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1-Aminopropane, 2-aminopropane, and 2-methyl-2-aminopropane: vibrational assignments, conformational analyses, and chemical thermodynamic properties†‡

D. W. SCOTT

Bartlesville Petroleum Research Center, Bureau of Mines,
U.S. Department of the Interior, Bartlesville, Oklahoma 74003, U.S.A.

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Molecular spectra of the three title compounds and of aminoethane, included for comparison, were interpreted by molecular vibrational analyses. Calorimetric entropy values for the three title compounds were used to obtain further understanding of the molecular energetics. Tables of the chemical thermodynamic properties were compiled.

1. Introduction

Simple aliphatic amines were included in this laboratory's program of thermodynamic studies of nitrogen compounds, because an understanding of the simple compounds would provide a foundation for understanding the more complex nitrogen compounds that actually occur in petroleum or in refinery streams. Calorimetric values for the vapor state at 298.15 K were obtained for the entropy and the enthalpy of formation(1) of 1-aminopropane (*n*-propylamine), 2-aminopropane (isopropylamine), and 2-methyl-2-aminopropane (*t*-butylamine). This paper reports statistical thermodynamic treatments by which the calorimetric values of the two properties at a single temperature were extended to other properties and to the whole temperature range of practical interest. These treatments required interpretation of the molecular spectra to obtain the needed vibrational assignments.

In what follows, the interpretation of the spectra will be discussed first, and then the statistical thermodynamic treatments that resulted in tables of the chemical thermodynamic properties.

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2. Interpretation of the molecular spectra

Molecular vibrational analyses were employed in interpreting the molecular spectra. They were performed with the aid of digital-computer programs SD-4064 (G-matrix), SD-4082 (Z-matrix symmetrization), and SD-9032-VII (eigenvalue perturbation) supplied by J. H. Schachtschneider of Shell Development Company. The calculations were made for assumed structures with tetrahedral angles and staggered configurations about single bonds throughout, and with the following values of bond distances: C—C, 1.53 Å; C—N, 1.47 Å; C—H, 1.10 Å; and N—H, 1.01 Å.† Although no calorimetric data were available for aminoethane (ethylamine), the advantages of having a simpler compound for comparison purposes led to the inclusion of aminoethane with the other three compounds.

As 2-methyl-2-aminopropane can exist in only one conformation, whereas the other three compounds present conformational problems, 2-methyl-2-aminopropane was the logical compound with which to start the analyses, and the interpretation of its spectra will be discussed first.

2-METHYL-2-AMINOPROPANE

Values of observed wavenumbers were obtained from the published vapor-state far-infrared spectrum(2) and from an unpublished vapor-state infrared spectrum for the analytical region obtained by James E. Stewart of Beckman Instruments, Inc., as part of a study of the vibrational spectra of primary and secondary amines.(3)

The force field selected for the molecular vibrational analysis was based on ones known to be satisfactory for structurally related molecules. For the "hydrocarbon" part of the molecule, this force field was that obtained earlier in studies of aliphatic sulfur compounds,(4) and all of the force constants were transferred. The definitions were broadened so that No. 18 (table 2 of reference 4) included C—C, ∠HCN with C common and C—N, ∠HCC with C common; No. 23 included ∠HCC, ∠HCN with C—H common; and No. 30 included ∠HCC, ∠HCN *trans* double prime and ∠HCC, ∠HCN *gauche* double prime. For the "primary amine" part of the molecule, the force field of Dellepiane and Zerbi(5) was selected, and their values of K_R, F_R, $F_{R\theta}$, $F_{\beta\beta}$, and $H_{\tau 1}$ were transferred. Three more constants not included in either field were introduced for the interface between the "hydrocarbon" and "primary amine" parts of the molecule: ∠CCN; C—N, ∠CCN with C—N common; and ∠CCN, ∠CCN with C—N common. Also, C—C, ∠CCN with C—C common was constrained to the mean of C—C, ∠CCC with C—C common and C—N, ∠CCN with C—N common; and ∠CCC, ∠CCN with C—C common was constrained to the mean of ∠CCC, ∠CCC with C—C common and ∠CCN, ∠CCN with C—N common. A fourth additional constant, C—C, C—N with C common, was tried initially and eliminated as being poorly determined. A few of the constants in this field do not apply to 2-methyl-2-aminopropane itself, but were included in anticipation of later transfer to the other three compounds for which they do apply.

Dellepiane and Zerbi(5) were unable to assign the NH_2 and ND_2 twisting wavenumbers in methylamine and its deuterium derivatives that they included in their

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† Å = 0.1 nm.

molecular vibrational analysis of simple aliphatic amines. They therefore lacked confidence in their value of the $F_{\theta\theta}$ force constant, which is not well determined by the other fundamentals. In the more complex molecule of 2-methyl-2-aminopropane, the NH_2 twisting mode can gain infrared intensity by interaction with other modes, and it appears unequivocally as one of the weaker infrared bands at 1111 cm^{-1}. This circumstance provided means to obtain more reliable values of $F_{\theta\theta}$ and other force constants of the NH_2 group that are correlated with $F_{\theta\theta}$.

The force field described above contains 30 force constants, of which 23 apply to 2-methyl-2-aminopropane. Sixteen of the 23 constants were constrained to their

TABLE 1. Adjusted force constants Φ_i of 2-methyl-2-aminopropane and errors $\sigma(\Phi_i)$

Force constant[a]	This research $\Phi_i \pm \sigma(\Phi_i)$	Dellepiane and Zerbi[(5)] $\Phi_i \pm \sigma(\Phi_i)$[b]
K_s	5.943 ± 0.055	6.421 ± 0.025
H_η	0.669 ± 0.022	0.643 ± 0.011
H_θ	0.610 ± 0.029	0.578 ± 0.013
$F_{\theta\theta}$	-0.140 ± 0.029	-0.050 ± 0.017
∠CCN	1.456 ± 0.148	
C—N, ∠CCN; C—N common	0.585 ± 0.155	
∠CCN, ∠CCN; C—N common	0.371 ± 0.137	

[a] Units: stretch, mdyn Å^{-1}; stretch-bend, mdyn rad^{-1}; bend, mdyn Å rad^{-2}.
[b] Not strictly comparable because of differences in assumed molecular geometry.

TABLE 2. Observed and calculated wavenumbers $\tilde{\nu}$ of 2-methyl-2-aminopropane and differences, $\Delta\tilde{\nu} = \tilde{\nu}(\text{obs}) - \tilde{\nu}(\text{calc})$

$\tilde{\nu}/cm^{-1}$		$\frac{\Delta\tilde{\nu}}{cm^{-1}}$	$\tilde{\nu}/cm^{-1}$		$\frac{\Delta\tilde{\nu}}{cm^{-1}}$	$\tilde{\nu}/cm^{-1}$		$\frac{\Delta\tilde{\nu}}{cm^{-1}}$
obs.	calc.		obs.	calc.		obs.	calc.	
a′			a′ (contd)			a″ (contd)		
[≈ 251][a, b]	234	—	1492	1464	28	—	910	—
337	338	−1	1635	1635	0	1000	996	4
446	437	9	2915	2862	53	(1033)[c]	1022	11
456	460	−4	(2915)[c]	2863	52	1111	1114	−3
743	741	2	2975	2955	20	1312	1300	12
812	811	1	(2975)[c]	2958	17	1390	1379	11
—	921	—	(2975)[c]	2958	17	(1460)[c]	1446	14
942	947	−5	3240	3244	−4	(1460)[c]	1447	13
1033	1025	8				(1477)[c]	1456	21
1234	1223	11	a″			(2915)[c]	2862	53
1329	1317	12	[253][b]	213	—	(2975)[c]	2953	22
1379	1373	6	[200][b]	231	—	(2975)[c]	2955	20
(1379)[c]	1373	6	[279][b]	234	—	(2975)[c]	2958	17
1460	1447	13	346	342	−4	3320	3316	4
1477	1454	23	(456)[c]	459	−3			

[a] Inferred from calorimetric entropy value.
[b] Not used in adjustment of force constants,
[c] Used more than once.

transferred values, and the remaining seven, Dellepiane and Zerbi's K_s, H_η, H_θ, and $F_{\theta\theta}$ and the three "interface" force constants, were adjusted to give the best least-squares fit to the observed wavenumbers of 2-methyl-2-aminopropane. The values obtained for the adjusted force constants are listed in table 1, and the calculated values of wavenumbers are compared with the observed values in table 2.

The assignment of table 2 accounts for all of the prominent features of the vapor-state infrared spectra; remaining weak bands have plausible explanations as sum-combinations:

$\tilde{\nu}$/cm^{-1}

1152; 337 + 812 = 1149
1754; 812 + 942 = 1754
2062; 2 × 1033 = 2066
2119; 812 + 1312 = 2124
2294; 812 + 1477 = 2289
2421; 942 + 1477 = 2419
2632; 1000 + 1635 = 2635
2755; 2 × 1379 = 2758

In some instances, the degeneracy of the *t*-butyl group is not split enough by the off-axis NH_2 group for the a′ and a″ components to be resolved in the observed spectra.

AMINOETHANE, 1-AMINOPROPANE, AND 2-AMINOPROPANE

Values of observed wavenumbers were obtained from vapor-state infrared spectra in the analytical region obtained by Carlos Ellis of this center, and, for the last two compounds, from the published vapor-state far-infrared spectra.(2)

The force field derived for 2-methyl-2-aminopropane was used to calculate wavenumbers of the two possible conformations of aminoethane, the five possible conformations of 1-aminopropane, and the two possible conformations of 2-aminopropane. The calculated wavenumbers are compared with the observed values in tables 3, 4, and 5. In the designations of the conformations of 1-aminopropane in

TABLE 3. Calculated and observed wavenumbers of aminoethane

$\tilde{\nu}(C_s)$/cm^{-1}	$\tilde{\nu}(C_1)$/cm^{-1}		$\tilde{\nu}(C_s)$/cm^{-1}	$\tilde{\nu}(C_1)$/cm^{-1}	
calc.	calc.	obs.	calc.	calc.	obs.
216 a″	220	234[a]	1408 a′	1413	1399
258 a″	250	262[b]	1446 a′	1447	1456
461 a′	479	491[c]	1449 a″	1449	
785 a″	758	782[d]	1462 a′	1463	1464
810 a′	812	817	1636 a′	1635	1622
890 a′	887	888[e]	2862 a′	2862	2876
1069 a′	1027	1056	2896 a′	2897	2902
1073 a″	1105	1087	2952 a″	2951	2971
1104 a′	1130	1118	2957 a′	2957	
1249 a″	1228	1239	2961 a″	2960	
1308 a″	1306	1294	3243 a′	3244	3210
1328 a′	1339	1351	3316 a″	3316	3345

[a] From sum-combination [234] + 782 = 1016.
[b] From sum-combination [262] + 782 = 1044.
[c] From sum-combination [491] + 888 = 1379.
[d] Mean of inversion doublet, 774–790.
[e] Mean of inversion doublet, 883–893.

TABLE 4. Calculated and observed wavenumbers of 1-aminopropane

$\tilde{\nu}$(T—T)/cm^{-1}	$\tilde{\nu}$(G—T)/cm^{-1}	$\tilde{\nu}$(G—G′)/cm^{-1}	$\tilde{\nu}$(T—G)/cm^{-1}		$\tilde{\nu}$(G—G)/cm^{-1}	
calc.	calc.	calc.	calc.	obs.	calc.	obs.
120 a″	117	122	123	$<$ 101[a]	122	—
222 a″	222	216	216	210	210	203
249 a″	229	232	247	252	230	232
316 a′	337	337	315	323	342	327
465 a′	504	521	482	454	519	541
740 a″	763	764	737	722[b]	758	751
799 a′	814	781	777	775[c]	793	786[d]
872 a″	871	865	865	878	845	843
893 a′	891	901	895	887	908	893
1020 a′	980	982	1016	1023	978	980
1074 a′	1062	1058	1061	1077	1052	1047
1092 a″	1095	1093	1084	1087	1114	1108
1092 a′	1116	1118	1137	1142 ?	1130	1122 ?
1230 a″	1216	1225	1215	1220	1202	—
1271 a′	1263	1264	1268	1275	1256	—
1286 a″	1286	1276	1289	1302	1284	—
1321 a″	1332	1332	1316	—	1333	—
1368 a′	1371	1380	1371	1354[e]	1382	1387
1419 a′	1395	1397	1421	1400	1398	1394
1435 a′	1438	1438	1437	—	1438	—
1449 a″	1449	1449	1449	1460	1449	(1460)[f]
1454 a′	1453	1453	1456	1466	1454	(1466)[f]
1462 a′	1457	1458	1463	1475	1458	(1475)[f]
1636 a′	1636	1635	1635	1626	1635	(1626)[f]
2862 a′	2862	2862	2862	2885	2862	(2885)[f]
2893 a′	2896	2896	2893	2892	2896	(2892)[f]
2899 a′	2897	2897	2899	2902	2897	(2902)[f]
2950 a″	2952	2952	2950	2943	2952	(2943)[f]
2956 a′	2955	2955	2956	2954	2955	(2954)[f]
2956 a″	2958	2957	2956		2957	
2963 a″	2962	2962	2963	2972	2962	(2972)[f]
3243 a′	3244	3244	3244	—	3244	—
3316 a″	3316	3316	3316	3347	3316	(3347)[f]

[a] Inferred from calorimetric entropy value.

[b] From sum-combination, 210 + [722] = 932.

[c] Mean of inversion doublet, 772–778.

[d] Mean of inversion doublet, 783–788.

[e] Mean of 1350–1358 doublet from Fermi resonance with 323 + 1023 = 1346.

[f] Used a second time.

table 4, the first letter (T or G) refers to the *trans* or *gauche* orientation of the C—C—C—N chain, and the second letter (T, G, or G′) refers to the *trans* or one of the two non-equivalent *gauche* orientations of the C—C—N—: chain. (The symbol for an electron pair, :, designates the vacant corner of the nitrogen tetrahedron.)

The observed spectra of aminoethane clearly can be interpreted as arising from a single conformation, but comparison of the calculated and observed wavenumbers does not provide a clear-cut distinction between the C_1 and C_s conformations. However, two observations identify the observed spectrum with the C_1 conformation.

TABLE 5. Calculated and observed wavenumbers of 2-aminopropane

$\tilde{\nu}(C_s)/\mathrm{cm}^{-1}$	$\tilde{\nu}(C_1)/\mathrm{cm}^{-1}$		$\tilde{\nu}(C_s)/\mathrm{cm}^{-1}$	$\tilde{\nu}(C_1)/\mathrm{cm}^{-1}$	
calc.	calc.	obs.	calc.	calc.	obs.
217 a″	215	234	1378 a″	1377	1381
232 a″	233	201	1393 a′	1397	1389
236 a′	237	263	1447 a″	1447	1462
380 a′	375	371[a]	1450 a′	1450	
408 a″	407	403	1454 a″	1453	1466
514 a′	517	471	1463 a′	1464	1473
764 a′	798	787	1635 a′	1635	1623
837 a′	819	827	2862 a′	2862	2860
931 a″	935	946[b]	2862 a″	2862	
961 a″	965	965	2927 a′	2929	2932
973 a′	973	978	2954 a″	2954	2959
1054 a″	1069	1086	2956 a″	2956	2970
1154 a′	1114	1130	2957 a′	2957	
1190 a′	1191	1177	2958 a′	2958	2983
1204 a″	1243	1243	3244 a′	3244	3200[c]
1346 a″	1324	1335	3316 a″	3317	3342
1357 a′	1362	1344			

[a] From Raman spectrum of liquid(6) and infrared spectrum of solution.(2)

[b] From Raman spectrum of liquid.(6)

[c] Not resolved from sum-combinations, $201 + 2970 = 3171$, $234 + 2970 = 3204$, and $263 + 2970 = 3233$.

(a) The bands at 782 and 888 cm^{-1} both exhibit inversion doubling and, therefore, must be of the same symmetry species, as they would be for the C_1 but not the C_s conformation. (b) The potential energy distribution shows that the C_s mode of calculated wavenumber 785 cm^{-1} is predominately CH_2 and CH_3 rock, whereas the C_1 mode of calculated wavenumber 758 cm^{-1} is predominantly NH_2 wag, as expected from the high intensity and inversion doubling of the corresponding observed band at 782 cm^{-1}.

The observed spectra of 1-aminopropane are too complex to interpret as arising from a single conformation. The statistical-thermodynamic treatment to be discussed later implies that the T—T, T—G, G—T, G—G, and G—G′ conformations have approximately the same energy and are present in about the proportions 1,2,2,2,2, determined by symmetry alone. However, only two of the five conformations are needed to explain the spectra. Comparison of observed and calculated wavenumbers (the observed bands at 980 and 1023 cm^{-1} are the most diagnostic) shows that one conformation has the *trans* and the other one the *gauche* orientation of the C—C—C—N chain. As shown in table 4, the observed wavenumbers are satisfactorily explained as arising from the T—G and G—G conformations. This interpretation is consistent with the fact that in the lower homologue, aminoethane, the observed wavenumbers arise solely from the C_1 conformation, which has the *gauche* orientation of the C—C—N—: chain. Table 4 with its footnotes provides an explanation of all features of the observed spectra except a few weak bands, for which plausible explanations can be found as sum-combinations:

$\tilde{\nu}/\text{cm}^{-1}$

1855; 775 + 1087 = 1862
1955; 2 × 980 = 1960
2760; 1354 + 1400 = 2754
3100; 1475 + 1626 = 3101
$3180; \left\{\begin{matrix} 203 \\ 210 \end{matrix}\right\} + 2972 = \left\{\begin{matrix} 3175 \\ 3182 \end{matrix}\right\}$
3410; 454 + 2972 = 3426

The observed spectra of 2-aminopropane can be interpreted as arising from a single conformation, despite evidence from the statistical-thermodynamic treatment to be discussed later that the C_s and C_1 conformations are present in about the ratio 1/2, determined by symmetry alone. In the region 1000 to 1300 cm^{-1}, the pattern of observed wavenumbers has more similarity to that calculated for the C_1 than for the C_s conformation. This circumstance lends support to the tentative conclusion arrived at previously from the far-infrared spectra alone[(2)] that the C_1 conformation is the one appearing in the infrared spectra. Weak bands not accounted for in table 5 and its footnotes have plausible explanations as sum-combinations:

$\tilde{\nu}/\text{cm}^{-1}$

1032; 234 + 787 = 1021
1051; 263 + 787 = 1050
1745; 403 + 1344 = 1747
3435; 471 + 2970 = 3441

COMMENTS ON THE FORCE FIELD

The force field based on 2-methyl-2-aminopropane is seen to predict wavenumbers of other primary amines well enough to be useful in arriving at vibrational assignments. However, some differences between observed and calculated wavenumbers are rather large. Also, in a related study of piperidine,[(7)] significantly different values of some force constants were required to fit the observed wavenumbers of that secondary amine. These observations serve as a reminder that a force field satisfactorily transferable among all aliphatic amines remains to be found.

3. Statistical-thermodynamic treatments

Tables of chemical thermodynamic properties of 1-aminopropane, 2-aminopropane, and 2-methyl-2-aminopropane were calculated by standard methods. The calorimetric data used are summarized in table 6. The product of moments of inertia for over-all

TABLE 6. Calorimetric data at 298.15 K

	1-Aminopropane	2-Aminopropane	2-Methyl-2-aminopropane
$S^\circ/\text{cal K}^{-1}\,\text{mol}^{-1}$[a]	77.9 ± 0.2	74.7 ± 0.2	78.3 ± 0.2
ΔH_f(real gas, sat.)/kcal mol^{-1}[b]	-16.7_7	-20.0_2	-28.9_0
$(\Delta H_\text{f}^\circ - \Delta H_\text{f})$/kcal mol^{-1}[c]	0.0_4	0.0_5	0.0_6
ΔH_f°/kcal mol^{-1}	−16.7 ± 0.2	−20.0 ± 0.2	−28.8 ± 0.2

[a] Observed values from calorimetric studies in this laboratory.
[b] Reference 1.
[c] Estimated.

rotation, and reduced moments of inertia for internal rotation, were calculated with the same structural assumptions used for the molecular vibrational analyses. Individual treatments now will be considered.

1-AMINOPROPANE

The T—G conformation was selected as the one for which the momental quantities and vibrational assignment (table 4) were used. For the three unobserved wavenumbers above 1300 cm^{-1}, the calculated values were used. The CH_3 and NH_2 torsions were treated as restricted internal rotations with simple, threefold, cosine-type potential barriers. Barrier heights of 3.7 and 1.7 kcal mol^{-1} were calculated from the observed torsional fundamentals of 252 and 210 cm^{-1}, respectively. The skeletal torsion was treated as an harmonic oscillator, and $R \ln 3$ was included in $-(G^\circ - H_0^\circ)/T$ and S° to take account of mixing of the *trans* and *d* and *l gauche* orientations of the C—C—C—N chain. The wavenumber for skeletal torsion was taken as 101 cm^{-1} to give agreement with the calorimetric entropy value. That is a maximum value; if the conformational entropy actually is any less than the $R \ln 9$ implicit in the treatment of the NH_2 and skeletal torsions, then a wavenumber less than 101 cm^{-1} would be required for agreement with the calorimetric entropy.

2-AMINOPROPANE

The C_1 conformation was selected as the one for which the momental quantities and vibrational assignment (table 5) were used. The two CH_3 torsions were treated as hindered by simple, threefold, cosine-type barriers. Barrier heights of 4.4 and 2.7 kcal mol^{-1} were calculated from the assigned torsional fundamentals of 263 and 201 cm^{-1}. The calorimetric entropy value requires that the C_s and C_1 conformations differ little in energy; in fact, satisfactory agreement is obtained by use for the NH_2 torsion of a simple, threefold, cosine-type barrier of height 2.1_4 kcal mol^{-1} evaluated from the observed torsional fundamental of 234 cm^{-1}. This conclusion about a small energy difference in the *vapor* accords with the observation of Krueger and Jan(9) of a difference of only (0.12 ± 0.02) kcal mol^{-1} for $(CH_3)_2CDNH_2$ in CCl_4 *solution.* The contributions of NH_2 torsion actually were obtained by summing over a set of Mathieu-like energy levels based on all of the observed transitions in the far-infrared spectrum attributed to that mode. In view of remaining ambiguities in interpreting the far-infrared spectrum, that refinement may have been more elaborate than justified. In any event, the results were insignificantly different than if the simple barrier mentioned above had been used instead. This treatment of 2-aminopropane is based solely on spectroscopic data and contains no parameter adjusted to fit the calorimetric entropy value; of course, this entropy value was used as a guide to the proper interpretation of the spectroscopic data.

2-METHYL-2-AMINOPROPANE

The vibrational assignment was that of table 2, with the calculated values used for the two unobserved fundamentals. The NH_2 torsion and all three CH_3 torsions were treated as hindered by simple, threefold, cosine-type barriers. The barrier height for the NH_2 torsion, 2.5 kcal mol^{-1}, and two of the CH_3 torsions, 5.0 and 2.7 kcal mol^{-1}, were calculated from the observed fundamentals of 253, 279, and 200 cm^{-1}, respectively. The barrier height for the third, unobserved, CH_3 torsion was taken as 4.1 kcal mol^{-1} to give agreement with the calorimetric entropy value.

CHEMICAL THERMODYNAMIC PROPERTIES

The values of enthalpy of formation in table 6, of the thermodynamic functions of the amines from the treatments just mentioned, and of the thermodynamic functions of C (c, graphite), $H_2(g)$, and $N_2(g)$(10) were used to compute the enthalpy, Gibbs energy, and common logarithm of the equilibrium constant of formation. The chemical thermodynamic properties of the three amines, for selected temperatures between 200 and 1000 K, are listed in tables 7, 8 and 9.

TABLE 7. Standard chemical thermodynamic properties of 1-aminopropane in the ideal gas state

T K	$-(G^\circ - H_0^\circ)/T$ cal K^{-1} mol^{-1}	$(H^\circ - H_0^\circ)/T$ cal K^{-1} mol^{-1}	$H^\circ - H_0^\circ$ kcal mol^{-1}	S° cal K^{-1} mol^{-1}	C_p° cal K^{-1} mol^{-1}	ΔH_f° [a] kcal mol^{-1}	ΔG_f° [a] kcal mol^{-1}	$\log_{10} K_f^\circ$ [a]
0	0	0	0	0	0	−10.1	−10.1	∞
200	58.3	12.0	2.39	70.3	16.7	−14.8	+1.5	−1.7
273.15	62.3	13.7	3.75	76.0	20.4	−16.3	8.4	−6.2
298.15	63.6	14.3	4.27	77.9	21.8	−16.7	10.0	−7.3
300	63.6	14.4	4.32	78.0	21.9	−16.8	10.1	−7.4
400	68.1	17.0	6.79	85.1	27.6	−18.5	19.4	−10.6
500	72.2	19.7	9.83	91.9	33.0	−19.9	29.0	−12.7
600	76.0	22.3	13.4	98.3	37.6	−21.0	38.9	−14.2
700	79.6	24.8	17.3	104.4	41.6	−21.9	48.9	−15.3
800	83.1	27.1	21.7	110.2	45.0	−22.4	59.1	−16.1
900	86.4	29.2	26.3	115.6	48.0	−22.8	69.3	−16.8
1000	89.6	31.2	31.2	120.8	50.5	−23.1	79.6	−17.4

[a] The standard enthalpy, Gibbs energy, and common logarithm of the equilibrium constant of formation by the reaction: 3 C (c, graphite) + $(9/2)H_2(g)$ + $(1/2)N_2(g)$ = $C_3H_9N(g)$.

TABLE 8. Standard chemical thermodynamic properties of 2-aminopropane in the ideal gas state

T K	$-(G^\circ - H_0^\circ)/T$ cal K^{-1} mol^{-1}	$(H^\circ - H_0^\circ)/T$ cal K^{-1} mol^{-1}	$H^\circ - H_0^\circ$ kcal mol^{-1}	S° cal K^{-1} mol^{-1}	C_p° cal K^{-1} mol^{-1}	ΔH_f° [a] kcal mol^{-1}	ΔG° [a] kcal mol^{-1}	$\log_{10} K_f^\circ$ [a]
0	0	0	0	0	0	−13.3	−13.3	∞
200	55.3	11.5	2.30	66.8	17.1	−18.1	− 1.1	1.2
273.15	59.2	13.5	3.70	72.7	21.2	−19.5	5.4	− 4.3
298.15	60.4	14.2	4.25	74.6	22.6	−20.0	7.7	− 5.6
300	60.5	14.3	4.29	74.8	22.7	−20.0	7.9	− 5.7
400	65.0	17.1	6.85	82.1	28.5	−21.7	17.4	− 9.5
500	69.1	19.9	9.96	89.0	33.6	−23.0	27.3	−11.9
600	73.0	22.6	13.6	95.6	38.1	−24.0	37.5	−13.7
700	76.6	25.1	17.6	101.7	41.9	−24.8	47.8	−14.9
800	80.2	27.4	21.9	107.6	45.1	−25.4	58.2	−15.9
900	83.5	29.5	26.6	113.0	48.0	−25.8	68.7	−16.7
1000	86.7	31.5	31.5	118.2	50.4	−26.0	79.2	−17.3

[a] The standard enthalpy, Gibbs energy, and common logarithm of the equilibrium constant of formation by the reaction: 3 C (c, graphite) + $(9/2)H_2(g)$ + $(1/2)N_2(g)$ = $C_3H_9N(g)$.

TABLE 9. Standard chemical thermodynamic properties of 2-methyl-2-aminopropane in the ideal gas state

$\frac{T}{\mathrm{K}}$	$-(G^\circ - H^\circ_0)/T$ cal K^{-1} mol^{-1}	$(H^\circ - H^\circ_0)/T$ cal K^{-1} mol^{-1}	$H^\circ - H^\circ_0$ kcal mol^{-1}	S° cal K^{-1} mol^{-1}	C°_p cal K^{-1} mol^{-1}	ΔH°_f [a] kcal mol^{-1}	ΔG° [a] kcal mol^{-1}	$\log_{10}K^\circ_f$ [a]
0	0	0	0	0	0	−20.7	−20.7	∞
200	55.5	13.0	2.59	68.5	21.1	−26.7	−4.1	4.5
273.15	60.0	15.9	4.35	75.9	26.8	−28.3	+4.4	−3.5
298.15	61.4	16.9	5.04	78.3	28.8	−28.8	7.4	−5.4
300	61.5	17.0	5.10	78.5	28.9	−28.9	7.7	−5.6
400	67.0	20.9	8.37	87.9	36.4	−30.8	20.1	−11.0
500	72.0	24.7	12.3	96.7	42.8	−32.3	33.0	−14.4
600	76.8	28.2	16.9	105.0	48.3	−33.4	46.2	−16.8
700	81.4	31.4	22.0	112.8	52.9	−34.3	59.5	−18.6
800	85.8	34.3	27.5	120.1	56.8	−34.9	73.0	−19.9
900	90.0	37.0	33.3	127.0	60.2	−35.3	86.5	−21.0
1000	94.0	39.5	39.5	133.5	63.2	−35.5	100.0	−21.9

[a] The standard enthalpy, Gibbs energy, and common logarithm of the equilibrium constant of formation by the reaction: 3 C (c, graphite) + (11/2)H_2(g) + (1/2)N_2(g) = $C_4H_{11}N$(g).

The thermodynamic functions were calculated, as already described, with the harmonic-oscillator, rigid-rotator, independent-internal-rotator approximation and are based solely on calorimetric values of entropy, as no experimental values of C°_p, the heat capacity in the ideal gas state, were available for estimating the effects of anharmonicity and other phenomena not included in the simplified treatment. The entries in tables 7, 8, and 9 are given to one less than the customary number of decimal places as a reminder that they are not as reliable as values based on more complete calorimetric data. Despite the evident shortcomings, the tabulated chemical thermodynamic properties of the three primary amines are superior to any values available heretofore and should suffice for nearly all practical chemical thermodynamic applications.

Results of low-temperature calorimetry provided by staff members of this laboratory are intended for later, separate, publication.

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