RI 7499

Bureau of Mines Report of Investigations/April 1971

Heat of Formation of Cuprous Cyanide and Its Heat Capacity From 10° to 400° K

UNITED STATES DEPARTMENT OF THE INTERIOR

Report of Investigations 7499

Heat of Formation of Cuprous Cyanide and Its Heat Capacity From 10° to 400° K

By A. R. Taylor, Jr., Mary H. Brown,
and Estelle G. Taylor

MARCH 3, 1849

UNITED STATES DEPARTMENT OF THE INTERIOR
Rogers C. B. Morton, Secretary

BUREAU OF MINES
Elburt F. Osborn, Director

The work upon which this report is based was done under a cooperative agreement between the Bureau of Mines, U.S. Department of the Interior, and the University of Alabama.

This publication has been cataloged as follows:

Taylor, Arthur R

Heat of formation of cuprous cyanide and its heat capacity from 10° to 400° K, by A. R. Taylor, Jr., Mary H. Brown, and Estelle G. Taylor. [Washington] U.S. Dept. of the Interior, Bureau of Mines [1971]

12 p. illus., tables. (U.S. Bureau of Mines. Report of investigations 7499)

Includes bibliography.

Based on work done in cooperation with the University of Alabama.

1. Cuprous cyanide. I. Brown, Mary H., jt. auth. II. Taylor, Estelle G., jt. auth. III. Title. (Series)

TN23.U7 no. 7499 622.06173

U.S. Dept. of the Int. Library

CONTENTS

ILLUSTRATION

TABLES

HEAT OF FORMATION OF CUPROUS CYANIDE AND ITS HEAT CAPACITY FROM 10° TO 400° K

by

A. R. Taylor, Jr.,[1] Mary H. Brown,[2] and Estelle G. Taylor[3]

ABSTRACT

Using solution calorimetry, the following heats of reaction were determined:

$$(1)\quad NaCN(c) + 1/2Cu_2O(c) + 129H_2O(\ell) \rightarrow CuCN(c) + NaOH\cdot 128.5H_2O \qquad \Delta H = -13.44\pm 0.10 \text{ kcal/mole.}$$

$$(2)\quad HCN(\ell) + NaOH\cdot 128.5H_2O \rightarrow NaCN(c) + 129.5H_2O(\ell) \qquad \Delta H = -2.52\pm 0.02 \text{ kcal/mole.}$$

From these reactions, the heats of formation for CuCN(c) and HCN(ℓ) were calculated to be 22.7±0.4 kcal/mole and 24.9±0.4 kcal/mole, respectively. Reaction 2 was made to check the consistency of literature values for heats of formation of HCN and NaCN.

Adiabatic calorimetric measurements between 10° and 400° K showed the entropy and heat capacity of CuCN(c) to be 21.51±0.06 eu and 14.58±0.04 cal/mole deg, respectively, at 298° K. A broad anomaly in the heat capacity was found in the temperature range 285°-320° K. The heat of transition associated with this anomaly was less than 1 cal/mole, the sensitivity of the measurements.

INTRODUCTION

The cyanide compounds are of importance to metallurgists studying the hydrometallurgical and pyrometallurgical beneficiation of several metallic ores. When this Bureau of Mines work was begun there were no thermochemical

---

[1] Research chemist, Tuscaloosa Metallurgy Research Laboratory, Bureau of Mines, Tuscaloosa, Ala.

[2] Former Bureau of Mines chemist, Tuscaloosa Metallurgy Research Laboratory, Tuscaloosa, Ala., now located at Ames, Iowa.

[3] Former Bureau of Mines chemist, Tuscaloosa Metallurgy Research Laboratory, Tuscaloosa, Ala., now located at Demopolis, Ala.

data available in the literature on CuCN except the heat of formation values for CuCN(aq) reported in NBS Circular 500 (12).[4] This value is based on measurements made in 1895 by Varet (15).

To determine the heat of formation of CuCN(c) by solution calorimetry, the reaction between NaCN and Cu_2O was selected because the heats of formation of these two compounds appeared to be established in the literature. As a check on the heat for formation of NaCN, the heat of the reaction between HCN and NaOH was measured.

APPARATUS

Heat of solution measurements were made with a glass dewar-type calorimeter using thermistors connected in opposite arms of a Wheatstone bridge circuit for temperature sensing. The off-balance signal from the bridge was amplified and fed to a recording potentiometer to provide a visual indication of temperature changes inside the calorimeter. Additional details are described in the literature (3, 7).

Low-temperature heat capacity measurements were made in an adiabatic calorimeter differing only slightly from many described in the literature (13). The calorimeter was a gold-plated copper can with a volume of about 95 ml. Mounted concentrically inside the can were a 25-ohm capsule-type platinum resistance thermometer and a 250-ohm constantan heater. At room temperature, the heat capacity of the calorimeter with thermometer and heater in place was 6.1 cal/deg. Surrounding the calorimeter was an adiabatic shield wound with three separate, manually controlled heater windings. Copper-constantan difference thermocouples were used to monitor the temperature difference between selected points on the shield and between the calorimeter and shield. A G-2 Muller[5] bridge was used to read the resistance of the NBS calibrated resistance thermometer.

MATERIALS

Cuprous cyanide used for this study was a fluffy white powder supplied by the Treadwell Corp. The CuCN was a precipitate obtained by treating a cupric sulfate solution with HCN and SO_2. Information supplied with the compound indicated that it was better than 99.9 percent CuCN. Spectrographic analysis revealed no metallic impurities, and the X-ray diffraction pattern agreed with the ASTM card (1).

Cuprous oxide was prepared in this laboratory using the same procedure that was used by Mah and her coworkers (8), who prepared Cu_2O to measure its heat of formation. First, CuO was made by heating turnings from a 99.999-percent copper rod in a porcelain crucible in air at 800° C. The heating process was interrupted at intervals for grinding and mixing of the sample. Next,

---

[4] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

[5] Reference to specific companies and trade names is made to facilitate understanding and does not imply endorsement by the Bureau of Mines.

the Cu_2O was prepared by heating the CuO in an alumina boat for several days at 1,010° C in a stream of dry nitrogen. This heating process also was interrupted for grinding and mixing the sample. No CuO could be detected in the final Cu_2O sample by X-ray diffraction.

Reagent-grade NaCN was purified by adding absolute ethanol to a nearly saturated water solution of NaCN and cooling the solution to 10° C. The sodium cyanide precipitate was filtered, washed with ethanol, dried in a vacuum desiccator, and finally dried at 110° C. Titration with standard silver nitrate solution indicated that the product was 99.1 percent NaCN. Since no significant metallic impurity was detected by spectrographic analysis, the 0.9 percent impurity was assumed to be Na_2CO_3.

Preliminary tests showed that CuCN and Cu_2O would dissolve satisfactorily in 1 M NaCN solution, so this was selected as the solvent for the reaction scheme. Because aqueous cyanide solutions decompose on standing owing to volatilization of molecular hydrogen cyanide and to hydrolytic decomposition of the cyanide ion (5), no attempt was made to prepare the solution in bulk, but fresh solution was prepared immediately before each run.

$HCN(\ell)$ was prepared using an adaption of Ziegler's method (17).[6] Concentrated sulfuric acid was placed in a 500-ml flask, and a saturated aqueous solution of NaCN was added dropwise, resulting in the evolution of HCN. The hydrogen cyanide was passed through a drying tube and condensed in a trap cooled by liquid nitrogen. Impurities more volatile than HCN were removed by recondensing the HCN at -78° C in a trap cooled with Dry Ice and 2-propanol. Less volatile impurities were condensed from the HCN by passing the gas through a trap cooled with carbon tetrachloride slush to -23° C. The purity of the HCN was checked by both infrared spectroscopy and gas chromatography. No impurities were detected in the gas phase infrared spectrum as compared with the published spectrum (11). No impurity peaks occurred in the gas chromatographic analysis using either Kel-F or Apiezon L columns. Thin-walled, glass ampoules were attached to the vacuum line and filled approximately half full with HCN. The ampoules were immersed in liquid nitrogen and heat-sealed about 15 mm from the bulb.

The 0.4327 M sodium hydroxide solution used in the reaction scheme was made from reagent-grade 50-percent sodium hydroxide solution.

SOLUTION MEASUREMENTS

Cuprous Cyanide

The reaction scheme for determining the heat of formation of CuCN(c) and the average heat measured for each reaction are shown in table 1. Reaction 1 represents the average heat of dissolution of four samples of purified NaCN(c) weighing from 0.5 to 1.1 g in a solution containing 36.78 g of reagent-grade NaCN and 745.8 g of water. The heat of this reaction was not corrected for

---

[6] The HCN used in this study was prepared and analyzed by Dr. C. L. Bramlett and his group at the University of Alabama Chemistry Department.

the heat of solution of the 0.9 percent Na_2CO_3 found in the purified NaCN because the presence of this quantity of sodium carbonate was determined to exert a negligible effect on the heat of solution. Reaction 2 represents the average heat of dissolution of five samples of $Cu_2O(c)$ weighing 1.0 to 1.4 g in a solution identical to that formed in reaction 1. Reaction 3 represents the average heat of mixing water with the final solution of reaction 2 to make it equivalent to the final solution of reaction 5; four measurements of this reaction were made. Reaction 4 represents the average heat of dissolution of 10 samples of CuCN(c) weighing from 1.2 to 1.5 g in the same solvent used for reaction 1. Reaction 5 represents the average heat of mixing four samples of an appropriate amount of 0.4327 $\underline{M}$ NaOH with a solution equivalent to the final solution of reaction 4. The sum of reactions 1 through 5 gives reaction 6 from which the heat of formation of CuCN(c) may be calculated. Using recent heat of formation values for $Cu_2O(c)$, $NaOH\cdot 128.5H_2O$, and NaCN(c), given in table 2, the heat of formation for CuCN(c) is calculated to be +22,684±340 cal/mole from reaction 7.

All deviations listed are equal to two standard deviation units, in agreement with the reporting of such values in previous publications.

TABLE 1. - Reaction scheme for the determination of the standard heat of formation of CuCN(c)

	Reaction			$\Delta H_{298.15}$, cal
(1)	$NaCN(c) + \begin{Bmatrix}46.91NaCN\\2,587.5H_2O\end{Bmatrix}$	→	$\begin{Bmatrix}47.91NaCN\\2,587.5H_2O\end{Bmatrix}$	-628± 2
(2)	$0.5Cu_2O(c) + \begin{Bmatrix}47.91NaCN\\2,587.5H_2O\end{Bmatrix}$	→	$\begin{Bmatrix}CuCN\\NaOH\\46.91NaCN\\2,587H_2O\end{Bmatrix}$	-43,762± 67
(3)	$\begin{Bmatrix}CuCN\\NaOH\\46.91NaCN\\2,587H_2O\end{Bmatrix} + 129H_2O(\ell)$	→	$\begin{Bmatrix}CuCN\\NaOH\\46.91NaCN\\2,716H_2O\end{Bmatrix}$	254± 3
(4)	$CuCN(c) + \begin{Bmatrix}46.91NaCN\\2,587.5H_2O\end{Bmatrix}$	→	$\begin{Bmatrix}CuCN\\46.91NaCN\\2,587.5H_2O\end{Bmatrix}$	-30,401± 74
(5)	$NaOH\cdot 128.5H_2O + \begin{Bmatrix}CuCN\\46.91NaCN\\2,587.5H_2O\end{Bmatrix}$	→	$\begin{Bmatrix}CuCN\\NaOH\\46.91NaCN\\2,716H_2O\end{Bmatrix}$	-298± 2
(6)	$NaCN(c) + 0.5Cu_2O(c) + 129H_2O(\ell)$	→	$CuCN(c) + NaOH\cdot 128.5H_2O$	[1] -13,437±100
(7)	$Cu(c) + 0.5N_2(g) + C(graphite)$	→	CuCN(c)	22,684±340

[1] $\Delta H_6 = \Delta H_1 + \Delta H_2 + \Delta H_3 - \Delta H_4 - \Delta H_5$.

Hydrogen Cyanide

To check the consistency of heats of formation of cyanides reported in the literature, the heat of formation of NaCN(c) was related to that of $HCN(\ell)$. Using the reaction scheme shown in table 3, a heat of formation value can be calculated for either NaCN(c) or $HCN(\ell)$, depending on which literature value is considered more reliable. Reaction 10 is identical to reaction 1 in table 1, and reactions 9 and 11 are similar to reactions 5 and 3 from table 1 except for the absence of CuCN. The heat of reaction 12 was negligible.

TABLE 2. - Heat of formation values used from the literature

Compound	ΔHf, cal/mole	Reference
Cu_2O(c)........................	-40,760±100	(6)
$H_2O(\ell)$........................	-68,315± 20	(16)
$NaOH\cdot 128.5H_2O$..................	-112,339±100	(4)
NaCN(c)........................	-21,680±300	(4)

TABLE 3. - Reaction scheme for the determination of the standard heat of formation of $HCN(\ell)$

	Reaction					$\Delta H_{298.15}$, cal
(8)	$HCN(\ell)$	+	NaOH 46.91NaCN $2{,}587.5H_2O$	→	NaCN 46.91NaCN $2{,}588.5H_2O$	-2,600± 13
(9)	$NaOH\cdot 128.5H_2O$	+	46.91NaCN $2{,}587.5H_2O$	→	NaOH 46.91NaCN $2{,}716H_2O$	-298± 2
(10)	NaCN(c)	+	46.91NaCN $2{,}587.5H_2O$	→	NaCN 46.91NaCN $2{,}587.5H_2O$	-628± 2
(11)	NaOH 46.91NaCN $2{,}587.5H_2O$	+	$128.5H_2O(\ell)$	→	NaOH 46.91NaCN $2{,}716H_2O$	253± 3
(12)	NaCN 46.91NaCN $2{,}587.5H_2O$	+	$H_2O(\ell)$	→	NaCN 46.91NaCN $2{,}588.5H_2O$	2± 1
(13)	$HCN(\ell)$ + $NaOH\cdot 128.5H_2O$			→	NaCN(c) + $129.5H_2O(\ell)$	[1] -2,525± 14
(14)	$0.5H_2(g)$ + C(graphite) + $0.5N_2(g)$			→	$HCN(\ell)$	24,869±318

[1] $\Delta H_{13} = \Delta H_8 + \Delta H_9 - \Delta H_{10} - \Delta H_{11} - \Delta H_{12}$.

Reaction 8 represents the average heat of solution of five samples of HCN weighing from 0.37 to 0.44 g in NaCN solution containing a stoichiometric amount of NaOH. Each heat of solution run for reaction 8 was corrected for the heat of vaporization of HCN. In making this correction, the ideal gas law was assumed to apply to HCN(g), and the density, vapor pressure, and heat of vaporization of $HCN(\ell)$ were assumed to be 0.699 g/ml, 739.4 torr, and 6.03 kcal/mole, respectively. This correction ranged from 2 to 4 cal/mole, depending upon bulb volume and sample size.

Reaction 13 is obtained by combining reactions 8 through 12. Using the heat of reaction 13 with the heats of formation of $NaOH\cdot 128.5H_2O$, $H_2O(\ell)$, and NaCN given in table 2, the heat of formation of HCN(ℓ) can be calculated to be 24.87±0.32 kcal/mole. This number is considerably smaller than the 26.02±0.20 kcal/mole reported in the literature (16). The literature value is apparently based on combustion work by Berthelot (2) and Thomsen (14) prior to 1900.

HEAT CAPACITY MEASUREMENTS

Heat capacity measurements were made on a 53.1816-g sample of CuCN sealed in the calorimeter under 1 atm of helium pressure. These data are recorded in table 4. Figure 1 shows a plot of heat capacity versus temperature with an insert showing an enlargement of the 260°-350° K range. The lower temperature portion of the plot is smooth and "s" shaped, typical of the behavior of the heat capacity of many compounds. In the 280°-320° K temperature region, over 30 minutes was necessary to establish thermal equilibrium after an energy input. Outside this particular interval, only 10 minutes or less was needed for the establishment of equilibrium. To establish the enthalpy change associated with this anomalous temperature region, three "enthalpy" runs were made, starting at a temperature below the lowest temperature at which the equilibration time became noticeably longer and extending to a higher temperature at which the equilibration was again normal. These data are presented in table 5. The expected enthalpy increment, assuming no heat of transition effect, was estimated from the area under a "normal" heat capacity curve obtained by extrapolating the experimental curves to 300° K, approximately the midpoint of the anomalous region. The heat of transition, ΔH, is the difference between the measured heat input and the expected heat absorbed. The errors involved in extrapolating the heat capacity curves, determining the area under them, etc., would amount to at least 1 or 2 cal/mole, indicating that ΔH is 0 within the accuracy of these measurements.

TABLE 4. - Measured heat capacity data for cuprous cyanide

T, ° K	C_p, cal/mole deg	T, ° K	C_p, cal/mole deg	T, ° K	C_p, cal/mole deg
7.23	0.239	114.34	9.196	262.34	13.957
7.72	.272	117.95	9.383	266.77	14.033
8.24	.353	118.65	9.420	272.95	14.130
8.84	.403	121.90	9.589	277.34	14.213
9.69	.513	122.85	9.629	279.01	14.242
10.95	.673	126.69	9.831	281.70	14.297
12.44	.872	130.46	10.006	[1] 283.47	14.343
14.03	1.131	134.16	10.185	286.04	14.366
15.66	1.385	138.05	10.360	290.36	14.462
17.17	1.627	138.49	10.378	294.65	14.590
18.53	1.824	142.16	10.540	297.27	14.626
19.85	2.019	142.52	10.559	298.91	14.732
21.19	2.211	143.80	10.608	298.94	14.866
22.76	2.430	146.18	10.707	299.87	14.727
24.65	2.657	147.22	10.752	300.11	14.801
26.61	2.876	151.83	10.941	302.16	14.828
28.89	3.134	156.37	11.120	303.17	14.949
31.38	3.388	160.85	11.283	305.40	14.972
33.77	3.639	165.26	11.448	310.81	15.001
36.14	3.868	169.62	11.608	313.60	15.046
38.49	4.085	173.22	11.722	316.88	15.068
40.85	4.294	173.93	11.753	324.34	15.158
43.22	4.498	176.19	11.828	[2] 330.08	15.225
45.58	4.700	178.19	11.889	335.78	15.301
47.88	4.892	179.59	11.938	341.47	15.363
50.16	5.076	183.43	12.057	345.69	15.417
50.65	5.111	187.56	12.187	349.26	15.454
53.29	5.321	191.70	12.313	352.83	15.483
56.16	5.547	195.80	12.436	355.39	15.514
59.28	5.786	199.79	12.542	359.80	15.553
62.46	6.024	204.55	12.672	364.15	15.597
65.70	6.261	209.33	12.800	364.46	15.601
69.07	6.490	213.13	12.886	368.73	15.648
72.50	6.719	213.30	12.894	369.15	15.658
75.95	6.945	217.05	12.984	373.00	15.690
78.97	7.149	217.46	12.999	376.78	15.728
79.39	7.176	220.95	13.090	381.02	15.774
82.43	7.381	224.82	13.169	385.26	15.812
83.09	7.423	226.35	13.204	389.01	15.868
85.75	7.598	228.67	13.260	393.22	15.888
89.23	7.810	230.16	13.288	397.42	15.927
92.86	8.012	233.94	13.381	401.60	15.969
95.35	8.154	237.71	13.464		
99.28	8.378	241.45	13.541		
103.10	8.590	245.39	13.620		
106.81	8.794	249.50	13.704		
110.43	8.998	253.60	13.789		
114.09	9.191	257.88	13.873		

[1] Long drifts begin.

[2] Drifts return to normal.

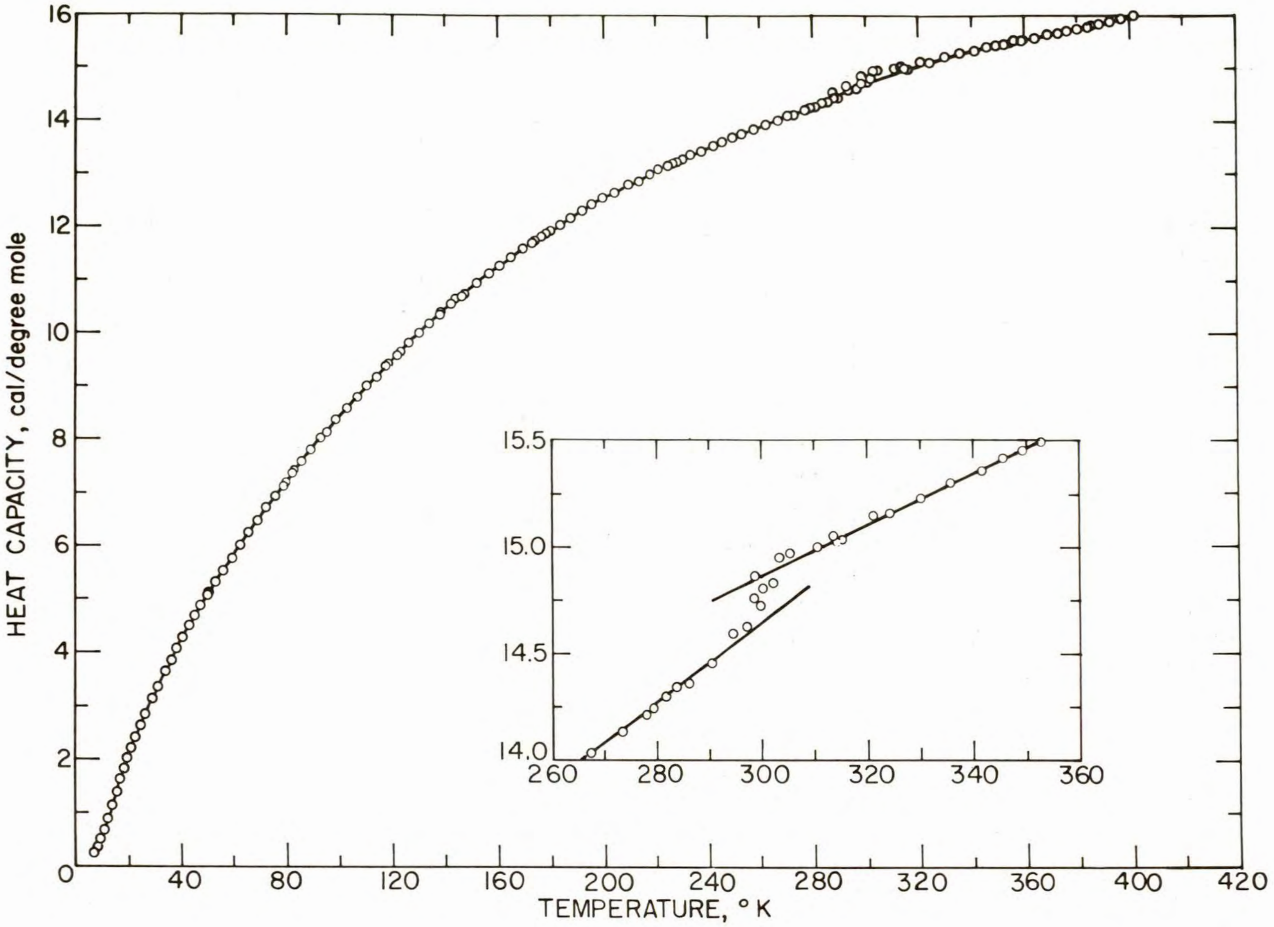

FIGURE 1. - Heat Capacity of CuCN.

TABLE 5. - Enthalpy runs

Initial temp, ° K	Final temp, ° K	Heat input, cal/mole	Expected heat absorbed, cal/mole	ΔH, cal/mole
266.1804	336.4965	1,035.0	1,034.9	0.1
271.3591	334.2713	928.9	928.2	.7
266.8615	336.6630	1,029.7	1,031.0	-1.3
261.3657	338.6454	1,134.2	1,135.2	-1.0

DISCUSSION

The anomalous heat capacity of CuCN between 280° and 320° K does not show the "peaks" usually associated with transitions, but rather manifests itself as a displacement of the "normal" heat capacity curve. McBride (9) found a similar anomaly for AgCN between 250° and 280° K.

Table 6 lists smooth values for the various thermodynamic functions obtained from the low-temperature data. These smooth values were calculated by the Thermal Research Laboratory of the Dow Chemical Co. using the polynomial curve-fitting routine used in preparing the JANAF tables. The entropy at 8° K, 0.0104 cal/mole deg, was obtained by using a T^3 extrapolation to 0° K.

TABLE 6. - Smoothed thermodynamic functions for cuprous cyanide

(Parentheses indicate extrapolated values)

T, ° K	C_p, cal/deg mole	S°, eu	$H^\circ_T - H^\circ_0$, cal/mole	$\frac{H^\circ_T - H^\circ_0}{T}$, cal/deg mole	$\frac{F_T - H^\circ_0}{T}$, cal/deg mole
8	0.310	0.104	0.626	0.078	-0.026
10	.545	.198	1.474	.147	-.050
12	.818	.321	2.830	.236	-.085
14	1.121	.469	4.765	.340	-.129
16	1.437	.639	7.322	.458	-.182
18	1.749	.827	10.510	.584	-.243
20	2.046	1.026	14.308	.715	-.311
22	2.322	1.235	18.679	.849	-.386
24	2.577	1.448	23.581	.983	-.465
26	2.814	1.663	28.974	1.114	-.549
28	3.037	1.880	34.828	1.244	-.636
30	3.250	2.097	41.116	1.371	-.726
35	3.756	2.637	58.65	1.676	-.961
40	4.220	3.169	78.60	1.965	-1.204
45	4.651	3.691	100.79	2.240	-1.451
50	5.062	4.202	125.08	2.502	-1.701
60	5.837	5.195	179.63	2.994	-2.201
70	6.556	6.149	241.64	3.452	-2.697
80	7.222	7.069	310.58	3.882	-3.187
90	7.841	7.956	385.92	4.288	-3.668
100	8.422	8.812	467.27	4.673	-4.139
110	8.972	9.641	554.3	5.039	-4.602
120	9.493	10.444	646.6	5.388	-5.056
130	9.983	11.223	744.0	5.723	-5.500
140	10.442	11.980	846.2	6.044	-5.936
150	10.867	12.715	952.7	6.352	-6.364
160	11.259	13.429	1,063.4	6.646	-6.783
170	11.620	14.123	1,177.8	6.928	-7.195
180	11.952	14.797	1,295.7	7.198	-7.598
190	12.259	15.451	1,416.8	7.457	-7.994
200	12.544	16.087	1,540.8	7.704	-8.383
210	12.810	16.706	1,667.6	7.941	-8.765
220	13.060	17.308	1,797.0	8.168	-9.140
230	13.293	17.893	1,928.7	8.386	-9.508
240	13.511	18.464	2,062.8	8.595	-9.869

TABLE 6. - Smoothed thermodynamic functions for cuprous cyanide--Continued

T, ° K	C_p, cal/deg mole	S°, eu	$H_T^\circ - H_0^\circ$, cal/mole	$\frac{H_T^\circ - H_0^\circ}{T}$, cal/deg mole	$\frac{F_T - H_0^\circ}{T}$, cal/deg mole
250	13.715	19.020	2,198.9	8.796	-10.224
260	13.906	19.561	2,337.0	8.989	-10.573
270	14.088	20.089	2,477.0	9.174	-10.915
273.15	14.144	20.253	2,521.5	9.231	-11.022
280	14.264	20.605	2,618.8	9.353	-11.252
290	14.441	21.109	2,762.3	9.525	-11.583
298.15	14.585	21.511	2,880.6	9.661	-11.849
300α	14.617	21.601	2,907.6	9.692	-11.909
300β	(14.865)	(21.601)	(2,907.6)	(9.692)	(-11.909)
310	(14.991)	(22.091)	(3,056.9)	(9.861)	(-12.230)
320	15.11	22.569	3,207.4	10.023	-12.545
330	15.23	23.035	3,359.1	10.179	-12.856
340	15.34	23.492	3,512.0	10.329	-13.162
350	15.45	23.938	3,666.0	10.474	-13.464
360	15.56	24.375	3,821.1	10.614	-13.761
370	15.66	24.803	3,977.2	10.749	-14.054
380	15.76	25.222	4,134.3	10.880	-14.342
390	15.86	25.633	4,292.4	11.006	-14.626
400	15.95	26.035	4,451.5	11.129	-14.906
410	(16.05)	(26.430)	(4,611.5)	(11.248)	(-15.183)
420	(16.14)	(26.818)	(4,772.4)	(11.363)	(-15.455)
430	(16.22)	(27.199)	(4,934.2)	(11.475)	(-15.724)
440	(16.31)	(27.573)	(5,097.)	(11.584)	(-15.989)
450	(16.39)	(27.940)	(5,260.)	(11.690)	(-16.250)

From the solution studies presented in this work, it must be concluded that an error of over 1 kcal/mole exists in the literature values for the heat of formation of either NaCN or HCN. Probably the major error lies in the value for HCN because this value was obtained prior to 1900 by combustion of gas of unknown purity. If this is true, the heat of formation values for many cyanide compounds reported in the literature must be wrong because these values are based on HCN.

The free energy of formation of CuCN can be calculated using the data in this report with JANAF values for the standard entropy of nitrogen and copper and the NBS value for carbon. This calculation yields ΔG_{298}° = 26.0 kcal/mole.

REFERENCES[7]

1. American Society for Testing and Materials. Seventeenth Set of the Powder Diffraction File. Philadelphia, Pa., 1968.

2. Berthelot, M. Sur la Chaleur de Formation de L'Acide Cyanhydrique et des Cyanures (The Heat of Formation of Hydrogen Cyanide and Other Cyanides). Ann. Chem. Phys., series 5, v. 23, 1881, pp. 252-268.

3. Brown, Mary H. The Heats of Formation of Selected Cyanide and Oxalate Compounds. Ph.D. Thesis, Univ. of Alabama, 1968, 78 pp.; Dissertation Abs., v. 29, No. 10, April 1969, p. 3696B.

4. Dow Chemical Co. JANAF Thermochemical Tables. Midland, Mich., Sept. 30, 1964, and Mar. 31, 1966.

5. Izatt, R., J. J. Christensen, R. T. Park, and R. Bench. Thermodynamics of Metal--Cyanide Coordination. I. pK, $\Delta H°$, and $\Delta S°$ Values as a Function of Temperature for Hydrocyanic Acid Dissociation in Aqueous Solution. Inorg. Chem., v. 1, 1962, pp. 828-831.

6. Kellog, H. H. Thermodynamic Properties of the Oxides of Copper and Nickel. J. Chem. and Eng. Data, v. 14, No. 1, January 1969, pp. 41-44.

7. Letson, B. B., and A. R. Taylor, Jr. Heats of Formation of Lithium Chloride and Lithium Oxalate, Including Details on the Construction and Operation of a Solution Calorimeter. BuMines Rept. of Inv. 6583, 1965, 12 pp.

8. Mah, A. D., L. B. Pankratz, W. W. Weller, and E. G. King. Thermodynamic Data for Cuprous and Cupric Oxides. BuMines Rept. of Inv. 7026, 1967, 20 pp.

9. McBride, J. J. Low Temperature Heat Capacities of Layer and Chain Type Crystalline Structures. Ph.D. Thesis, Univ. of Michigan, 1956, 131 pp.; Dissertation Abs., v. 18, April 1958, p. 1276.

10. Parker, V. B. Thermal Properties of Aqueous Uni-univalent Electrolytes. National Reference Data Series NBS 2, 1965, 66 pp.

11. Pierson, R. H., A. N. Fletcher, and E. S. Gontz. Catalog of Infrared Spectra for Qualitative Analysis of Gases. Anal. Chem., v. 28, 1956, p. 1218.

12. Rossini, Frederick D., Donald D. Wagman, William H. Evans, Samuel Levine, and Irving Jaffee. Selected Values of Chemical Thermodynamic Properties. NBS Circ. 500, 1952, 1268 pp.

---

[7] Titles in parentheses are translations from the language in which the item was published.

13. Taylor, A. R., Jr., T. Estelle Gardner, and D. F. Smith. Thermodynamic Properties of Beryllium Sulfate From 0° to 900° K. BuMines Rept. of Inv. 6240, 1963, 8 pp.

14. Thomsen, J. Thermochemische Untersuchungen (Thermochemical Investigations). J. Barth Verlag, Leipzig, v. I, 1882; v. II, 1882; v. III, 1884; v. IV, 1886.

15. Varet, R. Thermochimie--Recherches sur les Cyanures de Lithium, de Magnesium, de Cuivre (Thermochemical Research on the Cyanides of Lithium, Magnesium, and Copper). Compt. Rend., v. 121, 1895, p. 121.

16. Wagman, D. D., W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm. Selected Values of Chemical Thermodynamic Properties. NBS Tech. Note 270-3, 1968, 263 pp.

17. Ziegler, K. Organic Synthesis. John Wiley & Sons, Inc., New York, v. 7, 1927, ch. 18.

INT.-BU.OF MINES,PGH.,PA. 15937