

Thermodynamic properties of acrylonitrile, 1-aminopropane, 2-aminopropane, and 2-methyl-2-aminopropane^{a, b}

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Low-temperature calorimetric quantities were determined for acrylonitrile, 1-aminopropane, 2-aminopropane, and 2-methyl-2-aminopropane from 12 K to near their respective normal boiling temperatures. Values of molar heat capacity at saturation pressure of the condensed phases, transition and melting temperatures, and enthalpies of transition and fusion were measured by adiabatic calorimetry. From these data the thermodynamic quantities $-\{G_s(T) - H^\circ(0)\}/T$, $\{H_s(T) - H^\circ(0)\}/T$, $\{H_s(T) - H^\circ(0)\}$, S_s , and C_s were evaluated for the solid and liquid states. For acrylonitrile a revised vibrational assignment was made from Raman and infrared wavenumbers reported in the literature, and a table of thermodynamic functions for the ideal gas state from 0 to 1000 K was prepared. Values of the enthalpy, Gibbs energy, and logarithm of equilibrium constant of formation for acrylonitrile also were computed for the range 0 to 1000 K.

1. Introduction

As part of a program of study of the thermochemical and thermophysical properties of organic nitrogen compounds, low-temperature thermal properties of acrylonitrile (propenenitrile), 1-aminopropane (*n*-propylamine), 2-aminopropane (isopropylamine), and 2-methyl-2-aminopropane (*t*-butylamine) were studied. The derived results were used to calculate the thermodynamic properties of the condensed phases from 12 K to near the respective boiling temperatures. Third-law entropies of the four compounds in the ideal gas state at 298.15 K were calculated from the present data combined with values of enthalpy of vaporization and vapor pressures from the literature. The thermodynamic functions for acrylonitrile in the vapor state were recalculated from a revised interpretation of the published molecular spectra.

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^b Contribution No. 193 from the thermodynamics laboratory of the Bartlesville Energy Research Center.

2. Experimental

MATERIALS

The sample of acrylonitrile was provided by the Monsanto Chemical Co. through the courtesy of Mr G. D. Oliver. The three amine samples used were standard samples of organic nitrogen compounds API-USBM, prepared at the Laramie (Wyo.) Energy Research Center of the Bureau of Mines. The samples were dried by passing the vapors through activated molecular sieves. An estimate of the purity of each sample is given in a later section.

APPARATUS AND METHOD

The measurements were carried out in an adiabatic cryostat very similar in principle and design to that previously described.^(1, 2) The temperatures of the three sections of the adiabatic shield and the tempering ring of wires were controlled to within 1 mK with separate electronic controls which operated automatically with individual channels of recording circuitry provided with proportional, rate, and reset control action. The sample (about 0.85 mol of acrylonitrile, 0.67 mol of 1-aminopropane, 0.66 mol of 2-aminopropane, or 0.51 mol of 2-methyl-2-aminopropane) was sealed in a platinum vessel equipped with horizontal, perforated heat-distributing disks of gold. A small pressure of helium (about 40 Torr) was left in the calorimetric vessel to promote thermal equilibration at low temperatures.† The electrical power supplied to the calorimeter heater and the resistance of the platinum resistance thermometer were measured with a White double potentiometer. Measurements of potential were in terms of a bank of six saturated cadmium cells calibrated at the National Bureau of Standards. The duration of each heating interval was determined by an electrical stopclock driven by a constant-frequency, (50 ± 0.001) Hz, a.c. power source which was checked against radio station WWV, National Bureau of Standards, Boulder, Colorado; the estimated uncertainty in time measurements was less than 0.01 per cent. Temperatures were measured with platinum resistance thermometers calibrated in terms of the International Practical Scale of 1948, text revision of 1960,⁽³⁾ from 90 to 400 K, and in terms of the provisional scale of the National Bureau of Standards⁽⁴⁾ from 11 to 90 K. Celsius temperatures were converted to thermodynamic temperatures by adding 273.15 K.⁽⁵⁾ Energy was measured in joules and converted to calories by the relation, $1 \text{ cal}_{18} = 4.184 \text{ J}$. The 1961 International Atomic Weights⁽⁶⁾ and the 1963 values of the fundamental constants⁽⁷⁾ were used.

3. Results

HEAT CAPACITY

The observed values of heat capacity at saturation, C_s , of solid and liquid acrylonitrile, 1-aminopropane, 2-aminopropane, and 2-methyl-2-aminopropane are listed in table 1. Where necessary, the differences between C_s and C_p may be calculated from the thermodynamic relation:⁽⁸⁾

$$C_p - C_s = T(\partial V/\partial T)_p(\partial p/\partial T)_s.$$

† Torr = $(101\,325/760)$ Pa.

TABLE 1. Molar heat capacity ($\text{cal}_{\text{th}} = 4.184 \text{ J}$)

T^a K	C_p^b $\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}$	T^a K	C_p^b $\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}$	T^a K	C_p^b $\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}$
Acrylonitrile (crystals II)					
12.47	0.394	30.67	3.777	93.79	12.488
12.83	0.416	33.58	4.402	95.60	12.670
13.91	0.548	34.03	4.492	96.71	12.761
14.46	0.617	37.22	5.143	99.53	13.038
15.37	0.743	37.77	5.251	102.84	13.354
15.90	0.818	42.03	6.037	105.55	13.623
16.99	0.988	47.05	6.885	109.32	13.987
17.40	1.053	50.62	7.450	111.94	14.254
18.80	1.297	52.53	7.734	116.12	14.654
19.04	1.339	54.09	7.959	118.73	14.936
20.78	1.668	55.36	8.132	125.97	15.679
20.87	1.685	58.57	8.574	127.48	15.556
22.92	2.103	64.28	9.310	133.62	16.493
22.95	2.107	70.54	10.027	134.78	16.402
25.16	2.585	76.92	10.725	140.63	16.675
25.31	2.613	83.17	11.418	141.24	17.305
27.58	3.108	88.53	11.981	146.07	17.474
27.82	3.161	89.31	12.063	151.28	18.234
30.33	3.702				
Acrylonitrile (crystals I)					
163.92	17.038 ^c	171.17	17.759 ^c	176.75	18.411 ^c
165.80	17.238 ^c	171.60	17.578 ^c	178.72	18.237 ^c
166.30	17.090 ^c	173.60	17.882 ^c	179.88	18.266 ^c
167.98	17.278 ^c	174.01	17.888 ^c	180.66	18.350 ^c
168.36	17.231 ^c	174.45	18.367 ^c	181.25	18.603 ^c
169.26	17.482 ^c	175.57	18.503 ^c	181.75	18.836 ^c
170.80	17.273 ^c	176.22	18.259 ^c	183.69	19.211 ^c
171.07	17.631 ^c				
Acrylonitrile (liquid)					
196.69	24.421	233.45	24.731	284.39	25.660
203.32	24.458	243.53	24.880	293.09	25.877
203.70	24.454	253.53	25.045	303.27	26.131
209.36	24.492	263.45	25.232	324.74	26.696
213.11	24.513	274.10	25.441	335.99	27.011
223.31	24.612	283.28	25.667	347.10	27.341
1-Aminopropane (crystals)					
11.65	0.436	24.73	2.689	94.88	13.298
12.26	0.503	27.22	3.203	97.20	13.513
13.05	0.598	29.88	3.751	104.86	14.259 ^d
13.62	0.674	32.92	4.375	112.84	15.012 ^d
14.46	0.793	36.36	5.069	121.12	15.783 ^d
15.06	0.885	40.29	5.823	129.55	16.534 ^d
15.98	1.029	44.78	6.627	138.22	17.317 ^d
16.52	1.117	49.80	7.490	146.89	18.114 ^d
17.70	1.319	49.84	7.499	155.66	18.971 ^d
18.25	1.415	54.76	8.289	164.46	19.896 ^d
19.59	1.661	60.41	9.153	167.86	20.209 ^d
20.25	1.786	66.49	10.008	173.23	20.943 ^d
21.60	2.050	73.16	10.848	176.57	21.400 ^d
22.38	2.203	80.27	11.713	181.81	22.558 ^d
23.87	2.508	87.47	12.551		

TABLE 1—Continued

T^a K	C_p^b cal _{th} K ⁻¹ mol ⁻¹	T^c K	C_p^b cal _{th} K ⁻¹ mol ⁻¹	T^a K	C_p^b cal _{th} K ⁻¹ mol ⁻¹
1-Aminopropane (liquid)					
189.96	36.842	234.63	37.859	299.69	38.876
197.14	37.047	245.29	38.025	300.55	38.886
200.61	37.148	256.30	38.170	308.93	39.078
205.09	37.264	267.25	38.326	317.66	39.301
209.47	37.365	278.13	38.482	326.33	39.558
215.71	37.510	288.95	38.664	334.56	39.824
224.77	37.688				
2-Aminopropane (crystals)					
11.56	0.829	25.24	3.749	84.34	11.887
12.39	0.966	26.25	3.966	92.25	12.674
12.70	1.024	27.88	4.306	94.04	12.845
13.67	1.212	29.09	4.552	96.17	13.046
14.02	1.282	30.94	4.917	104.26	13.830 ^e
15.08	1.506	34.20	5.542	112.30	14.635 ^e
15.64	1.620	37.66	6.156	120.31	15.423 ^e
16.75	1.865	41.67	6.797	128.80	16.302 ^e
17.52	2.032	46.11	7.450	137.40	17.230 ^e
18.69	2.293	51.02	8.127	145.56	18.158 ^e
19.44	2.460	52.19	8.279	153.81	19.193 ^e
20.77	2.755	57.09	8.896	162.06	20.349 ^e
21.52	2.921	62.67	9.571	164.79	20.777 ^e
22.91	3.222	69.10	10.274	170.22	21.758 ^e
23.75	3.404	76.51	11.047	172.50	22.347 ^e
2-Aminopropane (liquid)					
181.48	35.194	215.46	37.021	278.92	38.674
185.32	35.446	226.30	37.413	289.20	38.929
188.41	35.645	236.96	37.730	299.41	39.202
193.07	35.931	247.58	37.990	299.90	39.200
195.22	36.055	258.10	38.221	309.06	39.469
204.95	36.550	268.55	38.456	318.16	39.763
2-Methyl-2-aminopropane (crystals III)					
11.80	0.938	24.44	4.359	66.52	11.742
12.90	1.191	27.13	5.062	70.67	12.360
12.96	1.204	30.21	5.804	72.33	12.629
14.17	1.505	33.50	6.533	77.53	13.561
14.36	1.554	36.98	7.233	79.65	14.011
15.62	1.894	41.02	7.952	80.82	14.258
15.95	1.982	45.50	8.660	81.78	14.525
17.23	2.338	49.37	9.252	82.61	14.698
17.72	2.475	50.45	9.415	84.36	15.226
18.97	2.830	53.18	9.799	86.30	15.932
19.63	3.014	54.50	9.979	87.92	16.813
20.87	3.363	58.19	10.517	89.46	18.384
21.90	3.654	60.28	10.832	90.62	27.392
23.04	3.974	64.15	11.390	91.30	45.316
2-Methyl-2-aminopropane (crystals II)					
91.51	18.863	124.29	18.007	161.95	22.660 ^f
92.10	15.159	131.90	18.918	164.54	22.964 ^f
95.21	14.715	139.54	19.847	170.46	23.798 ^f

TABLE 1—Continued

T^a K	C_p^b cal _{th} K ⁻¹ mol ⁻¹	T^a K	C_p^b cal _{th} K ⁻¹ mol ⁻¹	T^a K	C_p^b cal _{th} K ⁻¹ mol ⁻¹
2-Methyl-2-aminopropane (crystals II)—continued					
96.44	14.824	142.92	20.253	173.46	24.213 ^f
98.78	15.049	147.18	20.786	179.33	25.122 ^f
102.95	15.505	151.06	21.266	182.32	25.630 ^f
109.06	16.204	153.74	21.590	188.47	26.720 ^f
116.67	17.099	159.45	22.341 ^f	196.41	28.952 ^f
2-Methyl-2-aminopropane (crystals I)					
202.93	40.141 ^f	203.85	40.333 ^f	204.98	41.654 ^f
202.99	40.243 ^f	204.77	41.179 ^f		
2-Methyl-2-aminopropane (liquid)					
209.78	42.572	235.56	43.977	299.74	45.878
210.77	42.646	240.37	44.151	308.72	46.203
214.48	42.906	250.66	44.483	309.80	46.255
215.52	42.961	261.30	44.772	316.64	46.523
216.32	43.020	271.85	45.047	324.90	46.920
220.97	43.288	282.75	45.352	332.49	47.262
225.62	43.540	293.99	45.699		

^a T is the mean temperature of each heat capacity.

^b C_p is the heat capacity of each compound under its own vapor pressure. Results have *not* been corrected for the effects of premelting.

^c, ^d, ^e, ^f The temperature increments are in order of increasing T/K : ^c 5.410, 5.319, 5.368, 6.122, 5.335, 5.287, 4.467, 5.224, 4.019, 5.247, 5.162, 5.939, 5.080, 5.075, 5.075, 5.043, 5.074, 5.816, 5.076, 4.987, 4.957, 4.871; ^d 7.830, 8.142, 8.429, 8.437, 8.907, 8.568, 8.981, 8.627, 8.580, 8.954, 8.885, 8.433; ^e 8.256, 7.847, 8.172, 8.803, 8.402, 8.046, 8.453, 8.057, 9.434, 8.320, 8.909; ^f 8.496, 8.318, 9.116, 8.719, 8.727, 9.043, 9.034, 9.209, 7.320, 2.454, 1.729, 2.049, 1.851, 1.651.

The heat capacity values listed were corrected for vaporization into the gas space of the sample container. The temperature increments used in the experiments were small enough to ensure that corrections for nonlinear variation of C_p with T were unnecessary. With the exception of temperature regions near phase changes, the increments employed were approximately 10 per cent of the thermodynamic temperature below 50 K, 5 to 8 K from 50 to 150 K, and 8 to 10 K above 150 K. The imprecision of the heat capacity measurement was usually less than 0.1 per cent; above 30 K the accuracy uncertainty of the values of C_p should not exceed 0.2 per cent. The values of heat capacity determined in the premelting range were of lower precision and accuracy because of rapid changes in C_p with T , slow equilibration, and uncertainties caused by the presence of impurities. The results reported in table 1 are not corrected for any effect of premelting caused by impurities, but to permit this calculation, pertinent ΔT values are included as a footnote. Table 4 lists values at selected temperatures determined from smooth curves drawn through all the data from table 1 after corrections for premelting had been made.

The heat capacity curves for the liquid state of the four samples studied are of normal shape and may be represented by cubic equations in the thermodynamic

temperature. The constants for the equations, the temperature range, and deviations are given in table 2.

TABLE 2. Equations for the molar heat capacity of the liquid. $C_p/\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1} = A + B(T/\text{K}) + C(T/\text{K})^2 + D(T/\text{K})^3$; T_1 and T_2 are the lower and upper bounds of the temperature range; $\langle \delta \rangle$ is the average deviation, and δ_{max} the maximum deviation of the measured values of $C_p/\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}$ from the equation

	<i>A</i>	<i>B</i>	<i>C</i> × 10 ³	<i>D</i> × 10 ⁶	<i>T</i> ₁ /K	<i>T</i> ₂ /K	$\langle \delta \rangle$	δ_{max}
Acrylonitrile	31.664	-0.088 004 8	0.316 043	-0.283 584	193	352	0.007	0.018
1-Aminopropane	12.552	0.269 792	-0.989 730	1.276 414	185	340	0.005	0.008
2-Aminopropane	-8.896	0.486 376	-1.731 393	2.148 353	179	323	0.010	0.021
2-Methyl-2-amino- propane	-27.785	0.745 270	-2.621 559	3.186 123	207	337	0.024	0.047

SOLID-STATE PHASE TRANSFORMATIONS

Polymorphic crystalline states are observed for acrylonitrile and 2-methyl-2-amino-propane. Acrylonitrile exists in two enantiotropic crystalline modifications which transposed regularly, as would be expected for an isothermal or first-order transition (Type I, classification of McCullough⁽⁹⁾). Crystalline 2-methyl-2-aminopropane exhibited a second-order or lambda-type transition with a peak at 91.3 K and a first-order type I transition at less than 4 K below the melting temperature. These transitions were easily studied.

ENTHALPY OF FUSION, TRIPLE-POINT TEMPERATURE, CRYOSCOPIC CONSTANTS, AND SAMPLE PURITY

The enthalpy of fusion, ΔH_m , was determined from the total enthalpy difference between an equilibrium temperature below to one above the melting temperature. The isothermal increment was calculated by subtracting the sum of the enthalpies required to raise the temperature of the crystals from the initial temperature to the melting temperature and the liquid from the melting temperature to the final temperature. Appropriate correction for the effect of premelting⁽¹⁰⁾ caused by impurities

TABLE 3. Molar enthalpies of transition and fusion ($\text{cal}_{\text{th}} = 4.184 \text{ J}$)

<i>T</i> /K	$\Delta H/\text{cal}_{\text{th}} \text{mol}^{-1}$
	Acrylonitrile
162.50	284.0 ± 0.4 (transition)
189.63	1489.0 ± 0.8 (fusion)
	1-Aminopropane
188.36	2622.9 ± 0.8 (fusion)
	2-Aminopropane
177.99	1750.6 ± 0.2 (fusion)
	2-Methyl-2-aminopropane
91.30	27.13 ± 0.01 (transition)
202.27	1446.6 ± 0.1 (transition)
206.19	210.8 ± 0.2 (fusion)

was applied to each measurement of the enthalpy of fusion. Two or more measurements for each compound were averaged to obtain the results in table 3; the uncertainties are maximum deviations from the mean.

Equilibrium melting temperatures, T_F , as a function of fraction of total sample melted, F , are given in table 4. Also listed are values derived⁽¹⁰⁾ for the triple-point temperature T_{ip} , the mole fraction x_2 of impurity in the sample, and the cryoscopic constants, $A = \Delta H_m/RT_{ip}^2$ and $B = (1/T_{ip} - \Delta C_m/2\Delta H_m)$, calculated from the observed values of T_{ip} , ΔH_m , and ΔC_m (heat capacity difference in solid and liquid state at T_{ip}).

TABLE 4. Melting-temperature summaries

F	$1/F$	T_F/K	$T(\text{calc})/K$
Acrylonitrile			
$A = 0.02083 \text{ K}^{-1}$, $B = 0.00332 \text{ K}^{-1}$, $x_2 = 0.0008$			
0.1038 ^a	9.631	189.2406	189.2406
0.2682 ^b	3.728	189.4806	189.4793
0.3098 ^a	3.227	189.4952	189.4995
0.6253 ^a	1.599	189.5694	189.5653
0.8356 ^a	1.197	189.5795	189.5816
0.8961 ^b	1.116	189.5800	189.5849
1.0000	1.000		189.5896
Pure	0 (triple-point)		189.6300
1-Aminopropane			
$A = 0.03719 \text{ K}^{-1}$, $B = 0.00267 \text{ K}^{-1}$, $x_2 = 0.00028$			
0.1317	7.593	188.3001	188.3001
0.2672	3.743	188.3300	188.3292
0.4780	2.092	188.3418	188.3416
0.6899	1.449	188.3465	188.3465
0.9016	1.109	188.3484	188.3491
1.0000	1.000		188.3499
Pure	0 (triple-point)		188.3575
2-Aminopropane			
$A = 0.02794 \text{ K}^{-1}$, $B = 0.00220 \text{ K}^{-1}$, $x_2 = 0.00007$			
0.1272	7.861	177.9736	177.9728
0.2607	3.835	177.9831	177.9831
0.4894	2.043	177.9878	177.9877
0.6798	1.471	177.9889	177.9892
0.8701	1.149	177.9900	177.9900
1.0000	1.000		177.9904
Pure	0 (triple-point)		177.9930
2-Methyl-2-aminopropane			
$A = 0.00249 \text{ K}^{-1}$, $B = -0.00004 \text{ K}^{-1}$, $x_2 = 0.00007$			
0.1150	8.696	206.0278	205.9591
0.3667	2.727	206.1226	206.1227
0.6491	1.541	206.1528	206.1552
0.9353	1.069	206.1681	206.1681
1.0000	1.000		206.1700
Pure	0 (triple-point)		206.1974

^a From melting temperature studies at beginning of measurements.

^b From melting temperature studies near end of measurements to check extent of polymerization.

THE TRANSITION TEMPERATURES AND ENTHALPIES OF TRANSITION

The type I solid-solid phase transformation for acrylonitrile was nearly isothermal, taking place over less than 0.1 K temperature interval. From a study of equilibrium temperatures as a function of fraction transformed, 162.50 K was chosen as the temperature of the transition. For crystalline 2-methyl-2-aminopropane, the temperature of the "peak" of the lambda-type transition, 91.3 K, was obtained from heat capacity measurements on both sides of the lambda. The type I phase-transition temperature was determined as for acrylonitrile, and 202.27 K was chosen. Replicate measurements of the enthalpies of transition were made and calculated in a manner similar to that described for the enthalpies of fusion, and the results are in table 3.

THERMODYNAMIC PROPERTIES IN THE SOLID AND LIQUID STATES

The low-temperature results were used in calculating values of the "Gibbs energy function", "enthalpy function", enthalpy, entropy, and heat capacity for the solid and liquid states at selected temperatures from 10 to about 340 K for the four compounds. The thermodynamic properties at 10 K were calculated from a Debye function, the parameters of which were evaluated from the heat capacities between 11 and 20 K. The number of degrees of freedom used and the characteristic Debye temperatures are, respectively, acrylonitrile, 5.5 and 159.80 K; 1-aminopropane, 3.8 and 128.67 K; 2-aminopropane, 3.4 and 98.36 K; 2-methyl-2-aminopropane, 4.8 and 107.55 K. Thermodynamic properties above 10 K were calculated from values of enthalpy and temperature of phase changes and from appropriate integration of smoothed values of the heat capacity at regular intervals. The results are given in table 5; corrections for the effects of premelting were applied as necessary in computing the "smoothed" results.

COMPARISON WITH OTHER WORK

As far as the authors are aware, the low-temperature thermal properties of only one of the four compounds reported here have been determined in another laboratory. Lebedev, Rabinovich, and Martynenko (LRM)⁽¹¹⁾ measured, calorimetrically, the heat capacity and enthalpies plus temperatures of phase changes of acrylonitrile and polyacrylonitrile from 58 to 300 K. From the information given in their report, it is not possible to determine the purity of the acrylonitrile studied by LRM, who state that their precision uncertainty of measurements is about 0.2 per cent but did not exceed 0.5 per cent. LRM did not present their measured results; thus only the smoothed and derived data for acrylonitrile over the common temperature range of the measurements were compared. Figure 1 illustrates the deviation between the two sets of smoothed heat capacities, and table 6 presents a summary of the comparison of the temperatures and enthalpies of phase changes and derived enthalpies and entropies. Note that except for the region 0 to 60 K over which LRM made no observations, the enthalpy and entropy changes agree exceedingly well (0.10 per cent and 0.24 per cent, respectively) despite the wide variation in the reported values of the other physical properties.

TABLE 5. Molar thermodynamic functions for condensed phases ($\text{cal}_{\text{th}} = 4.184 \text{ J}$)

T K	$-\{G_s(T)-H^{\circ}(0)\}/T$ $\text{cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1}$	$\{H_s(T)-H^{\circ}(0)\}/T$ $\text{cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1}$	$\{H_s(T)-H^{\circ}(0)\}$ $\text{cal}_{\text{th}} \text{ mol}^{-1}$	S_s $\text{cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1}$	C_s $\text{cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1}$
Acrylonitrile (crystals II)					
10	0.017	0.052	0.52	0.070	0.209
12	0.030	0.090	1.08	0.120	0.360
14	0.048	0.143	1.99	0.190	0.567
16	0.071	0.212	3.38	0.283	0.834
18	0.101	0.298	5.37	0.399	1.156
20	0.138	0.402	8.03	0.539	1.518
25	0.260	0.726	18.14	0.986	2.549
30	0.427	1.120	33.59	1.547	3.632
35	0.632	1.555	54.43	2.187	4.694
40	0.869	2.010	80.39	2.879	5.670
45	1.132	2.466	110.97	3.598	6.548
50	1.415	2.915	145.75	4.330	7.354
60	2.024	3.775	226.50	5.799	8.765
70	2.666	4.576	320.35	7.243	9.967
80	3.327	5.319	425.5	8.646	11.069
90	3.994	6.018	541.6	10.012	12.126
100	4.662	6.676	667.6	11.339	13.084
110	5.328	7.303	803.3	12.631	14.061
120	5.990	7.908	948.9	13.898	15.065
130	6.646	8.498	1104.7	15.144	16.106
140	7.297	9.080	1271.1	16.377	17.173
150	7.943	9.654	1448.1	17.597	18.218
160	8.584	10.223	1635.7	18.808	19.332
162.50	8.744	10.366	1684.4	19.110	19.638
Acrylonitrile (crystals I)					
162.50	8.744	12.113	1968.4	20.857	16.878
170	9.296	12.337	2097.2	21.632	17.474
180	10.009	12.644	2275.9	22.654	18.269
189.63	10.676	12.949	2455.5	23.625	19.034
Acrylonitrile (liquid)					
189.63	10.68	20.80	3944	31.48	24.392
190	10.71	20.81	3953	31.52	24.394
200	11.79	20.99	4197	32.78	24.436
210	12.82	21.15	4442	33.97	24.491
220	13.80	21.31	4687	35.11	24.576
230	14.76	21.45	4933	36.21	24.688
240	15.67	21.59	5181	37.26	24.825
250	16.56	21.72	5430	38.28	24.985
260	17.41	21.85	5681	39.26	25.165
270	18.23	21.98	5933	40.21	25.359
273.15	18.49	22.02	6013	40.51	25.421
280	19.04	22.10	6188	41.14	25.563
290	19.82	22.22	6445	42.04	25.798
298.15	20.43	22.33	6656	42.76	26.003
300	20.57	22.35	6704	42.92	26.049
310	21.31	22.47	6966	43.78	26.303
320	22.02	22.60	7230	44.62	26.567
330	22.72	22.72	7497	45.44	26.841
340	23.40	22.84	7767	46.24	27.128
350	24.06	22.97	8040	47.03	27.430
360	24.71	23.10	8316	47.81	27.750

TABLE 5—Continued

T K	$-\{G_s(T)-H^\circ(0)\}/T$ cal _{th} K ⁻¹ mol ⁻¹	$\{H_s(T)-H^\circ(0)\}/T$ cal _{th} K ⁻¹ mol ⁻¹	$\{H_s(T)-H^\circ(0)\}$ cal _{th} mol ⁻¹	S_s cal _{th} K ⁻¹ mol ⁻¹	C_s cal _{th} K ⁻¹ mol ⁻¹
1-Aminopropane (crystals)					
10	0.023	0.069	0.69	0.092	0.275
12	0.040	0.119	1.42	0.158	0.469
14	0.063	0.187	2.61	0.249	0.726
16	0.093	0.273	4.36	0.366	1.033
18	0.131	0.376	6.76	0.507	1.371
20	0.177	0.493	9.86	0.670	1.738
25	0.323	0.841	21.03	1.164	2.744
30	0.511	1.244	37.33	1.756	3.776
35	0.735	1.679	58.77	2.415	4.797
40	0.989	2.131	85.22	3.120	5.768
45	1.266	2.585	116.33	3.851	6.666
50	1.562	3.036	151.82	4.598	7.522
60	2.194	3.917	235.03	6.111	9.092
70	2.861	4.757	332.98	7.618	10.458
80	3.549	5.547	443.7	9.095	11.682
90	4.246	6.293	566.3	10.538	12.814
100	4.945	6.995	699.5	11.940	13.795
110	5.643	7.656	842.1	13.299	14.744
120	6.337	8.286	994.2	14.622	15.676
130	7.024	8.889	1155.5	15.913	16.571
140	7.704	9.470	1325.7	17.174	17.472
150	8.377	10.034	1505.0	18.410	18.402
160	9.042	10.588	1694.0	19.629	19.399
170	9.700	11.137	1893.3	20.838	20.494
180	10.352	11.692	2104.5	22.045	21.779
188.36	10.894	12.165	2291.3	23.059	22.898
1-Aminopropane (liquid)					
188.36	10.89	26.09	4914	36.98	36.74
190	11.12	26.18	4974	37.30	36.80
200	12.47	26.72	5344	39.19	37.13
210	13.79	27.22	5716	41.01	37.38
220	15.07	27.69	6091	42.76	37.59
230	16.31	28.12	6468	44.43	37.78
240	17.51	28.53	6847	46.04	37.94
250	18.69	28.91	7227	47.60	38.08
260	19.83	29.26	7609	49.09	38.22
270	20.94	29.60	7992	50.54	38.36
273.15	21.28	29.70	8113	50.98	38.40
280	22.02	29.91	8376	51.93	38.51
290	23.08	30.21	8762	53.29	38.68
298.15	23.92	30.44	9078	54.36	38.84
300	24.10	30.50	9150	54.60	38.88
310	25.11	30.77	9540	55.88	39.10
320	26.09	31.04	9932	57.13	39.36
330	27.05	31.29	10327	58.34	39.67
340	27.99	31.54	10726	59.53	40.04
2-Aminopropane (crystals)					
10	0.046	0.137	1.368	0.183	0.537
12	0.079	0.231	2.769	0.310	0.879
14	0.123	0.352	4.934	0.476	1.281
16	0.179	0.495	7.914	0.674	1.703
18	0.247	0.653	11.755	0.900	2.140
20	0.324	0.824	16.478	1.148	2.584

TABLE 5—Continued

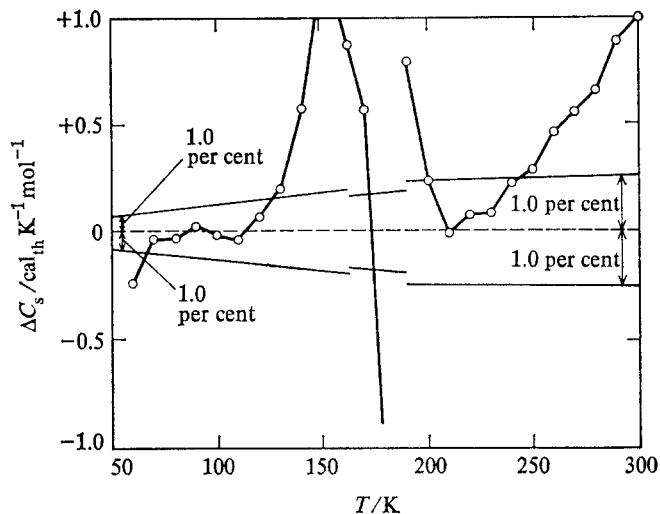
T K	$-\{G_s(T)-H^{\circ}(0)\}/T$ cal _{th} K ⁻¹ mol ⁻¹	$\{H_s(T)-H^{\circ}(0)\}/T$ cal _{th} K ⁻¹ mol ⁻¹	$\{H_s(T)-H^{\circ}(0)\}$ cal _{th} mol ⁻¹	S_s cal _{th} K ⁻¹ mol ⁻¹	C_s cal _{th} K ⁻¹ mol ⁻¹
2-Aminopropane (crystals)—continued					
25	0.557	1.286	32.153	1.843	3.694
30	0.834	1.776	53.27	2.610	4.734
35	1.145	2.267	79.35	3.413	5.688
40	1.480	2.749	109.97	4.229	6.538
45	1.830	3.213	144.57	5.043	7.291
50	2.192	3.656	182.79	5.848	7.989
60	2.933	4.485	269.11	7.418	9.254
70	3.682	5.248	367.3	8.931	10.369
80	4.430	5.954	476.3	10.384	11.424
90	5.170	6.620	595.7	11.790	12.455
100	5.900	7.251	725.1	13.152	13.415
110	6.620	7.856	864.2	14.476	14.403
120	7.329	8.443	1013.1	15.772	15.392
130	8.027	9.017	1172.2	17.045	16.428
140	8.716	9.585	1341.8	18.301	17.516
150	9.397	10.152	1522.8	19.549	18.697
160	10.071	10.727	1716.3	20.798	20.034
170	10.739	11.320	1924.4	22.059	21.639
177.99	11.270	11.812	2102.4	23.082	22.974
2-Aminopropane (liquid)					
177.99	11.27	21.64	3853	32.91	34.95
180	11.52	21.79	3923	33.31	35.09
190	12.71	22.51	4277	35.22	35.74
200	13.88	23.19	4637	37.07	36.30
210	15.03	23.82	5003	38.85	36.78
220	16.15	24.42	5373	40.57	37.19
230	17.25	24.98	5747	42.23	37.53
240	18.33	25.51	6123	43.84	37.80
250	19.38	26.01	6503	45.39	38.04
260	20.40	26.48	6884	46.88	38.26
270	21.41	26.92	7268	48.33	38.48
273.15	21.73	27.05	7389	48.78	38.55
280	22.40	27.33	7654	49.73	38.70
290	23.37	27.73	8042	51.10	38.94
298.15	24.14	28.04	8360	52.18	39.16
300	24.31	28.11	8433	52.42	39.21
310	25.24	28.47	8826	53.71	39.50
320	26.15	28.82	9223	54.97	39.82
2-Methyl-2-aminopropane (crystals III)					
10	0.050	0.149	1.49	0.198	0.588
12	0.085	0.253	3.03	0.339	0.979
14	0.134	0.391	5.47	0.525	1.463
16	0.197	0.558	8.92	0.755	1.996
18	0.274	0.748	13.47	1.022	2.554
20	0.363	0.957	19.14	1.320	3.119
25	0.637	1.530	38.24	2.167	4.510
30	0.969	2.133	63.98	3.102	5.756
35	1.343	2.730	95.54	4.073	6.844
40	1.745	3.304	132.16	5.050	7.779
45	2.166	3.847	173.11	6.013	8.586
50	2.598	4.359	217.96	6.958	9.346
60	3.478	5.309	318.54	8.788	10.787

TABLE 5—Continued

T K	$-\{G_s(T)-H^\circ(0)\}/T$ cal _{th} K ⁻¹ mol ⁻¹	$\{H_s(T)-H^\circ(0)\}/T$ cal _{th} K ⁻¹ mol ⁻¹	$\{H_s(T)-H^\circ(0)\}$ cal _{th} mol ⁻¹	S_s cal _{th} K ⁻¹ mol ⁻¹	C_s cal _{th} K ⁻¹ mol ⁻¹
2-Methyl-2-aminopropane (crystals III)—continued					
70	4.364	6.196	433.7	10.560	12.260
80	5.248	7.059	564.7	12.307	13.997
90	6.130	7.934	714.0	14.063	15.879
91.30	6.244	8.049	734.8	14.293	16.138
2-Methyl-2-aminopropane (crystals II)					
91.30	6.244	8.346	761.9	14.590	14.364
100	7.029	8.904	890.4	15.933	15.178
110	7.907	9.525	1047.7	17.432	16.313
120	8.762	10.140	1216.7	18.902	17.495
130	9.598	10.752	1397.7	20.349	18.690
140	10.417	11.362	1590.6	21.779	19.904
150	11.222	11.972	1795.8	23.194	21.129
160	12.014	12.584	2013.3	24.597	22.399
170	12.795	13.200	2243.9	25.995	23.734
180	13.567	13.826	2488.6	27.393	25.231
190	14.332	14.471	2749.6	28.803	26.999
200	15.091	15.148	3029.5	30.239	29.070
202.27	15.263	15.307	3096.1	30.570	29.584
2-Methyl-2-aminopropane (crystals I)					
202.27	15.26	22.46	4543	37.72	39.94
206.20	15.70	22.79	4699	38.49	40.24
2-Methyl-2-aminopropane (liquid)					
206.20	15.70	23.81	4910	39.51	42.30
220	17.28	25.00	5501	42.28	43.23
230	18.41	25.81	5936	44.22	43.74
240	19.52	26.57	6376	46.09	44.13
250	20.62	27.28	6819	47.90	44.46
260	21.71	27.94	7265	49.65	44.73
270	22.77	28.57	7714	51.34	44.99
273.15	23.10	28.76	7855	51.86	45.08
280	23.82	29.16	8165	52.98	45.27
290	24.85	29.72	8619	54.57	45.57
298.15	25.68	30.16	8992	55.84	45.82
300	25.87	30.25	9076	56.12	45.88
310	26.87	30.76	9537	57.63	46.25
320	27.86	31.25	10002	59.11	46.68
330	28.82	31.73	10471	60.55	47.14
340	29.78	32.19	10945	61.97	47.62

ENTROPY OF THE VAPOR

To calculate the entropies of the four compounds in the ideal gas state at 298.15 K (table 7), values of the enthalpies of vaporization and vapor pressure were required. For 1-aminopropane, 2-aminopropane, and 2-methyl-2-aminopropane, the enthalpy of vaporization was calculated by means of the Clapeyron equation and the Cox vapor-pressure equation given by Osborn and Douslin⁽¹²⁾ and estimated values of the second virial coefficient. The entropy of compression was obtained from these

FIGURE 1. Deviation of heat capacity measurements of Lebedev *et al.*⁽¹¹⁾ and this research.TABLE 6. Comparison of several properties of acrylonitrile ($\text{cal}_{\text{th}} = 4.184 \text{ J}$)

Property	This research	Lebedev <i>et al.</i> ⁽¹¹⁾
$T(\text{transition})/\text{K}$	162.5	162.8
$T(\text{triple point})/\text{K}$	189.63	190.10
$\Delta H(\text{transition})/\text{cal}_{\text{th}} \text{ mol}^{-1}$	284	390
$\Delta H(\text{fusion})/\text{cal}_{\text{th}} \text{ mol}^{-1}$	1489	1250
$\{H(60 \text{ K}) - H(0)\}/\text{cal}_{\text{th}} \text{ mol}^{-1}$	227	240 (extrapolated)
$\{S(60 \text{ K}) - S(0)\}/\text{cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1}$	5.80	6.59 (extrapolated)
$\{H(300 \text{ K}) - H(60 \text{ K})\}/\text{cal}_{\text{th}} \text{ mol}^{-1}$	6477	6470
$\{S(300 \text{ K}) - S(60 \text{ K})\}/\text{cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1}$	37.12	37.21

same vapor pressures. For acrylonitrile, the enthalpy of vaporization was derived from the vapor pressures of Davis and Wiedeman (DW)⁽¹³⁾ and D. R. Stull.⁽¹⁴⁾ DW report a value of $7800 \text{ cal}_{\text{th}} \text{ mol}^{-1}$ (273 to 353 K) as calculated from the slope of their vapor pressure–temperature curve by means of the Clausius–Clapeyron equation. If the assumption is made that the enthalpy of vaporization quoted is for the average temperature, 313 K, it can be corrected to 298.15 K to yield $8.00 \text{ kcal}_{\text{th}} \text{ mol}^{-1}$. A Cox equation was fitted to the data of Stull,⁽¹⁴⁾ and $7.99 \text{ kcal}_{\text{th}} \text{ mol}^{-1}$ was obtained by use of the Clapeyron equation with an estimated value of the second virial coefficient. An uncertainty of $\pm 0.10 \text{ kcal}_{\text{th}} \text{ mol}^{-1}$ was assigned to the enthalpy of vaporization, notwithstanding the fortuitous agreement.

CHEMICAL THERMODYNAMIC PROPERTIES OF THE VAPOR

For the three aminopropanes, Scott⁽¹⁵⁾ has computed the chemical thermodynamic properties of the vapor for selected temperatures between 200 and 1000 K with contributions of internal rotation selected to give agreement with the calorimetric

TABLE 7. Conversion of molar entropy values to the ideal gas state at 298.15 K
($\text{cal}_{\text{th}} = 4.184 \text{ J}$; atm = 101.325 kPa)

Compound	$S_g(l)$ $\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}$	ΔH_{vap} $\text{kcal}_{\text{th}} \text{mol}^{-1}$	ΔS_{vap} $\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}$	$(S_{\text{ideal}} - S_g)^a$ $\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}$	$R \ln(p/\text{atm})$ $\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}$	$S^{\circ}(298.15 \text{ K})$ $\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}$
Acrylonitrile	42.76 ± 0.09	8.00 ± 0.10	26.83 ± 0.3	0.07	-3.79 ± 0.02	65.87 ± 0.4
1-Aminopropane	54.36 ± 0.11	7.49 ± 0.05	25.12 ± 0.17	0.11	-1.74 ± 0.01	77.85 ± 0.21
2-Aminopropane	52.18 ± 0.10	6.81 ± 0.05	22.84 ± 0.17	0.16	-0.52 ± 0.00	74.66 ± 0.20
2-Methyl-2-aminopropane	55.84 ± 0.11	7.10 ± 0.05	23.81 ± 0.17	0.12	-1.44 ± 0.01	78.33 ± 0.21

^a Estimated.

TABLE 8. Chemical thermodynamic properties of acrylonitrile in the ideal gas state ($\text{cal}_{\text{th}} = 4.184 \text{ J}$)

T K	$-\{G^{\circ}(T) - H^{\circ}(0)\}/T$ $\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}$	$\{H^{\circ}(T) - H^{\circ}(0)\}/T$ $\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}$	S° $\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}$	C_p° $\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}$	$\Delta H_f^{\circ a}$ $\text{kcal}_{\text{th}} \text{mol}^{-1}$	$\Delta G_f^{\circ a}$ $\text{kcal}_{\text{th}} \text{mol}^{-1}$	$\log_{10} K_f^{\circ a}$
0	0	0	0	0	45.4	45.4	∞
200	50.68	9.64	60.33	12.32	44.3	45.6	-49.8
298.15	54.79	11.02	65.80	15.34	43.9	46.3	-33.9
300	54.86	11.04	65.90	15.40	43.9	46.3	-33.7
400	58.23	12.51	70.74	18.37	43.4	47.1	-25.8
500	61.18	13.95	75.13	20.93	43.0	48.1	-21.0
600	63.84	15.29	79.13	23.07	42.7	49.2	-17.9
700	66.30	16.54	82.84	24.87	42.4	50.3	-15.7
800	68.58	17.68	86.26	26.41	42.2	51.4	-14.0
900	70.72	18.72	89.44	27.72	42.0	52.6	-12.8
1000	72.75	19.68	92.43	28.86	41.8	53.7	-11.7

^a The standard enthalpy, Gibbs energy, and common logarithm of the equilibrium constant of formation by the reaction:
 $3 \text{ C (c, graphite)} + (3/2) \text{ H}_2(\text{g}) + (1/2) \text{ N}_2(\text{g}) = \text{C}_3\text{H}_3\text{N}(\text{g})$.

entropy values of this research. For acrylonitrile, Halverson, Stamm, and Whalen (HSW)⁽¹⁶⁾ have computed thermodynamic functions of the vapor from a vibrational assignment obtained from their studies and interpretation of the molecular spectra. The thermodynamic functions were recomputed with a slightly revised vibrational assignment based on the molecular spectra reported by HSW and those reported earlier by Thompson and Torkington.⁽¹⁷⁾ The 15 fundamental wavenumbers were taken to be 3124, 3078, 3042, 2239, 1616, 1416, 1282, 1096, 1033, 963, 869, 683, 566, 280, and 220 cm^{-1} . Ten of these wavenumbers are from the assignment of HSW. However, the doublet, 954 to 972 cm^{-1} , that they assigned to two separate modes is here interpreted as Fermi resonance of a single fundamental at about 963 cm^{-1} with a sum-combination. The other fundamental was taken to be 1033 cm^{-1} , observed as a weak infrared band. The liquid-state value of 566 cm^{-1} was used in the absence of a vapor-state value, since vapor-liquid shifts usually are small in the region of the spectrum involved. The two CCN bending wavenumbers have liquid-state values of 240 and 305 cm^{-1} . By analogy with the vapor-liquid shift observed for acetonitrile by Crowder and Cook,⁽¹⁸⁾ the vapor-state values would be expected to be about 16 cm^{-1} lower. They were estimated from the sum-combinations:

$$[220a''] + 566a' = 786A'' \quad \text{and} \quad [280a'] + 683a'' = 963A''.$$

The infrared band at 786 cm^{-1} does not have the C-type contour predicted by simple theory for the above interpretation, but a variety of effects not included in the simple theory can perturb band contours. Values of moments of inertia used in computing the thermodynamic functions were taken from the microwave studies of Costain and Stoicheff.⁽¹⁹⁾

Values of the thermodynamic functions for selected temperatures between 200 and 1000 K are given in columns 2 to 5 of table 8. The agreement between the observed (65.9 ± 0.4) and calculated ($65.8 \text{ cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1}$) values of the entropy at 298.15 K is well within experimental error.

Davis and Wiedeman⁽¹³⁾ have reported the enthalpy of combustion of the liquid, $-(420.5 \pm 0.7) \text{ kcal}_{\text{th}} \text{ mol}^{-1}$. This value, the enthalpy of vaporization from table 7, and values of the enthalpy of formation of $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$ ⁽²⁰⁾ were used to calculate the enthalpy of formation of the vapor at 298.15 K, $(43.9 \pm 0.7 \text{ kcal}_{\text{th}} \text{ mol}^{-1})$. This value of the enthalpy of formation, values of the thermodynamic functions of acrylonitrile from table 8, and values of the thermodynamic functions of C(c, graphite), $\text{H}_2(\text{g})$, and $\text{N}_2(\text{g})$ from the JANAF tables⁽²¹⁾ were used to compute the enthalpy, Gibbs energy, and logarithm of the equilibrium constant of formation for the same selected temperatures as for the thermodynamic functions. The results are given in columns 6 to 8 of table 8.

The thermodynamic functions of acrylonitrile were calculated with the rigid-rotator, harmonic-oscillator approximation and do not include the effects of anharmonicity and other effects neglected in this simple treatment. Also, the two thermodynamically important C—C—N bending wavenumbers were inferred from sum-combinations and not directly observed for the vapor. Moreover, the experimental uncertainties in the enthalpies of formation and vaporization are rather large. As a reminder that the entries in columns 6 to 8 of table 8, are not as reliable as values

based on more complete and accurate spectroscopic and calorimetric data, they are given to one less than the customary number of decimal places.

The authors are indebted to Dr D. W. Scott for the reassignment of the fundamental wavenumbers for acrylonitrile and for his many helpful suggestions and advice. The assistance of Mr David Bacon with some of the experimental measurements is gratefully acknowledged.

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