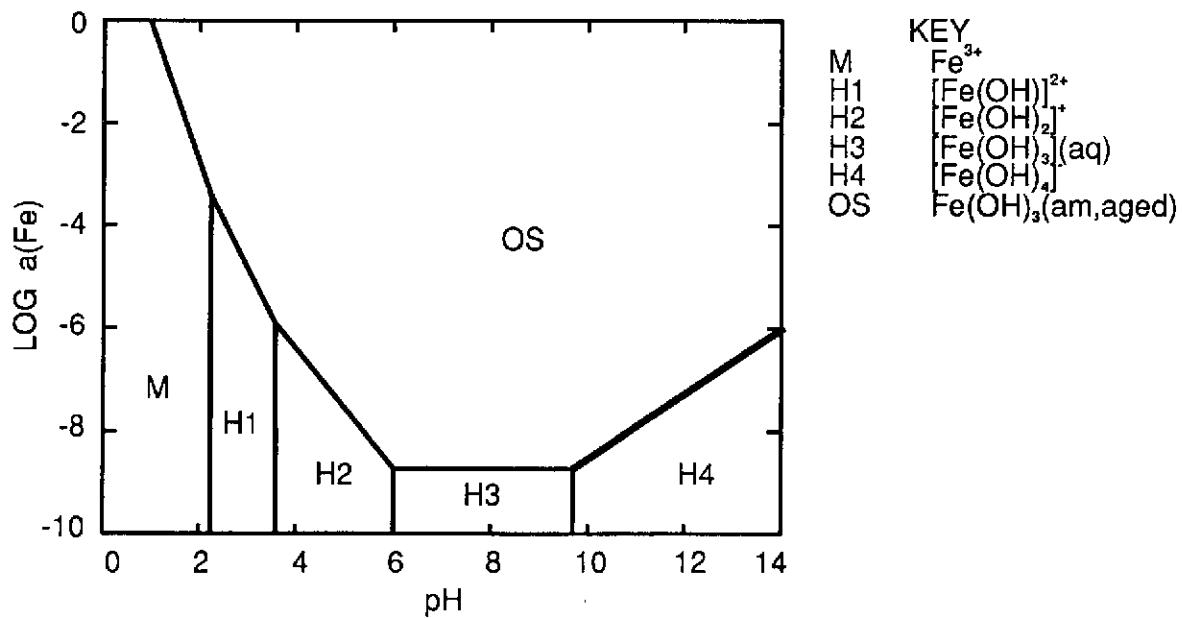
$p\text{Fe(II)}$ - pH diagram for $p\text{CO}_2 = 3.0$.

Figure E-165



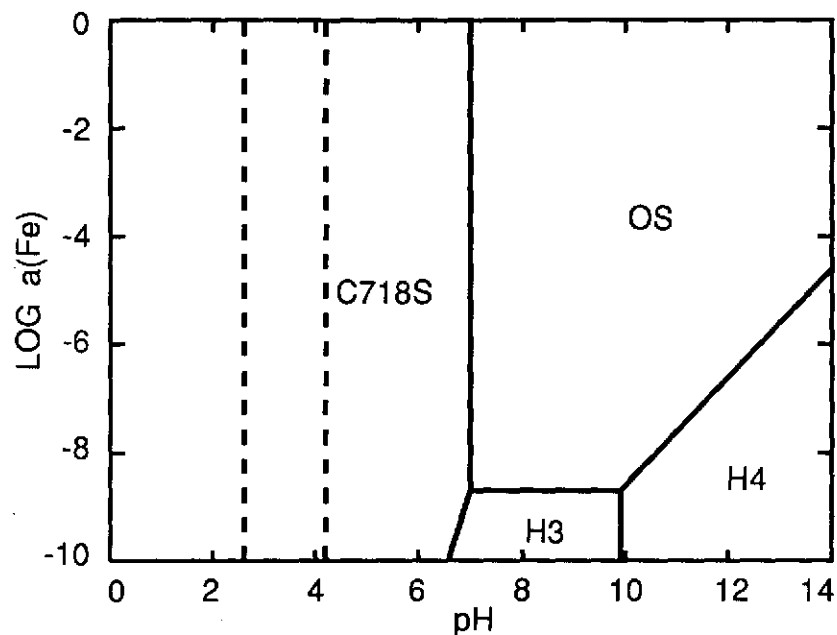
$p\text{Fe(II)}$ - pH diagram for $p[\text{Fe}(\text{CN})_6^{4-}] = 4.0$.

Figure E-166



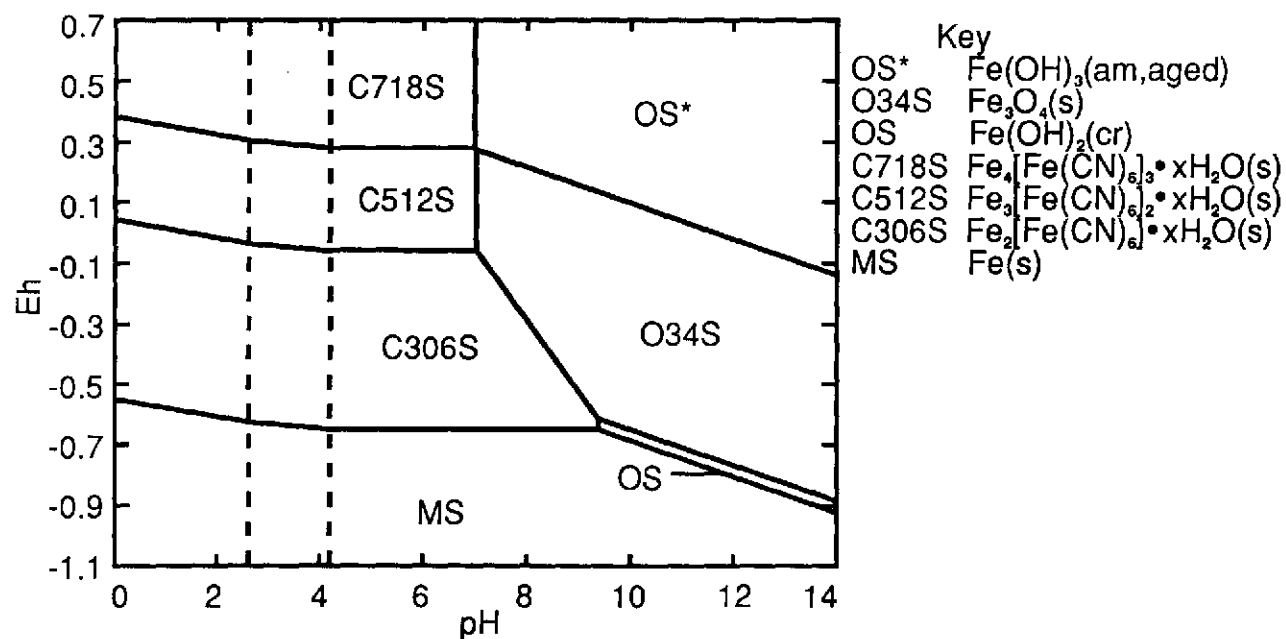
$p\text{Fe(III)}$ - pH diagram with no ligands.

Figure E-167



$p\text{Fe(III)}$ - pH diagram for $p[\text{Fe}(\text{CN})_6^{4-}] = 4.0$.

Figure E-168



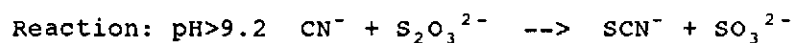
Eh - pH diagram for $p\text{Fe} = 2.0$ and $p[\text{Fe}(\text{CN})_6^{4-}] = 4.0$.

APPENDIX F.—RATE DATA FOR REACTIONS OF FREE CYANIDE AND DERIVED SPECIES

This appendix contains rate data for reactions of free cyanide and derived and related species. The data are compiled in tables F-1 through F-16. At the head of each table, the chemical reactions are given, written with the species predominant in the specified pH ranges at 25° C from the data in table B-2. Then the rate equation is given. In the rate equation, Z and R denote respectively the total substrate and reagent concentrations. Total substrate or reagent concentration means all species of substrate or reagent that are interrelated by hydrogen-ion gain or loss. For example, if Z is cyanide, $Z = [\text{CN}^-] + [\text{HCN}]$. For some hydrolysis reactions, the reagent R is H_2O and does not appear in the rate equation. The rate constants are designated by "k's" with different subscripts. Equilibrium constants for dissociation of H_2O or acid dissociation of substrate or reagent species are designated respectively by K_w , K_a , or K_{aR} . The units of concentration and time are respectively $\text{mol} \cdot \text{L}^{-1}$ and s throughout. Data are tabulated for each rate constant in the rate equation. The cited references are listed at the end of chapter 7.

The experimental conditions, namely, pH, ionic strength, and temperature, are given. The data were processed according to equation 7-7 in chapter 7. The linear least squares fit correlation coefficient r and the activation enthalpy ΔH^* and entropy ΔS^* are given if rate constants at three or more temperatures were reported. The values of ΔH^* and ΔS^* quoted in the references are also given. If the reference quotes a ΔE^* value instead of ΔH^* , that value is entered for the "Authors' data" ΔH^* , and the letter E is entered for "Authors' data" ΔS^* . Discrepancies between ΔH^* and ΔS^* values calculated here versus those quoted by the authors are attributed to unreported data for other temperatures or to differences in data treatment. Finally, rate constants at temperatures 0°, 10°, 25°, 40°, 60°, and 90° C, calculated from the statistical data treatment conducted here, are tabulated. Values at temperatures more than 20° C beyond the temperature range of the reported experimental data should be used cautiously, as indicated by the tabulated standard errors.

Table F-1.-Kinetic data for reaction of
cyanide with thiosulfate



Rate equation: $-\text{R}^{-1}\text{Z}^{-1}\text{dZ}/\text{dt} = k_1 K_a (K_a + [\text{H}^+])^{-1}$

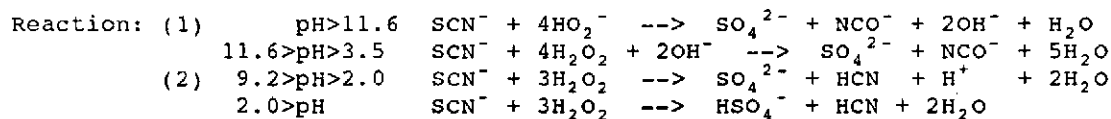
Reported rate constants	k_1	k_1
Reference	28	28
pH range	¹ 11	¹ 11
Ionic strength, M	0	0.09
Temperature, $^{\circ}\text{C}$	25-90	25-90
Statistical processing		
Number of points	3	3
Correlation coefficient	0.9986	0.9959
ΔH° , kJ	43.8	39.1
	± 2.3	± 3.5
ΔS° , J·K	-192.5	-198.5
	± 7.0	± 10.7
Authors' data		
ΔH° or ΔE° , kJ	51.9	N
	± 1.7	
ΔS° , J·K	-163.2	N
	± 12.6	
Calculated rate constants		
0 $^{\circ}$ C	(2.1 $\pm$ 0.5) E-6	(8.1 $\pm$ 2.8) E-6
10	(4.4 $\pm$ 0.8) E-6	(1.55 $\pm$ 4.4) E-5
25	(1.17 $\pm$ 1.5) E-5	(3.8 $\pm$ 0.8) E-5
40	(2.9 $\pm$ 0.3) E-5	(8.4 $\pm$ 1.2) E-5
60	(8.4 $\pm$ 0.6) E-5	(2.2 $\pm$ 0.3) E-4
90	(3.4 $\pm$ 0.4) E-4	(7.7 $\pm$ 1.3) E-4

N No data.

¹Estimated: not stated.

Note.—Cited references are listed at end of Chapter 7.

Table F-2.-Kinetic data for oxidation of
thiocyanate ion by hydrogen peroxide



Rate equation: (1) $-\text{R}^{-1}\text{Z}^{-1}\text{dZ}/\text{dt} = k_1[\text{H}^+](K_{a_r} + [\text{H}^+])^{-1}$
 (2) $-\text{R}^{-1}\text{Z}^{-1}\text{dZ}/\text{dt} = k_2[\text{H}^+][\text{H}_2\text{O}_2]([[\text{H}_2\text{O}_2]] + k_3[\text{HCN}])^{-1}$

Reported rate constants	k_1 29	k_2 30	k_3 30
Reference			
pH range	4-13	1	1
Ionic strength., M	0.27	0.1	0.1
Temperature °C	20-50	20, 30	20, 30
Statistical processing			
Number of points	3	2	2
Correlation coefficient	0.9998	¹ N	¹ N
$\Delta H^\ddagger$, kJ	62.1	36.7	N
	± 1.2		
$\Delta S^\ddagger$, J·K	-103.6	-151.4	N
	± 3.8		
Authors' data			
$\Delta H^\ddagger$ or $\Delta E^\ddagger$, kJ	64.9	46.0	N
$\Delta S^\ddagger$, J·K	E	E	N
Calculated rate constants			
0° C	(3.0 $\pm$ 1.2) E-5	(6.8) E-3	N
10	(8.1 $\pm$ 1.4) E-5	(1.24) E-2	N
25	(3.23 $\pm$ 0.07) E-4	(2.9) E-2	² 2
40	(1.12 $\pm$ 0.03) E-3	(6.1) E-2	N
60	(5.0 $\pm$ 1.2) E-3	(1.51) E-1	N
90	(3.5 $\pm$ 1.3) E-2	(4.9) E-1	N

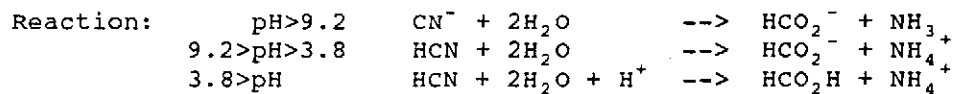
N No data.

¹Correlation coefficient and errors not determinable.

²Approximately constant at 20° and 30° C.

Note.—Cited references are listed at end of Chapter 7.

Table F-3.-Kinetic data for addition of water to cyanide



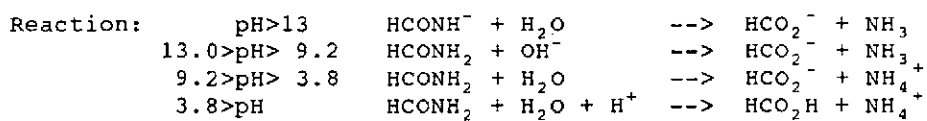
Rate equation: $-z^{-1}dz/dt = k_1 K_{a2} ([\text{H}^+] + K_{a2})^{-1} + k_2 [\text{H}^+]$

Reported rate constants	k_1	k_2
Reference	44	47
pH range	7-10	<0
Ionic strength, M	0.2	6.
Temperature, $^{\circ}\text{C}$	30-100	70-85
Statistical processing		
Number of points	3	3
Correlation coefficient	1.0000	0.9999
ΔH° , kJ	95.1	74.9
	± 8	± 9
ΔS° , J·K	-79.2	-116.4
	± 2.4	± 2.7
Authors' data		
ΔH° or ΔE° , kJ	N	77.8
ΔS° , J·K	N	E
Calculated rate constants		
0° C	(2.7 $\pm$ 2.2) E-10	(2.3 $\pm$ 2.2) E-8
10	(1.26 $\pm$ 0.07) E-9	(7.7 $\pm$ 6) E-8
25	(1.01 $\pm$ 0.05) E-8	(4.0 $\pm$ 2) E-7
40	(6.7 $\pm$ 2) E-8	(1.78 $\pm$ 0.07) E-6
60	(6.3 $\pm$ 2) E-7	(1.07 $\pm$ 0.02) E-5
90	(1.18 $\pm$ 0.04) E-5	(1.08 $\pm$ 0.01) E-4

N No data.

Note.—Cited references are listed at end of Chapter 7.

Table F-4.-Kinetic data for hydrolysis of formamide



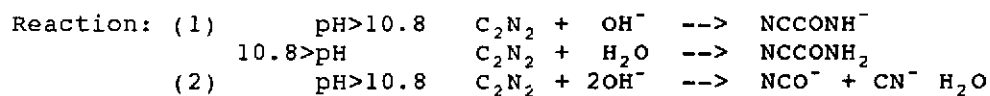
Rate equation: $-Z^{-1}dZ/dt = k_1[\text{H}^+] + k_2 + k_3[\text{OH}^-]$

Reported rate constants	k_1	k_2
Reference	62	61
pH range	1-9	1-9
Ionic strength, M	0.1	0.1
Temp., °C	80 only	80 only
Statistical processing		
Number of points	N	N
Correlation coefficient		
$\Delta H^\ddagger$, kJ	N	N
$\Delta S^\ddagger$, J·K	N	N
Authors' data		
$\Delta H^\ddagger$ or $\Delta E^\ddagger$, kJ	N	N
$\Delta S^\ddagger$, J·K	N	N
Calculated rate constants		
0° C	(1.05±.21) E-5	(1.66±.09) E-4
10	(3.33±.47) E-4	(4.8±1.8) E-3
25	(1.63±.11) E-4	(2.10±.35) E-3
40	(6.83±0.32) E-4	(8.0±.9) E-3
60	(3.8±0.4) E-3	(3.9±1.1) E-2
90	(3.5±0.8) E-25	(3.1±1.9) E-14

N No data.

Note.—Cited references are listed at end of Chapter 7.

Table F-5.-Kinetic data for hydrolysis of cyanogen



Rate equation: (1) $-Z^{-1}dz/dt = k_1 + k_2K_w[H^+]^{-1}$
 (2) $-Z^{-1}dz/dt = k_3K_w[H^+]^{-1}$

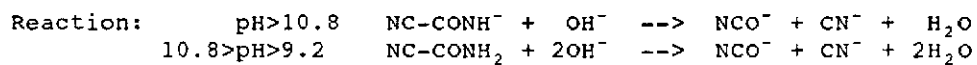
Reported rate constants	k_1	k_2	k_3
Reference	67	67	67
pH range	2.0	11-13	11-13
Ionic strength, M	0.01	0.01	0.01
Temperature, °C	25	5-45	5-45
Statistical processing			
Number of points	N	8	8
Correlation coefficient	N	0.9999	0.9999
$\Delta H^\ddagger$, kJ	N	55.2	63.7
		± 3	± 4
$\Delta S^\ddagger$, J·K	N	+4.4	+25.5
		± 1	± 1.3
Authors' data			
$\Delta H^\ddagger$ or $\Delta E^\ddagger$, kJ	N	55.3	63.8
		± 3	± 4
$\Delta S^\ddagger$, J·K	N	-33.8	-12.1
		± 3	± 1
Calculated rate constants			
0° C	N	(2.65 $\pm$.08) E+2	(8.2 $\pm$.3) E+1
10	N	(6.48 $\pm$.12) E+2	(2.28 $\pm$.05) E+2
25	¹ 5.3E-7	(2.22 $\pm$.03) E+3	(9.35 $\pm$.14) E+2
40	N	(6.79 $\pm$.15) E+3	(3.38 $\pm$.09) E+3
60	N	(2.58 $\pm$.10) E+4	(1.55 $\pm$.07) E+4
90	N	(1.46 $\pm$.09) E+5	(1.13 $\pm$.09) E+5

N No data.

¹Reported.

Note.—Cited references are listed at end of Chapter 7.

Table F-6.--Kinetic data for disproportionation
of cyanoformamide



Rate equation: $-Z^{-1}dZ/dt = k_1 K_{a2} ([H^+] + K_{a2})$

Reported rate constants	k_1
Reference	67
pH range	11-13
Ionic strength, M	0.01
Temperature, °C	5-45
Statistical processing	
Number of points	5
Correlation coefficient	¹ N
$\Delta H^\ddagger$, kJ	¹ N
$\Delta S^\ddagger$, J·K	¹ N
Authors' data	
$\Delta H^\ddagger$ or $\Delta E^\ddagger$, kJ	91.8
	±.4
$\Delta S^\ddagger$, J·K	+57.7
	±.3
Calculated rate constants	
0° C	² (1.64) E-2
10	² (7.1) E-2
25	² (5.3) E-1
40	² (3.28)
60	² (2.90) E+1
90	² (4.9) E+2

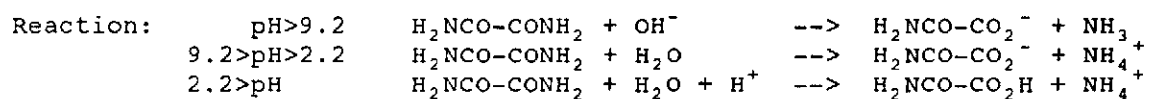
N No data.

¹Individual rate constants not reported.

²Calculated from authors' activation parameters.

Note.--Cited references are listed at end of Chapter 7.

Table F-7.-Kinetic data for hydrolysis of oxamide



Rate equation: $-Z^{-1}dZ/dt = k_1[\text{H}^+] + k_2[\text{OH}^-]$

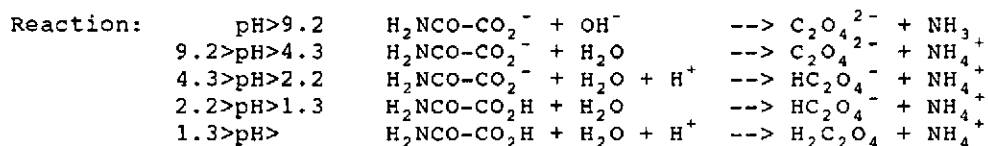
Reported rate constants	k_1	k_2
Reference	78	79, 80
pH range	0-2	12-13
Ionic strength, M	1.	1.
Temperature, °C	80, 98	0-30
Statistical processing		
Number of points	2	4
Correlation coefficient	¹ N	0.9994
ΔH° , kJ	79.2	38.3
		±1.0
ΔS° , J·K	-86.4	-149.8
		±3.3
Authors' data		
ΔH° or ΔE° , kJ	86	38.9
ΔS° , J·K	E	-156.9
Calculated rate constants		
0° C	(1.2) E-7	(4.0±.2) E-3
10	(4.4) E-7	(7.6±.2) E-3
25	(2.5) E-6	(1.81±.05) E-2
40	(1.22) E-5	(4.0±.2) E-2
60	(8.1) E-5	(1.03±.08) E-1
90	(9.3) E-4	(3.5±.4) E-1

N No data.

¹Correlation coefficient and errors not determinable.

Note.—Cited references are listed at end of Chapter 7.

Table F-8.--Kinetic data for hydrolysis of oxamic acid



$$\text{Rate equation: } -Z^{-1}dz/dt = k_1[\text{H}^+] + k_2 + k_3[\text{OH}^-]$$

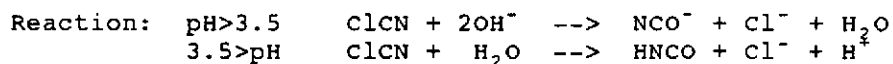
Reported rate constants	k_1	k_1	k_2	k_3
Reference	78	79, 80	79, 80	79, 80
pH range	0-2	0-1	0-1	13-14
Ionic strength., M	1.0	1.0	1.0	1.0
Temperature, °C	80, 98	60-98	60-98	40-60
Statistical processing				
Number of points	2	4	5	3
correlation coefficient	^1_N	0.9980	0.9975	0.9997
$\Delta H^\ddagger$, kJ	78.8	71.2	69.6	44.4
		± 3.2	± 2.9	± 1.0
$\Delta S^\ddagger$, J·K	-82.3	-103.2	-134.9	-165.8
		± 9.1	± 8.1	± 3.2
Authors' data				
$\Delta H^\ddagger$ or $\Delta E^\ddagger$, kJ	86	69.5	67.8	46.0
$\Delta S^\ddagger$, J·K	E	-60.7	-147.7	-169.9
Calculated rate constants				
0° C	(2.5) E-7	(5.6 $\pm$ 3.1) E-7	(2.5 $\pm$ 1.6) E-8	(4.0 $\pm$.3) E-5
10	(8.7) E-7	(1.8 $\pm$.8) E-6	(7.8 $\pm$ 4.0) E-8	(8.2 $\pm$.5) E-5
25	(4.9) E-6	(8.5 $\pm$ 2.7) E-6	(3.6 $\pm$ 1.3) E-7	(2,24 $\pm$.08) E-4
40	(2.4) E-5	(3.5 $\pm$.7) E-5	(1.46 $\pm$.36) E-6	(5.56 $\pm$.09) E-4
60	(1.55) E-4	(1.94 $\pm$.20) E-4	(7.7 $\pm$ 1.0) E-6	(1.65 $\pm$.03) E-3
90	(1.77) E-3	(1.77 $\pm$.16) E-3	(6.7 $\pm$.6) E-5	(6.8 $\pm$.3) E-3

N No data.

¹Correlation coefficient and errors not determinable.

Note.—Cited references are listed at end of Chapter 7.

Table F-9.-Kinetic data for hydrolysis of cyanogen chloride



Rate equation: $-Z^{-1}dZ/dt = k_1 + k_2[\text{OH}^-]$

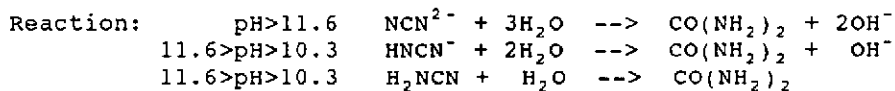
Reported rate constants	k_1	k_1	k_2
Reference	83	85	85
pH range	7	2-3	10
Ionic strength, M	0.	0.07	0.07
Temperature, $^{\circ}\text{C}$	40-60	18-41	20-40
Statistical processing			
Number of points	3	3	3
Correlation coefficient	0.9992	0.9998	0.9985
ΔH° , kJ	80.3	84.0	85.6
	± 3.2	± 1.6	± 4.6
ΔS° , J·K	-95.	-84.1	+63.
	$\pm 10.$	± 5.2	$\pm 15.$
Authors' data			
ΔH° or ΔE° , kJ	85.8	¹ 82, 86	¹ 83, 82
ΔS° , J·K	E	¹ -90, -77	¹ 53, 52
Calculated rate constants			
0 $^{\circ}$ C	(2.9 $\pm$.7) E-8	(2.0 $\pm$.2) E-8	(4.7 $\pm$ 1.1) E-1
10	(1.0 $\pm$.2) E-7	(7.7 $\pm$.4) E-8	(1.9 $\pm$.3)
25	(6.1 $\pm$.6) E-7	(4.9 $\pm$.1) E-7	(1.22 $\pm$.07) E+1
40	(3.02 $\pm$.15) E-6	(2.59 $\pm$.08) E-6	(6.7 $\pm$.5) E+1
60	(2.04 $\pm$.10) E-5	(1.91 $\pm$.12) E-5	(5.1 $\pm$ 1.0) E+2
90	(2.4 $\pm$.4) E-4	(2.6 $\pm$.3) E-4	(7.2 $\pm$ 2.6) E+3

N No data.

¹Two determinations.

Note.—Cited references are listed at end of Chapter 7.

Table F-10.--Kinetic data for addition of water to cyanamide



Rate equation: $-Z^{-1}dz/dt = k_1 + k_2(K_{az} + [\text{H}^+])^{-1}$

Reported rate constants	k_2	k_1	k_1
Reference	87	88	89
pH range	8-12	2	0
Ionic strength, M	0.1	0.02	1.0
Temperature, °C	60-90	60, 85	25-40
Statistical processing			
Number of points	4	2	6
Correlation coefficient	0.9995	¹ N	0.9936
$\Delta H^\ddagger$, kJ	89.5	115.5	71.3
	±1.9		±4.1
$\Delta S^\ddagger$, J·K	-69.5	+2.8	-91.
	±5.6		±13.
Authors' data			
$\Delta H^\ddagger$ or $\Delta E^\ddagger$, kJ	93.7	121.	² N
$\Delta S^\ddagger$, J·K	E	E	-90
Calculated rate constants			
0° C	(1.0±.3) E-8	(7.) E-10	(2.3±1.0) E-6
10	(4.3±1.1) E-8	(4.1) E-9	(7.1±2.0) E-6
25	(3.1±.5) E-7	(5.1) E-8	(3.4±.3) E-5
40	(1.82±.21) E-6	(5.0) E-7	(1.43±.15) E-4
60	(1.53±.08) E-5	(7.6) E-6	(7.9±2.5) E-4
90	(2.40±.13) E-4	(2.59) E-4	(7.2±4.9) E-3

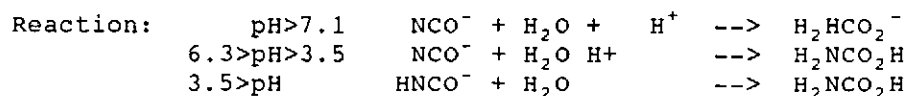
N No data.

¹Correlation coefficient and errors not determinable.

²Not reported.

Note.--Cited references are listed at end of Chapter 7.

Table F-11.--Kinetic data for addition of water to cyanate



$$\text{Rate equation: } -Z^{-1}dZ/dt = k_1[\text{H}^+]^2(K_{a_z} + [\text{H}^+])^{-1} + k_2K_{a_z}[\text{H}^+](K_{a_z} + [\text{H}^+])^{-1} + k_3; \quad k_2' = k_2K_{a_z}$$

Reported rate constants	k_1	k_2'	k_3	k_2
Reference	20	20	20	97
pH range	0	2-5	12-13	8-11
Ionic strength, M	1.0	0.1	0.3	0.25
Temperature, $^{\circ}\text{C}$	1-26	0-12	65-100	60, 80
Statistical processing				
Number of points	3	3	3	2
Correlation coefficient	0.9997	0.9993	1.0000	^{1N}
ΔH° , kJ	59.0	63.6	96.7	58.1
	± 1.4	± 2.4	$\pm .7$	
ΔS° , J·K	-64.9	-83.2	+70.0	-36.4
	± 4.9	± 8.6	± 1.9	
Authors' data				
ΔH° or ΔE° , kJ	61.	67.	98.	61.1
ΔS° , J·K	E	E	E	-36.9
Calculated rate constants				
0 $^{\circ}$ C	(1.22 $\pm$.04) E-2	(1.80 $\pm$.05) E-4	(4.1 $\pm$.3) E-10	(5.4) E-1
10	(3.16 $\pm$.07) E-2	(5.0 $\pm$.1) E-4	(1.9 $\pm$.1) E-9	(1.39)
25	(1.17 $\pm$.04) E-1	(2.1 $\pm$.2) E-3	(1.58 $\pm$.07) E-8	(5.1)
40	(3.9 $\pm$.2) E-1	(7.4 $\pm$.9) E-3	(1.08 $\pm$.03) E-7	(1.64) E+1
60	(1.60 $\pm$.14) E-2	(3.4 $\pm$.6) E-2	(1.07 $\pm$.02) E-6	(6.7) E+1
90	(1.01 $\pm$.14) E+1	(2.5 $\pm$.7) E-1	(2.08 $\pm$.02) E-5	(4.1) E+2

Table F-11.-Kinetic data for addition of water to cyanate--Continued

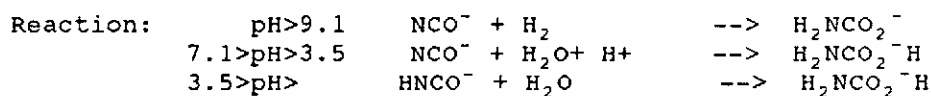
Reported rate constants	k_3	k_1	k_2'	k_3
Reference	97	98	98	98
pH range	8-11	1	1-5	13
Ionic strength, $\underline{M}$	0.25	0.2	0.2	0.2
Temperature, $^{\circ}\text{C}$	60, 80	4-18	10, 18	70-94
Statistical processing				
Number of points	2	3	2	3
Correlation coefficient	^1N	0.9998	N	0.9999
ΔH° , kJ	100.0	60.0	80.6	97.6
		± 1.1		± 1.2
ΔS° , J-K	-60.2	-62.0	-28.5	-67.9
		± 3.9		± 3.3
Authors' data				
ΔH° or ΔE° , kJ	102.9	63.2	83.3	100.0
ΔS° , J-K	60.7	E	E	E
Calculated rate constants				
0°C	(3.1) E-10	(1.10 $\pm$.02) E-2	(7.2) E-5	(3.6 $\pm$.5) E-10
10	(1.5) E-9	(2.89 $\pm$.03) E-2	(2.62) E-4	(1.7 $\pm$.2) E-9
25	(1.35) E-8	(1.10 $\pm$.03) E-1	(1.54) E-3	(1.42 $\pm$.11) E-8
40	(9.8) E-8	(3.7 $\pm$.2) E-1	(7.7) E-3	(9.8 $\pm$.6) E-8
60	(1.05) E-6	(1.56 $\pm$.12) E-2	(5.2) E-2	(9.9 $\pm$.3) E-7
90	(2.25) E-5	(1.02 $\pm$.11) E+1	(6.3) E-1	(1.98 $\pm$.03) E-5

N No data.

¹Correlation coefficient and errors not determinable.

Note.—Cited references are listed at end of Chapter 7.

Table F-12.--Kinetic data for bicarbonate-catalyzed
addition of water to cyanate



Rate equation: $-Z^{-1}dz/dt = k_1[\text{HCO}_3^-]$

Reported rate constants	k_1	k_1
Reference	97	99
pH range	8-9	8-10
Ionic strength, $\underline{M}$	0.25	0.2
Temperature, $^{\circ}\text{C}$	60, 80	18-50
Statistical processing		
Number of points	2	3
Correlation coefficient	^1N	1.0000
ΔH^* , kJ	65.8	65.2
		± 2
ΔS^* , J·K	-116.1	-118.4
		± 6
Authors' data		
ΔH^* or ΔE^* , kJ	67.4	67.8
ΔS^* , J·K	E	E
Calculated rate constants		
0 $^{\circ}$ C	(1.3) E-6	(1.27 $\pm$.01) E-6
10	(3.7) E-6	(3.62 $\pm$.02) E-6
25	(1.6) E-5	(1.53 $\pm$.01) E-5
40	(6.0) E-5	(5.68 $\pm$.02) E-5
60	(2.9) E-4	(2.72 $\pm$.02) E-4
90	(2.25) E-3	(2.07 $\pm$.02) E-3

N No data.

^{1} Correlation coefficient and errors not determinable.

Note.—Cited references are listed at end of Chapter 7.

Table F-13.-Kinetic data for formation
of urea from cyanate and ammonia

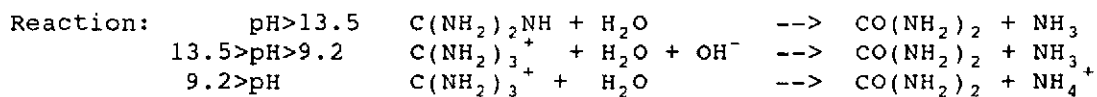
Reaction: $9.2 > \text{pH} > 3.5$ $\text{NCO}^- + \text{NH}_4^+ \rightarrow \text{CO}(\text{NH}_2)_2$

Rate equation: $-R^{-1}Z^{-1}dz/dt = k_1[\text{H}^+](K_{a_z} + [\text{H}^+])^{-1}$

Reported rate constants	k_1
Reference	90
pH range	8-9
Ionic strength, M	0.25
Temperature, $^{\circ}\text{C}$	60, 80
statistical processing	
Number of points	2
Correlation coefficient	^{1}N
ΔH° , kJ	94.9
ΔS° , J·K	-16.5
Authors' data	
ΔH° or ΔE° , kJ	97.5
ΔS° , J·K	17.0
Calculated rate constants	
0 $^{\circ}$ C	(4.0) E-7
10	(2.5) E-6
25	(2.0) E-5
40	(1.3) E-4
60	(1.24) E-3
90	(2.29) E-2

Note.--Cited references are listed at
end of Chapter 7.

Table F-14.-Kinetic data for hydrolysis of guanidine ion



Rate equation: $-Z^{-1}dz/dt = k_1 K_{az} [\text{OH}^-] (K_w + K_{az} [\text{OH}^-])^{-1}$

Reported rate constants	k_1	$k_1 K_{az} / K_w$
Reference	104	105
pH range	14	12
Ionic strength, M	3.0	0.04
Temperature, $^{\circ}\text{C}$	15-78	100-135
Statistical processing		
Number of points	¹ N	3
Correlation coefficient	¹ N	0.9999
ΔH^* , kJ	¹ N	130.4
		± 1.4
ΔS^* , J·K	¹ N	+33.9
		± 3.5
Authors' data		
ΔH^* or ΔE^* , kJ	85.4	133.5
ΔS^* , J·K	E	E
Calculated rate constants		
0° C	(5.2) E-8	(3.9 $\pm$.8) E-11
10	(1.9) E-7	(3.1 $\pm$.6) E-10
25	(1.21) E-6	(5.3 $\pm$.8) E-9
40	(6.3) E-6	(6.9 $\pm$.8) E-8
60	(4.5) E-5	(1.48 $\pm$.12) E-6
90	(5.7) E-4	(7.9 $\pm$.3) E-5

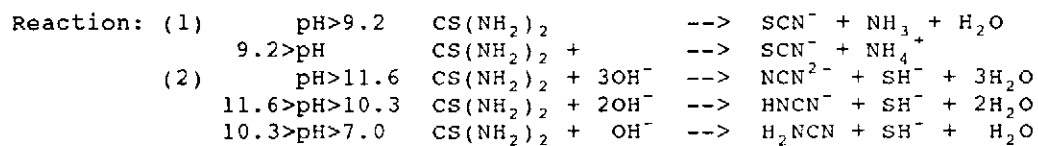
N No data.

¹Rate constant reported only for 60° C.

Calculated rate constants from this value and authors' ΔE^* .

Note.—Cited references are listed at end of Chapter 7.

Table F-15.-Kinetic data for decomposition of thiourea

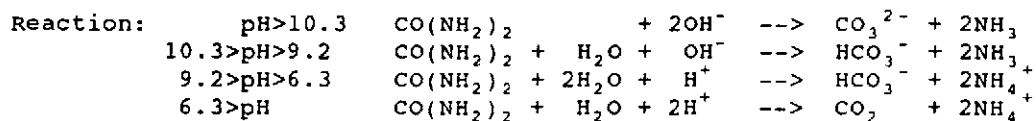


Rate equation: (1) $-z^{-1}dz/dt = k_1$
 (2) $-z^{-1}dz/dt = k_2[OH^-]$

Reported rate constants	k_1	k_2
Reference	95	106
pH range	2-10	12-13
Ionic strength, M	0.0	0.1
Temperature, °C	90-130	80-100
Statistical processing		
Number of points	5	3
Correlation coefficient	1.0000	0.9994
$\Delta H^\ddagger$, kJ	-146.2	71.8
	±2	±2.4
$\Delta S^\ddagger$, J·K	+15.3	-131.
	±4	±7.
Authors' data		
$\Delta H^\ddagger$ or $\Delta E^\ddagger$, kJ	149.8	75.
		±4.
$\Delta S^\ddagger$, J·K	E	E
Calculated rate constants		
0° C	(4.0±.2) E-15	(1.6±.5) E-8
10	(4.0±.1) E-14	(5.1±1.3) E-8
25	(9.7±.2) E-13	(2.5±.5) E-7
40	(1.71±.03) E-11	(1.04±.14) E-6
60	(5.30±.07) E-10	(5.8±.5) E-6
90	(4.52±.03) E-8	(5.37±.10) E-5

Note.—Cited references are listed at end of Chapter 7.

Table F-16.-Kinetic data for hydrolysis of urea



$$\text{Rate equation: } -z^{-1}dz/dt = k_1 + k_2[\text{OH}^-] + k_3[\text{OH}^-]^2$$

Reported rate constants	k_1	k_2	k_1	k_1	k_3
Reference	88	105	109	110	110
pH range	2	12	1-7	14	14
Ionic strength, M	0.02	0.04	0.1	2.0	2.0
Temperature, °C	60, 85	90-120	60-100	33-70	
Statistical processing					
Number of points	2	3	6	4	6
Correlation coefficient	¹ N	0.9996	0.9997	0.9905	0.9864
$\Delta H^\ddagger$, kJ	134.3	105.8 ±2.9	133.5 ±1.6	93.5 ±7.5	85.7 ±7.1
$\Delta S^\ddagger$, J·K	+29.7	-53.5 ±7.7	+26.8 ±4.5	-85. ±23.	-112. ±22.
Authors' data					
$\Delta H^\ddagger$ or $\Delta E^\ddagger$, kJ	N	108.8	136.8 ±.9	90.3	89.9
$\Delta S^\ddagger$, J·K	E	E	E	-83.7	-89.5
Calculated rate constants					
0° C	(4.0) E-12	(5.±2.) E-11	(4.2±1.6) E-12	³ N	³ N
10	(3.5) E-11	(2.9±1.0) E-10	(3.4±1.1) E-11	³ N	³ N
25	(6.5) E-10	(2.9±.8) E-9	(6.3±1.5) E-10	(1.0±.6) E-8	(9.±6.) E-9
40	(9.2) E-9	(2.4±.5) E-8	(8.7±1.4) E-9	(6.2±1.9) E-8	(5.0±1.6) E-8
60	(2.16) E-7	(2.9±.4) E-7	(2.02±.18) E-7	(5.7±1.5) E-7	(3.8±1.1) E-7
90	(1.29) E-5	(7.4±.4) E-6	(1.18±.06) E-5	¹ N	¹ N

N No data.

¹Correlation coefficient and errors not determinable.

²Not reported.

³Error larger than value.

Note.—Cited references are listed at end of Chapter 7.