Chemical Thermodynamic Properties of Aniline

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A COMPLETE VIBRATIONAL ASSIGNMENT for aniline, reported by Evans (*5*), allows calculation of the thermodynamic functions of the ideal gas. The low temperature heat capacity, heat of vaporization, and heat of combustion of the condensed phases are reported here and combined with the ideal gas values to give a consistent table of the chemical thermodynamic properties.

LOW TEMPERATURE HEAT CAPACITY AND HEAT OF FUSION

The low temperature heat capacity and heat of fusion were measured using previously described equipment and techniques (*7, 9, 17, 18*). The experimental heat capacities are given in chronological order in Table I. The temperature rises may be inferred from the average temperatures listed.

Table I. Experimental Heat Capacity of Aniline

T, °K.	C_p, Cal. Mole^{-1} °K.$^{-1}$	T, °K.	C_p, Cal. Mole^{-1} °K.$^{-1}$	T, °K.	C_p, Cal. Mole^{-1} °K.$^{-1}$
Series I					
		171.10	19.42	46.55	7.141
13.49	0.797	176.85	20.04	51.37	7.838
15.49	1.119	182.48	20.69	56.78	8.522
17.51	1.518	187.98	21.31	62.75	9.200
19.57	1.971	193.38	21.97	68.76	9.695
21.97	2.490	198.68	22.56	74.37	10.25
24.96	3.134	203.87	23.18	80.34	10.79
28.14	3.894	208.98	23.79	86.85	11.42
31.16	4.457	214.00	24.42	150.09	17.18
34.38	5.138	218.93	25.08	154.85	17.56
37.94	5.776	223.78	25.61	159.77	18.12
49.97	7.592	228.55	26.28	164.61	18.65
35.14	5.247	237.84	27.49	169.89	19.24
38.21	5.796	242.39	28.11	175.65	19.95
42.14	6.444	247.32	28.61	181.29	20.54
46.49	7.177	252.63	29.40	186.81	21.25
56.15	8.409	257.83	30.25	192.22	21.82
61.35	8.957	270.22	44.74	197.53	22.46
67.51	9.624	274.85	44.86	202.74	23.04
73.86	10.16	279.46	45.06	207.86	23.61
79.80	10.76	284.05	45.25	212.89	24.29
85.40	11.31	288.63	45.27	217.83	24.87
90.75	11.77	293.19	45.51	222.70	25.48
95.89	12.17	297.72	45.86	227.48	26.17
100.86	12.53	302.24	45.95	236.78	27.27
105.69	12.96	306.73	46.16	241.34	28.06
110.37	13.38	Series II		245.84	28.52
114.93	13.77	13.67	0.827	250.28	28.96
119.37	14.21	15.79	1.155	255.04	29.86
123.71	14.56	17.83	1.591	272.59	44.84
128.64	14.99	20.21	2.117	278.44	45.16
134.15	15.57	22.82	2.710	284.27	45.09
139.51	16.06	25.66	3.272	290.09	45.40
144.75	16.63	28.59	3.963	295.88	45.60
149.88	17.14	31.54	4.524	301.63	45.87
154.90	17.64	34.73	5.183	307.36	46.10
159.82	18.14	38.26	5.808	313.06	46.29
165.22	18.76	42.19	6.502		

In the temperature range 100° to 300° K., the data are in excellent agreement with values determined by Parks, Huffman, and Barmore (*13*). Below 100° there are no previous measurements. There was no evidence of any transition or unusual behavior in the solid state, the heat capacity curve showing the usual sigmoid shape except for premelting behavior a few degrees below the melting point. Smoothed heat capacities for the solid were derived from a large scale plot of the data and were extrapolated to the melting point, A combination of a Debye function ($\Theta = 110$) in three degrees of freedom and an Einstein function ($\Theta = 152$) in three degrees of freedom gave a good fit over the range 13° to 27° K. and was used to extrapolate to 0° K. The ice point was taken as 273.15° K. and the molecular weight of aniline as 93.130.

The melting point was derived by the usual extrapolation of a plot of the equilibrium temperature *vs.* the reciprocal of the fraction melted as 267.13° ± 0.05° K. The slope of the plot indicated 0.02 mole % of liquid-soluble solid-insoluble impurity. Three determinations of the heat of fusion were in good agreement at 2.519 ± 0.001 kcal. mole^{-1}, compared to 2.523 kcal. mole^{-1} measured by Parks, Huffman, and Barmore (*13*). The liquid heat capacities of Table I and the higher temperature data of Hough, Mason, and Sage (*10*) could be reasonable well represented by C_p (cal. mole^{-1} ° K.$^{-1}$) = 33.71 + 0.0409 T and smoothed liquid heat capacities were calculated from this equation.

Smoothed thermodynamic functions were calculated using an electronic computer which fitted the smoothed heat capacities over short ranges of temperature with quadratic equations and integrated over the middle portion of the range. Results are given in Table II for the range below room temperature and in Table VI above room temperature.

Table II. Smoothed Thermodynamic Functions of Aniline

Cal. mole^{-1} ° K.$^{-1}$

T, ° K.	C°_p	S°_T	$\frac{(H^\circ_T - H^\circ_0)}{T}$	$-\frac{(F^\circ_T - H^\circ_0)}{T}$
15	1.056	0.373	0.277	0.096
20	2.036	0.808	0.591	0.216
25	3.147	1.379	0.989	0.390
30	4.223	2.049	1.440	0.609
35	5.216	2.776	1.909	0.867
40	6.123	3.532	2.380	1.152
50	7.633	5.069	3.287	1.782
60	8.824	6.568	4.112	2.455
70	9.852	8.007	4.861	3.147
80	10.78	9.384	5.543	3.841
90	11.66	10.705	6.174	4.531
100	12.50	11.977	6.765	5.212
120	14.22	14.407	7.863	6.544
140	16.13	16.741	8.906	7.835
160	18.20	19.028	9.937	9.091
180	20.40	21.297	10.976	10.321
200	22.74	23.566	12.034	11.532
220	25.20	25.848	13.118	12.730
240	27.78	28.151	14.232	13.919
260	30.51	30.481	15.378	15.103
267.13(c)	31.53	31.320	15.795	15.525
267.13(l)	44.63	40.750	25.225	15.525
280	45.16	42.862	26.129	16.733
298.15	45.90	45.721	27.310	18.411
300	45.98	46.006	27.425	18.581

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HEAT OF VAPORIZATION

The heat of vaporization at 60° C. was measured using a calorimeter which was checked with benzene and gave good performance (*8*). The results for aniline are given in Table III. The deviation from ideality was checked using the Berthelot equation and found to be negligibly small. The column ΔH_v at 60° C. includes corrections to exactly 60° by means of heat capacity data and correction for the vaporization to fill the space left by vaporized sample.

The spectroscopic and molecular data of Evans (*5*) were used to calculate thermodynamic functions of the ideal gas. Free energy functions based on 298.15° K. were derived from these calculated functions. The third-law entropy and the heat capacity equation given above were used to obtain corresponding free energy functions based on 298.15° K. for the liquid.

These free energy functions and vapor pressures from the literature (*2, 6, 11, 12, 14, 15*) were then used to calculate the heat of vaporization at 298.15° K. The most nearly constant heat of vaporization at 298.15° K. was judged to be obtained if the barrier to internal rotation was lowered slightly to 3.43 kcal. mole^{-1}. The selected result, 13.325 kcal. mole^{-1}, is compared with representative individual points in Figure 1. With the revised barrier, the calorimetric value calculated to 298.15° K. is 13.328 kcal. mole^{-1}, in excellent agreement, and confirming the selected result from free energy functions and vapor pressure data.

Smoothed values of the vapor pressure and heat of vaporization were calculated from the thermodynamic functions for liquid and gas states and a heat of vaporization at 298.15° K. of 13.325 kcal. mole^{-1} and are given in Table IV. The calculated boiling point at 760 mm. is 457.55° K., in excellent agreement with selected values listed by Timmermans (*20*).

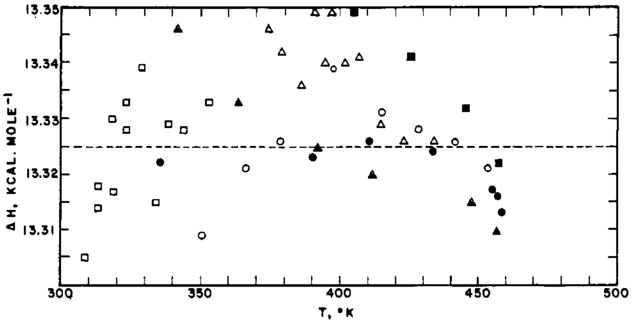

Figure 1. Heat of vaporization of aniline at 25° C.

Calculated from vapor pressure data at temperatures shown by third law methods

○ Ramsay and Young (*14*)
□ Rock (*15*)
● McDonald, Shrader, and Stull (*12*)
▲ Kahlbaum (*11*)
▽ Garrick (*6*)
--- Selected value
■ Beckmann and Liesche (*2*)

Table III. Calorimetric Heat of Vaporization of Aniline

$t_{exp.}$, ° C.	Grams Vaporized	ΔH_v, Cal. Mole^{-1} Uncorr.	ΔH_v, Cal. Mole^{-1} At 60° C.
60.53	2.3941	12,653	12,664
61.23	2.4004	12,630	12,655
59.79	2.4179	12,651	12,647
60.29	2.4308	12,654	12,660
		Av.	12,656

Table IV. Calculated Vapor Pressures and Heats of Vaporization of Aniline

T, ° K.	t, ° C.	p, Mm.	ΔH_v, Cal. Mole^{-1}
304.70	31.55	1	13,195
314.77	41.62	2	13,000
325.74	52.59	4	12,791
341.77	68.62	10	12,496
355.26	82.11	20	12,255
370.17	97.02	40	11,998
392.56	119.41	100	11,627
412.05	138.90	200	11,319
434.20	161.05	400	10,983
457.55	184.40	760	10,643

HEAT OF COMBUSTION AND HEAT OF FORMATION

The calorimetric system and techniques for the heat of combustion have been described (*9, 16, 17*). The combustion bomb volume was 0.340 liter and was charged with 1 gram of water and 30 atm. of oxygen in all experiments. The temperature rise was measured with a Western Electric Type 14B thermistor with a temperature coefficient of 90 ohms ° C.$^{-1}$ Initial temperature was 24.0° C. and the temperature rise was 2.00° ± 0.02° C. The calorimetric system was calibrated with National Bureau of Standards benzoic acid 39 g, which under the above conditions has a heat of combustion of 6317.8 defined thermochemical calories per gram mass. The sample was ignited by electrically fusing a 0.004-inch platinum wire to which was tied a strip of Mylar film as a fuse. The ignition energy was small and assumed constant in all experiments. The energy equivalent of the system was 34.539 cal. ohm^{-1} with a standard deviation of 0.003 cal. ohm^{-1}.

The heat of combustion and carbon content of the Mylar film were measured in separate experiments as 5473.8 ± 0.9 cal. gram^{-1} under standard conditions and 62.304 ± 0.040% carbon. The hydrogen content was determined by standard analytical techniques as 4.18%, and the remainder was assumed to be oxygen.

The heat of combustion of aniline was measured by enclosing the sample in a bag of Mylar film. The sample

Table V. Heat of Combustion of Aniline

ΔT, Ohms	Mylar, Grams	q_{Total}, Cal.	q_{Mylar}, Cal.	q_{HNO_3}, Cal.	$q_{Washburn}$, Cal.	Sample Mass, Gram	$-\Delta E_c^\circ/M$, Cal. G.$^{-1}$
180.993	0.19302	6252.48	1057.38	10.51	3.64	0.59537	8702.1
178.742	0.13426	6174.70	735.49	10.74	3.40	0.62346	8701.6
180.056	0.18127	6220.11	993.02	10.74	3.62	0.59929	8698.2
179.986	0.16691	6217.69	914.35	11.25	3.60	0.60804	8697.6
179.832	0.14912	6212.37	816.89	10.89	3.60	0.61841	8701.3
178.852	0.33934	6178.50	1857.48	9.66	3.87	0.49518	8698.8
						Av.	8699.9
						Std. dev.	0.8

Table VI. Molal Chemical Thermodynamic Properties of Aniline Liquid

T, ° K.	C_p, Cal. Deg.$^{-1}$	S_T, Cal. Deg.$^{-1}$	$H_T - H_0$, Cal.	$-(F_T - H_0)/T$, Cal. Deg.$^{-1}$	ΔH_f, Kcal.	ΔF_f, Kcal.	$\log_{10} K_p$
298.15	45.90	45.72	8,143	18.41	+7.47	+35.68	−26.154
300	45.98	46.01	8,228	18.58	7.48	35.85	−26.116
350	48.03	53.25	10,578	23.03	7.77	40.56	−25.326
400	50.07	59.79	13,030	27.21	8.03	45.24	−24.723
450	52.12	65.81	15,585	31.18	8.28	49.86	−24.215
500	54.16	71.41	18,242	34.93	8.53	54.49	−23.817

Table VII. Molal Chemical Thermodynamic Properties of Aniline Ideal Gas

T, ° K.	C_p°, Cal. Deg.$^{-1}$	S_T°, Cal. Deg.$^{-1}$	$H_T^\circ - H_0^\circ$, Cal.	$-(F_T^\circ - H_0^\circ)/T$, Cal. Deg.$^{-1}$	ΔH_f°, Kcal.	ΔF_f°, Kcal.	$\log_{10} K_p$
298.15	25.91	76.28	4,349	61.69	+20.80	+39.90	−29.246
300	26.07	76.44	4,397	61.78	20.78	40.01	−29.148
350	30.28	80.78	5,807	64.19	20.12	43.36	−27.075
400	34.17	85.08	7,421	66.53	19.54	46.64	−25.482
450	37.68	89.31	9,218	68.83	19.03	50.10	−24.331
500	40.81	93.45	11,182	71.09	18.59	53.53	−23.398
600	46.09	101.37	15,536	75.48	17.88	60.59	−22.070
700	50.32	108.81	20,365	79.72	17.34	67.76	−21.156
800	53.79	115.76	25,575	83.79	16.95	74.97	−20.480
900	56.71	122.27	31,105	87.71	16.69	82.28	−19.979
1000	59.18	128.37	36,903	91.47	16.55	89.55	−19.571

mass was determined by direct weighing. The calorimeter equivalent for the aniline experiments was 34.545 cal. ohm^{-1}, which includes 6 grams of platinum not used in the calibration experiments. Washburn corrections were calculated by the method of Cox, Challoner, and Meetham (*4*). Combustion results are given in Table V. With atomic weights of C = 12.011, H = 1.008, and N = 14.008, the heat of combustion at constant volume is −810.22 ± 0.24 kcal. mole^{-1}, referring to the reaction:

$$C_6H_7N(liq) + \frac{31}{4}\,O_2(g) \rightarrow 6CO_2(g) + \frac{7}{2}\,H_2O(liq) + \frac{1}{2}\,N_2(g)$$

The heat of combustion at constant pressure is then $\Delta H^\circ_{c298}(liq) = -810.96 \pm 0.24$ kcal. mole^{-1}. The uncertainty is taken as twice the standard deviation. The result is in excellent agreement with −810.81 kcal. mole^{-1} from Anderson and Gilbert (*1*) as revised by Cole and Gilbert (*3*) and corrected to $C = 12.011$. Employing an average value of −810.90 and heats of formation of gaseous carbon dioxide and liquid water of −94.054 and −68.317 kcal. mole^{-1}, respectively, yields the heat of formation of liquid aniline as $\Delta H_{f298}(liq) = +7.47 \pm 0.20$ kcal. mole^{-1}. The standard heat of vaporization given above is used to derive $\Delta H^\circ_{f298}(g) = +20.80 \pm 0.21$ kcal. mole.$^{-1}$

CHEMICAL THERMODYNAMIC PROPERTIES

The foregoing experimental data and the spectroscopic and molecular data of Evans (*5*) with the revised barrier to internal rotation were used to calculate consistent tables of thermodynamic properties for the liquid and ideal gas states of aniline in Tables VI and VII. Reference states for the elements were taken from Stull and Sinke (*19*).

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