[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Heat Capacity of Mercury from 15 to 330°K. Thermodynamic Properties of Solid Liquid and Gas. Heat of Fusion and Vaporization[1]

BY R. H. BUSEY AND W. F. GIAUQUE

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The heat capacity of mercury has been measured from 15 to 330°K. The heat of fusion was found to be 548.6 cal. mole^{-1} at the m.p. The observations have been combined with available calorimetric and vapor pressure data at higher temperatures, and the Sackur–Tetrode equation, to determine the thermodynamic properties of solid, liquid and gaseous mercury. The entropy of liquid mercury at 298.16°K. was found to be 18.19 cal. deg.$^{-1}$ mole^{-1}. The heat of vaporization at the boiling point is 14,127 cal. mole^{-1}.

The change in the heat content of liquid mercury has recently been measured by Douglas, Ball and Ginnings.[2] Their measurements were made at 50° intervals between 0 and 450°. They have been used to calculate various thermodynamic quantities and by correlation of the results with available vapor pressure data, an estimate of gas imperfection, and the Sackur–Tetrode equation, they obtain a value for the entropy of liquid mercury. Their value of 18.12 cal. deg.$^{-1}$ mole^{-1} at 25° is 0.36 lower than one published by Pickard and Simon[3] and 0.22 cal. deg.$^{-1}$ mole^{-1} lower than a value which they obtain by recalculating the existing low temperature data which were also available to Pickard and Simon. We have recalculated the data used by Pickard and Simon[3] and agree with their original result. In remaking this calculation the entropy of fusion, 2.44 cal. deg.$^{-1}$ mole^{-1}, used by Pickard and Simon, was adopted for consistency although the available data indicate 2.38 as the value. Thus the two contradictory values were 18.12 (D., B. and G.) and 18.48 (P. and S.). Since the entropy of liquid mercury can be determined with an accuracy of a few hundredths of a cal. deg.$^{-1}$ mole^{-1} by means of present low temperature technique we decided to redetermine the value of this important quantity.

Apparatus.—The calorimetric apparatus and method were the same as those used recently for heat capacity measurements on nickel[4] except that the calorimeter was made from "18-8" stainless steel. It has been shown by Marshall, Epstein and Norton[5] that iron is soluble in mercury to less than one part in 10^8.

A gold resistance-thermometer heater of the type ordinarily used in this Laboratory was wound on the outside of the steel calorimeter. This is not a very good combination since strain is certain to develop in the thermometer because of the difference in the coefficients of expansion. However, the resistance thermometer was compared with the standard thermocouple almost continuously except when heat was being introduced to the calorimeter or to its surrounding heavy copper-lead cylinder. Thus there were two good equilibrium calibrations for each heat capacity measurement. No sudden changes in resistance were found and any resistance changes due to strain should cause no error. All resistance change corrections used in correcting for the heat leak were exceptionally smooth. The thermocouple W-26 was compared directly with the melting (13.92°K.) and boiling (20.36°K.) points of hydrogen and the melting (63.15°K.) and boiling (77.34°K.) points of nitrogen as well as the melting point (234.29°K.) of mercury. The hydrogen and nitrogen were solidified in the space surrounding the calorimeter.

The standard thermocouple read 0.01° high at each point except the melting point of mercury where it read 0.03° high. 0°C. was taken as 273.16°K. and one calorie was defined as 4.1840 absolute joules.

The calorimeter was made from a seamless tube which had a diameter of 4.5 cm. and was 11 cm. long. The wall thickness was 0.08 cm. and the ends were 0.10 cm. thick. The ends were welded into the tube in a helium arc. The heat capacity of the empty calorimeter was measured over the entire range as usual.

Mercury Sample.—The mercury was Mallinckrodt analytical reagent which was stated to have a maximum total impurity of 0.0006%. It melted very sharply. The absence of any detectable calorimetric premelting effect in the region immediately below the melting point indicated a very high purity with respect to any liquid-soluble solid-insoluble impurity. The weight of the sample used was 2189.31 g. *in vacuo* and the atomic weight was taken as 200.61.

The Heat Capacity Measurements.—The heat capacity observations are recorded in Table I. The observations were made continuously in the sense that each run commenced where the previous one ended so that there was no possibility of overlooking a transition. Since there were no complicating factors in the heat capacity measurements the temperature rise for each run is not given but

TABLE I

HEAT CAPACITY (IN CAL. DEG.$^{-1}$ MOLE^{-1}) OF MERCURY

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
Series 1		Series 4 (contd.)		Series 6 (contd.)	
197.57	6.505	304.99	6.679	62.27	5.179
203.71	6.548	311.35	6.662	67.89	5.315
209.92	6.599	317.77	6.652	73.21	5.430
216.42	6.654	Series 5		78.68	5.514
222.94	6.712	222.46	6.701	84.48	5.603
229.26	6.761	229.09	6.764	90.64	5.685
249.35	6.770	239.02	6.814	97.08	5.764
255.80	6.777	Series 6		103.84	5.847
Series 2		14.90	1.779	110.84	5.904
288.00	6.709	16.28	1.977	117.69	5.964
Series 3		17.90	2.184	124.52	6.015
325.89	6.633	19.84	2.438	131.52	6.068
Series 4		22.02	2.714	138.81	6.116
242.17	6.795	24.31	2.962	146.32	6.163
248.18	6.786	27.04	3.236	161.89	6.266
254.32	6.764	30.20	3.541	170.04	6.302
261.79	6.746	33.54	3.844	178.00	6.368
268.04	6.740	37.35	4.120	186.27	6.421
274.22	6.730	41.60	4.378	194.44	6.479
280.50	6.726	46.20	4.602	202.89	6.540
286.50	6.713	51.16	4.808	211.39	6.608
293.03	6.697	56.53	5.005	219.79	6.676
298.49	6.685			228.13	6.751
299.48	6.684			241.86	6.802

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[1] This work was supported in part by the Office of Naval Research, United States Navy.

[2] T. B. Douglas, A. F. Ball and D. F. Ginnings, *J. Research Natl. Bur. Standards*, **46**, 334 (1951).

[3] L. Pickard and F. E. Simon, *Proc. Phys. Soc.*, **61**, 1 (1948).

[4] R. H. Busey and W. F. Giauque, THIS JOURNAL, **74**, 3157 (1952).

[5] A. L. Marshall L. F. Epstein and F. J. Norton, *ibid.*, **72**, 3514 (1950).

may be estimated from the spacing. Values taken from a smooth curve through the data should be accurate to 0.1% above 35°, at 20°K. may be 1% and at 15° may be 3% due to decreasing sensitivity of the resistance thermometer. The entropy increase from 0 to 330°K. should be accurate to 0.1% since any high or low results due to lack of thermometer sensitivity would largely compensate in the entropy calculation.

This follows from the fact that the over-all temperature interval is known to about 0.01%.

Heat of Fusion of Mercury.—The heat of fusion of mercury was measured in the usual manner of starting below and ending somewhat above the melting point with appropriate corrections. The values are given in Table II where they are compared with previous values.

TABLE II

HEAT OF FUSION (IN CAL. DEG.$^{-1}$ MOLE^{-1}) OF MERCURY (M.P. 234.29°K.)

T_1	T_2	ΔH	Series
232.39	246.38	548.5	1
232.83	236.09	548.7	5
232.28	237.88	548.6	6
	Average	548.6	
	Pollitzer[6]	554.5	
	Bridgman[7]	560	

Thermodynamic Functions.—Values of the several thermodynamic functions are given in Table III.

In computing the several properties the data of Simon and Pickard[3] were used below 15°K., the results of the present research were given 100% weight between 15 and 330°K. Above this temperature the results were joined as smoothly as possible with the data of Douglas, Ball and Ginnings.[2] These authors estimate that their error may be several tenths of a per cent. at ordinary temperature, but is 0.1% above 100°. The agreement of the heat content data of D., B. and G., $H_t - H_{0^\circ}$ at values of t for 50° intervals to 450°, with the values in Table III is as follows: -0.50, -0.19, -0.07, -0.04, $+0.02$, $+0.05$, $+0.02$, 0.00 and 0.00%.

Since the standard state for liquid or solid mercury corresponds to the phase under a pressure of one atmosphere the amount $-V\alpha(1 - P)|_{0^\circ}^{t}$ should be added to the entropy difference along the saturation curve. The quantity $V(1 - T\alpha)(1 - P)|_{0^\circ}^{t}$ should be added to $H|_{0^\circ}^{t}$ to obtain $H^\circ|_{0^\circ}^{t}$ where α is the coefficient of expansion, $1/V\,(\partial V/\partial T)_P$, and P is the vapor pressure.

The entropy of liquid mercury at 298.16°K. was found to be 18.19 cal. deg.$^{-1}$ mole^{-1} which is 0.07 cal. deg.$^{-1}$ mole^{-1} above the value of Douglas, Ball and Ginnings.[2] It appears that the high value of 18.48 reported by Pickard and Simon[3] must be due to experimental error in the data which they utilized.

TABLE III

THERMODYNAMIC FUNCTIONS OF MERCURY

T	C_p°	S^0	$\frac{H^\circ - H_0^\circ}{T}$	$\frac{F^\circ - H_0^\circ}{T}$
15	1.754	1.251	0.719	0.532
20	2.462	1.856	1.069	0.787
25	3.035	2.469	1.407	1.062
30	3.531	3.067	1.722	1.345
35	3.951	3.645	2.013	1.632
40	4.288	4.196	2.278	1.918
45	4.547	4.716	2.516	2.200
50	4.762	5.207	2.730	2.477
60	5.119	6.110	3.102	3.008
70	5.358	6.918	3.408	3.510
80	5.536	7.645	3.664	3.981
90	5.678	8.306	3.881	4.425
100	5.797	8.911	4.067	4.844
110	5.896	9.468	4.229	5.239
120	5.983	9.985	4.372	5.613
130	6.057	10.467	4.499	5.968
140	6.123	10.919	4.614	6.305
150	6.185	11.343	4.716	6.627
160	6.245	11.744	4.810	6.934
170	6.309	12.124	4.895	7.229
180	6.377	12.486	4.975	7.511
190	6.447	12.832	5.050	7.782
200	6.519	13.164	5.121	8.043
210	6.597	13.484	5.190	8.294
220	6.679	13.793	5.256	8.537
230	6.769	14.092	5.320	8.772
234.29(s)	6.808	14.217	5.346	8.871
234.29(1)	6.806	16.559	7.688	8.871
240	6.795	16.723	7.667	9.056
250	6.776	17.000	7.632	9.368
260	6.758	17.265	7.599	9.666
270	6.739	17.520	7.567	9.953
280	6.721	17.765	7.537	10.228
290	6.702	18.001	7.509	10.492
298.16	6.688	18.187	7.486	10.701
300	6.684	18.228	7.482	10.746
350	6.598	19.251	7.362	11.889
400	6.539	20.128	7.262	12.866
450	6.502	20.896	7.180	13.716
500	6.484	21.580	7.111	14.469
550	6.481	22.198	7.054	15.144
600	6.488	22.762	7.006	15.756
650	6.505	23.281	6.967	16.314
700	6.534	23.763	6.935	16.828
750	6.576	24.215	6.909	17.306

The Heat of Vaporization of Mercury.—The vapor pressure of mercury has been measured by a number of observers but of these the data of Smith and Menzies[8,9] and Beattie, Blaisdell and Kaminsky[10] are so outstanding that they alone will be considered. Douglas, Ball and Ginnings[2] have compared the data of various other observers and given references. They have also given temperature corrections to be applied to the 1927 temperature scale used by Menzies.[9]

Apparently, essentially nothing is known concerning the gas imperfection of mercury. Douglas, Ball and Ginnings have in effect assumed a second virial coefficient, based on a three constant equation derived from rather uncertain stability data

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(6) F. Pollitzer, *Z. Elektrochem.*, **17**, 5 (1911).

(7) P. W. Bridgman, *Proc. Am. Acad. Sci.*, **47**, 347 (1911).

(8) A. Smith and A. W. C. Menzies, THIS JOURNAL, **32**, 1434 (1910).

(9) A. W. C. Menzies, *Z. physik. Chem.*, **130**, 90 (1927).

(10) J. A. Beattie, B. E. Blaisdell and J. Kaminsky, *Proc. Am. Acad. Arts Sci.*, **71**, 361, 375 (1937).

for diatomic mercury gas, and combined the various results to obtain the best over-all fit for the heat of dissociation of Hg_2 and the entropy of the liquid.

The present work has the advantage of a reliable value for the entropy of liquid mercury. D., B. and G. point out that they could not use Berthelot's equation to estimate gas imperfection, because the critical constants for mercury are unknown. However, Berthelot's equation can be reduced to a simpler form involving one undetermined constant without appreciable loss of accuracy in the present case.

$$PV = RT + \frac{9R\,T_c}{128\,P_c}\left(1 - \frac{6T_c^2}{T^2}\right)P \qquad (1)$$

$$= RT + BP \qquad (2)$$

The term $6\,T^2_c/T^2$ is relatively large compared to 1 near the boiling point of a wide variety of gases. If the 1 is neglected, we may write

$$PV = RT + (bP/T^2) \qquad (3)$$

We estimate that if the constant b is evaluated near the boiling point, the expression will represent a B consistent with Berthelot's equation to about 2% along the vapor pressure curve at several atmospheres above the boiling point. At lower temperatures the 1 becomes even more negligible compared to $6\,T^2_c/T^2$. Moreover, the P decreases so rapidly below the boiling point that the gas imperfection becomes of minor importance.

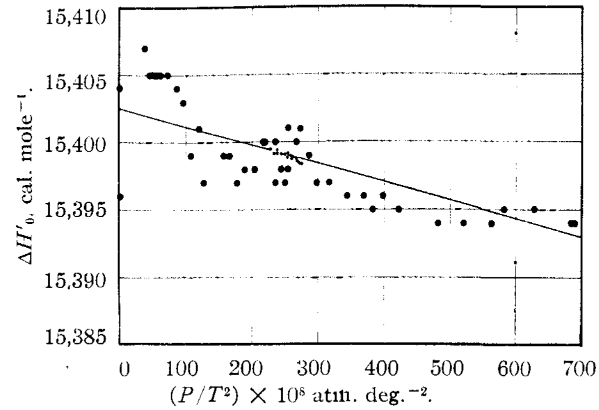

Fig. 1.—Heat of vaporization and gas imperfection of mercury: ●, data of Smith and Menzies; ·, data of Beattie, Blaisdale and Kaminsky.

In the present case one might wonder if the specific association to Hg_2 might not invalidate the use of $b/T^2 = B$. A simple way to show that this is not the case is to use the estimated B values which D., B. and G. have tabulated. They should have the right form for an imperfection based on such an association. We find the following correspondence based on const.$/T^2 = B$ cm.^{3}:

t, °C.	100	200	300	400	500
$-B_{\text{D.B.G.}}$	197	118	81	60	46
Const.$/T^2$	197	122	83	60	46

When $PV = RT + BP$, it may be shown[11] that the fugacity f is represented by

$$\ln\frac{f}{p} = \frac{BP}{RT} = \frac{bP}{RT^3} \qquad (4)$$

The quantity $(F^\circ - H^\circ_0)/T$ for ideal mercury vapor may be calculated from the Sackur–Tetrode equation

$$-\frac{F^\circ - H^\circ_0}{T} = \frac{3}{2}R\ln M + \frac{5}{2}R\ln T - 7.2819 \qquad (5)$$

$$= 11.4392\log T + 8.5203 \text{ cal. deg.}^{-1}\text{ mole}^{-1} \qquad (6)$$

We have used the same natural constants as D.. B. and G. in equations 5 and 6.

$$Hg_{(l)} = Hg_{(g)}$$

$$\frac{\Delta F^\circ}{T} = -R\ln\frac{f}{a_{(l)}} = -R\ln P - \frac{b'P}{T^3} - \frac{V(1-P)}{T} \qquad (7)$$

$a_{(l)}$ refers to the activity of liquid mercury under the saturation pressure.

The term $-V(1 - P)/T$ is required to correct for the change in free energy of liquid mercury when the pressure is increased from the vapor pressure P to 1 atmosphere, which is used as the standard state, $a = 1$, of thermodynamics for condensed phases.

A preliminary calculation of $\Delta H'_0$ − (= ΔH°_0 approx.) was made ignoring the term $b'P/T^3$. Values of $\Delta H'_0$ were plotted as ordinates against P/T^2. The axial intercept of a straight line through the data is ΔH°_0 and the slope is b'. The graph is shown in Fig. 1, where b' is taken as -1.35×10^6 cal. atm.$^{-1}$ deg.^{2}; $b = -55.7 \times 10^6$ cm.^{3} deg.^{2}; $\Delta H^\circ_0 = 15{,}402.5$ cal. mole^{-1}. The value of ΔH°_0 is given to tenths of calories only to give agreement to better than 0.1 mm. at the boiling point. The straight line represents the data within the limits of accuracy. The data at low values of pressure have a relatively low percentage accuracy and thus can be given practically no weight. The straight line was drawn through the data of Beat-

TABLE IV

HEAT OF VAPORIZATION AND VAPOR PRESSURE OF MERCURY

T, °K.	P, mm.	ΔH actual, cal. mole^{-1}
234.29 m.p.	2.30×10^{-6}	14,766
250	1.68×10^{-5}	14,737
275	2.48×10^{-4}	14,692
298.16	2.00×10^{-3}	14,652
300	2.33×10^{-3}	14,649
325	1.54×10^{-2}	14,606
350	7.71×10^{-2}	14,565
375	3.108×10^{-1}	14,525
400	1.048	14,485
425	3.058	14,446
450	7.903	14,407
475	18.44	14,369
500	39.42	14,330
525	78.32	14,292
550	146.0	14,253
575	257.2	14,213
600	431.8	14,173
625	695.6	14,132
629.88 b.p.	760.0	14,127
650	1078	14,089
675	1617	14,045
700	2355	13,999
725	3339	13,952
750	4624	13,901

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(11) G. N. Lewis and M. Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, N. Y., p. 198.

tie, Blaisdell and Kaminsky,[10] as nearly as possible. These data are very accurate but their range is too limited to define the slope. The slope selected corresponds to a gas imperfection of 0.27% at the boiling point. The most profitable additional contribution to the thermodynamics of mercury would be a direct determination of the gas imperfection at temperatures appreciably above the boiling point so that pressures considerably above one atmosphere could be used.

The ideal heat of vaporization of liquid mercury is given as a function of temperature by the equation

$$H^\circ_{(g)} - H^\circ_{(l)} = \Delta H_0^\circ + \frac{5}{2}RT - (H^\circ_{(l)} - \mathrm{H}_0^\circ) = \Delta H\ (\text{ideal}) \quad (8)$$

The thermodynamic equation

$$(\partial H/\partial P)_T = V - T(\partial V/\partial T)_P \quad (9)$$

may be combined with the equation for gas imperfection and the data of state for the liquid to obtain the actual heat of vaporization of liquid mercury to its equilibrium vapor.

$$\Delta H\ (\text{actual}) = \Delta H(\text{ideal}) + \frac{3b'P}{T^2} + V_{(l)}\,(1 - T\alpha)(1 - P) \quad (10)$$

Values of the actual heat of vaporization are given in Table IV along with values of the vapor pressure calculated by means of the $(F^\circ - H_0^\circ)/T$ function and equation 7.

ΔH(ideal) is identical with ΔH(actual) to within one cal. mole^{-1} up to 500°K. At the boiling point ΔH(ideal) is greater by 10 cal. mole^{-1} and at 750°K. it is 46 cal. mole^{-1} greater. The difference can be calculated by means of equation 10. The volume of the liquid and α, the coefficient of expansion at $t°$ may be obtained from the equation.[2]

$$V_{(l)} = 14.756 + 2.678 \times 10^{-3}t + 1.36 \times 10^{-7}t^2 + 9.8 \times 10^{-11}t^3 + 9.93 \times 10^{-13}t^4 \quad (11)$$

The heat content and entropy of actual mercury gas may be calculated from the equations

$$\frac{H_T - H_0^\circ}{T} = \frac{5}{2}R + \frac{3bP}{T^3} \quad (12)$$

$$S = \frac{3}{2}R\ln M + \frac{5}{2}R\ln T - R\ln P + \frac{5}{2}R + \frac{2bP}{T^3} - 7.2819 \quad (13)$$

We thank Dr. T. H. Geballe for assistance with the experimental measurements.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

A Study of Refractive Index Increments of Weak Acids and Buffer Mixtures

BY EDWARD B. DISMUKES[1] AND ROBERT A. ALBERTY

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A differential refractometer which is suitable for measuring refractive index increments at 1° in the range of $\Delta n = 10^{-3}$ to 5×10^{-3} with a precision of $\Delta n = 1 \times 10^{-6}$ is described. This instrument has been used to measure the refractive index increments of buffers formed by acetic, aspartic and glutamic acids and their sodium salts and of aqueous solutions of monochloroacetic, oxalic and phosphoric acids. The variation of the integral molar increment for a constituent with concentration is discussed for buffers and for aqueous solutions. It is shown that for a restricted concentration range the refractive index increment of a solution may be represented as a summation of products of molar increments and concentrations of the various salts and weak acids at equilibrium.

One of the problems in applying the theory of moving boundary systems formed by weak electrolytes is the prediction of changes in refractive index across boundaries. The present investigation was undertaken because there appears to be no previous work on the problems encountered in buffers. The difference between the refractive index (n) of a solution and that of the solvent (n_0) is a function of the concentrations of the added substances and will be referred to as the refractive index increment. The integral increment for a constituent A in a solvent is defined as

$$\bar{k}_A = (n - n_0)/\bar{c}_A \quad (1)$$

where $\bar{c}_A$ is the molar concentration of A including all ionized and un-ionized forms in the solution. Since we will deal here only with integral increments, the quantity defined by (1) will be referred to simply as the constituent increment.[2] If the solvent is a buffer it is to be understood that the total molar concentrations of the constituents of the buffer are to be held constant.

In general $\bar{k}_A$ is a function of $\bar{c}_A$, due to the fact that the relative concentrations of the various forms of the constituent A may vary and that these forms may have integral refractive index increments which are not equal. It is assumed that the increments of the individual species in the solution are additive, as expressed in equation (2).

$$n - n_0 = \sum_i^N k_i c_i \quad (2)$$

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(1) Wisconsin Alumni Research Foundation Research Fellow (1951–1952); Shell Fellow (1952–1953).

(2) The differential constituent increment is defined by

$$\bar{k}_{A,d} = \partial(n - n_0)/\partial\bar{c}_A$$

so that

$$\bar{k}_{A,d} = \bar{k}_{A,i} + \bar{c}_A(\partial\bar{k}_{A,i}/\partial\bar{c}_A)$$

where $\bar{k}_{A,i}$ is the integral increment.