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Heat Capacity of Liquid Mercury Between 0° and 450° C; Calculation of Certain Thermodynamic Properties of the Saturated Liquid and Vapor

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The enthalpy of liquid mercury was measured from 0° to 450° C by the "drop" method. These and other precise published data were used to calculate a number of thermodynamic properties of liquid and gaseous mercury at the vapor pressures from the triple point, −38.88°, to +500° C. The entropy calculated from data on the vapor and liquid was compared with that derived from published low-temperature heat-capacity data for the solid. The calculated values of vapor pressure, also using data on the vapor and liquid, were found to agree over a wide temperature range with certain published experimental values when independently derived gas-imperfection and published temperature-scale corrections were applied.

I. Introduction

It is of considerable practical and theoretical importance that the physical properties of mercury be known accurately. The element has found an important use as the fluid in certain heat engines operating at high temperatures. Furthermore, it can be highly purified, perhaps more easily than almost any other commonly available substance. Because of their reproducibility, the physical properties of mercury have often been used as standards.

The accuracy of the values of many thermodynamic properties, over a temperature range, often depends on how accurately the heat capacity is known. As various past observers have shown considerable disagreement above room temperature in their values for the heat capacity of mercury, the measurements reported in this paper were undertaken primarily to furnish accurate values of this property up to a vapor pressure of 4 atm. This investigation is the second in a current series of measurements at this Bureau of the heat capacities of liquid metals.

II. Experimental Procedure

1. Method and Apparatus

The method and apparatus have been described previously [1, 2, 3].[1]

In brief, the method consists in heating the sample in a furnace to a known temperature and dropping it into an ice calorimeter, thereby measuring the heat evolved in cooling the sample to 0° C. The calibration factor of the calorimeter was determined electrically to be 270.46 ±0.03 absolute joules per gram of mercury. The samples were sealed in cylindrical containers of stainless steel. The heat capacities of the empty containers were accounted for by "blank" experiments employing them, these experiments being carried out at the same temperatures as with the filled containers. The temperature of the sample in the furnace was measured by a platinum resistance thermometer that had been calibrated at this Bureau.

2. Samples

Two samples of mercury of about 130 g each were sealed in the containers made of stainless steel No. 347, each having about 10-cm^3 capacity. The capsules had the same mass (17 g) and composition as those used in the sodium investigation [3]. The samples, purified and sealed, were furnished by the Knolls Atomic Power Laboratory, of Schenectady, N. Y. Commercially pure mercury that was believed to have been triply distilled was redistilled four more times in vacuum. The samples were sealed in the containers under a pressure of helium of about $\frac{1}{30}$ atm. The sealing process [4] was completed by a pulse of high-frequency current induced locally at the top of the container. It was found possible to seal the containers in this manner without changing their weight by more than a milligram. The "empty" containers were sealed in the same manner with the same pressure of helium. The containers filled with mercury were tested for tightness at 450° C and were found to have a leakage rate of about 0.1 microgram of mercury per hour at this temperature, an amount that is without significant effect on the enthalpy measurements.

The mercury sample actually used for most of the thermal measurements was examined spectrochemically at this Bureau. Of 34 elements looked for as possible impurities, only copper and nickel were detected by this means, and these were found to be present only in traces amounting to less than 0.01 percent of the mass of the sample. The stock supply of mercury from which the sample for the thermal measurements had been taken was analyzed by the Knolls Atomic Power Laboratory. The total nonvolatile impurity found, mostly silver, amounted to 0.00001 percent. A mass-spectrographic examination by them for "volatile" impurities indicated the possible presence of traces of aluminum, manganese,

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[1] Figures in brackets indicate the literature references at the end of this paper.

iron, cobalt, nickel, zinc, and rhodium; the total amount of these, however, was shown not to exceed 0.001 percent.

III. Experimental Results

A total of 111 measurements of enthalpy was made, from 0° to 450° C (to about 4 atm pressure). Of these, 66 were made with the two empty capsules and 45 with the two capsules containing mercury. The average deviation of a single measurement from the mean at a given temperature was 0.03 percent. One of the mercury samples, measured at only 250° C (to ensure that no systematic error in mass was present), gave a mean value for the enthalpy of mercury that differed from that obtained when using the other sample by only 0.01 percent. The detailed results of individual runs are given in table 1.

No corrections for impurities were made, as these were undoubtedly so small as to lie well within the accidental error. All weights were corrected for buoyancy. No corrections for temperature were made, as the thermometer reading was held to within ±0.01 deg of the stated temperature in each case. The ice point of the resistance thermometer changed so slightly during the course of the measurements as to indicate a negligible error in computing the temperatures. Corrections were applied to account for small differences in masses of capsule and exterior oxide coatings. In addition, corrections were made at the higher temperatures for the small heats evolved in condensing some mercury vapor inside the container, in order that the results would refer to the liquid alone.

This last-mentioned correction, and that needed to evaluate the enthalpy change that would have resulted under maintenance of saturation from the heat measurements made on the system maintained at constant volume, were conveniently calculated by an equation given by Osborne [5],

$$[Q]_1^2=[q-PV+mH_{(l)}+(V-mv)L/(v'-v)]_1^2, \qquad (1)$$

where $[Q]_1^2$ is the heat evolved in cooling a closed container in which there is a liquid in equilibrium with its vapor from temperature 2 to temperature 1; $[q]_1^2$ is the contribution to $[Q]_1^2$ made by the empty container, shields, and suspension wire; P is the vapor pressure of the liquid; V is the internal volume of the container; m is the total mass of liquid and vapor; $H_{(l)}$ is the enthalpy, per unit mass, of the "saturated" liquid (i. e., at pressure P); v' and v are the specific volumes of saturated vapor and liquid, respectively; and L is the enthalpy of vaporization per unit mass.

The total of the various corrections did not exceed 0.03 percent of the enthalpy, except in the case of some of the first runs, where a correction of approximately 0.2 percent was necessitated by the use of a shield system that was later broken and so had to be replaced by one of different heat capacity.

TABLE 1. *Corrected heat and enthalpy values of individual experiments*

Furnace temperature	Measured heat		[a] Enthalpy change of mercury, H_t-H_0		
	Blank	With mercury	Observed	Calculated	Difference
°*C*	*abs j*	*abs j*	*abs-j g*$^{-1}$	*abs-j g*$^{-1}$	*abs-j g*$^{-1}$
50.00	400.5		6.942	6.946	−0.004
	403.4				
	401.6	[b](1269.3)			
	397.1	1298.7			
	401.1	1298.7			
	400.8	1298.1			
	[c] 401.0				
	[c] 401.0				
	[c] 399.2				
100.00	814.3		13.835	13.831	+0.004
	814.0				
	815.6				
	[c] 816.5	2605.0			
	[c] 815.9	2603.8			
	[c] 816.2	2604.8			
	813.2				
	814.4				
	814.6				
150.00	1238.6	3913.6	20.672	20.669	+0.003
	1242.0	3914.9			
	1239.9	3914.8			
	1241.9				
200.00	1676.6		[d] 27.461	27.470	−0.009
	1673.5	5223.9			
	1678.8	5228.9			
	1678.1	5226.4			
	1674.9	5223.0			
	1676.3	5230.2			
	1677.5	5227.4			
	[c] 1674.1	5228.6			
	[c] 1674.2	5228.1			
	[c] 1675.6				
250.00		6548.5	34.250	34.250	0.000
	2117.5	6548.0			
	2121.5	6549.3			
	2120.2	[e] 6484.0			
	2119.4	[e] 6481.9			
		[e] 6482.8			
300.00	2571.3		41.027	41.019	+0.008
	2567.0				
	2572.2	[b](7868.3)			
	2570.0	7875.9			
	2570.0	7874.8			
	2568.8	7877.9			
	[c] 2571.6	7875.3			
	[c] 2569.6				
	[c] 2569.1				
350.00	3030.5	9205.5	47.791	47.790	+0.001
	3028.0	9209.5			
	3028.2	9211.0			
	3029.1	9207.8			
400.00	3496.6		[d] 54.569	54.577	−0.008
	3493.5				
	3494.3	10548.9			
	3490.6	10544.6			
	3493.4	10550.8			
	3493.7	10553.0			
	3492.8	10548.2			
	[c] 3489.5	10547.5			
	[c] 3489.4				
	[c] 3491.2				
450.00	[b](3957.4)	11900.7	[d] 61.396	61.392	+0.004
	3964.1	11902.0			
	3965.6	11900.9			
	3964.1	11902.8			
	[c] 3965.0	11897.3			
	[c] 3965.9	11900.7			
	[c] 3964.3				

[a] Values apply to saturation (i. e., at the vapor pressure).

[b] Rejected by Chauvenet's criterion.

[c] On alternate capsule of same mass.

[d] This mean obtained by weighting each set proportionately to the number of measurements in the set and inversely proportionately to the average deviation from the mean of the set.

[e] On alternate capsule, containing 127.411 g Hg. The other capsule had the same mass of container but contained 129.344 g Hg.

Within the accidental error the heats of the empty containers ("blank" experiments) were found to vary perfectly smoothly with temperature up to 450° C. By plotting against $t(°C)$ the function

$$\frac{H_t-H_0}{1.86t+0.0025t^{1.73}}, \tag{2}$$

which varied only 1 percent between 50° and 450°, these blank values were thereby smoothed. The net enthalpies of mercury given in table 1 have been calculated by using the smoothed values for the empty container, although the heat values listed for the empty containers in the table are those actually obtained.

The experimental values of the enthalpy of liquid mercury (at saturation pressure), less the enthalpy at 0° C, are represented by the following equation, whose constants were fitted by least squares:

$$\left.\begin{aligned} H_t-H_0 &= 0.139612t-1.4673(10^{-5})t^2 \\ &+1.6874(10^{-8})t^3 \qquad (0° \text{ to } 450°\text{C}) \end{aligned}\right\}, \tag{3}$$

where H is in absolute joules per gram and t in deg C (International Temperature Scale). The values in the fifth column of table 1 were calculated from this equation.

IV. Calculation of Thermodynamic Properties

1. General Procedure

The more common thermodynamic properties of liquid and gaseous mercury, at the existing vapor pressures, were accurately calculated as a function of temperature over the range from the triple point, —38.88°, to 500° C. Except for what may be considered as minor but unavoidable correction terms, the calculated values of most of these properties rest on three sets of precise experimental data, namely, (1) the enthalpy measurements of the liquid reported in this paper, (2) a previously published series of vapor pressure measurements covering a 13-deg temperature range in the vicinity of the normal boiling point, and (3) the experimental values of the fundamental physical constants that made possible the statistical evaluation of the entropy of the ideal vapor. The additional experimental data employed, whose accuracy is of secondary effect on the accuracy of the calculated properties, are (1) those giving certain fundamental constants of the Hg_2 molecule (used to arrive at data of state for mercury vapor), (2) accurate gas-thermometer measurements of one laboratory (used to make corrections from the International to the thermodynamic temperature scale), and (3) PVT data for the liquid (necessary in an accurate evaluation of the heat capacities from the measured enthalpy).

The procedure of calculation followed will now be outlined. The heat capacities of liquid mercury were calculated from the enthalpy data by the usual thermodynamic relations. The changes with temperature of the entropy of the saturated liquid were next calculated from the values of heat capacity, and were combined with the statistically calculated value of the entropy of the vapor (at the vapor pressure) to give the absolute entropy of the liquid. The heat capacity (C_p) of the vapor was calculated by first assuming it to be an ideal monatomic gas and then making small corrections for imperfections of the gas. By integration of the resulting heat capacity equation and evaluation of the integration constant by using the value of the heat of vaporization at the normal boiling point calculated from the vapor-pressure data and the Clapeyron equation, values of enthalpy of the vapor (relative to the liquid at a fixed temperature) were obtained. The free energies of the liquid and vapor followed from the calculated entropy and enthalpy values. By equating the expressions for these free energies of "saturated" liquid and vapor, a vapor-pressure relation was obtained that is applicable over a much larger temperature range than the supporting vapor-pressure data.

At the present time, the uncertainty in the corrections for gas imperfection and temperature scale, referred to above, limit slightly the accuracy of the calculated properties. Because of these uncertainties it was considered advisable merely to indicate these two corrections in the equations derived. The values of the properties tabulated (in tables 3, 4, and 5) were arrived at, however, by assigning to the corresponding correction terms, on the basis of what are judged to be the best existing data, specific values that are separately listed (in tables 6 and 7 and in the text preceding them). This procedure facilitates an estimation of the uncertainties introduced into the present values and also should simplify any future desired revision of the values, should more accurate corrections become available.

2. Nomenclature and General Assumptions

In what follows, energy will be expressed in calories (1 cal=4.1840 abs j); all extensive properties, per gram-atom of mercury (atomic weight=200.61); and temperature (T), in degrees absolute (0° C=273.16° K), unless otherwise stated. Each value calculated from the equations applies at the existing vapor pressure, except in those cases where pressure is an explicit variable in the equations given. In addition, the subscripts in the heat capacities C_p, C_v, and C_s signify that the respective heat changes are those occurring under the maintenance of constant pressure, constant volume, and liquid-vapor equilibrium, respectively. The equations for relative enthalpy and relative free energy contain the term $H_{TP(l)}$, the enthalpy of the liquid at the triple point, $-38.88°$ C. Liquid and vapor are distinguished by the subscripts l and g, respectively. In the numerical equations (i. e., those in which some or all of the numerical constants have dimensions), P, the pressure, is to be expressed in millimeters of mercury (760 mm=1 standard atm); and V, the volume, in cm^3 g-atom^{-1}.

Log and *ln* indicate logarithms to the bases 10 and e, respectively.

Saturated mercury vapor at pressures not exceeding 2 atm has been found experimentally to have densities that differ from those calculated for an ideal gas by less than 2 percent (the uncertainty of the measurements). It is therefore permissible to assume that practically all of the gas imperfection arises from binary collisions only. Statistical mechanics shows that under this circumstance the correct form for the equation of state of the vapor is

$$PV_{(g)}=RT\left[1+\frac{B}{V}\right], \tag{4}$$

where B, the so-called "second" virial coefficient, is a function of temperature only. However, for convenience it will be used here in the approximately equivalent form

$$PV_{(g)}=RT+PB. \tag{5}$$

In the numerical equations of this paper, B is to be expressed in cm^3 g-atom^{-1}. The values of dB/dT and d^2B/dT^2 at the temperature at which the equation is applied will be designated by B' and B'', respectively, and the corresponding values at the normal boiling point, 629.74° K, will be designated by B_0, B_0', and B_0''.

θ and T will be used to designate the values of a given temperature on the International and thermodynamic absolute temperature scales, respectively.

3. Enthalpy and Heat Capacity of the Liquid

By extrapolating the experimental enthalpy values (represented by eq 3) to the triple point, $-38.88°$ C (234.28° K), and changing to the units as indicated above (to cal, g-atom, deg K), the enthalpy of the liquid $H_{(l)}$ at any temperature θ, relative to the enthalpy $H_{TP(l)}$ at the triple point, becomes

$$\begin{aligned}H_{(l)}-H_{TP(l)}=7.259390\theta-1.36651\ (10^{-3})\theta^2\\+8.0906(10^{-7})\theta^3-1636.13.\end{aligned} \tag{6}$$

The heat capacity equations that are derived from eq 6 must be multiplied by $d\theta/dT$ to account for the difference between thermodynamic (T) and International (θ) temperature scales. However, in the temperature range in which the equations are applicable, the heat capacity varies by only 3 percent. Since $d\theta/dT$ is, at all these temperatures, very close to unity, an error negligible in comparison with the experimental errors of the supporting data is introduced by the more convenient procedure of multiplying by $d\theta/dT$ only the average value of $(\partial H_{(l)}/\partial\theta)s$, taken to be 6.55. This is equivalent to adding as a correction term $6.55[(d\theta/dT)-1]$.

The "saturation" heat capacity ($C_{s(l)}$) can be found from the thermodynamic equation

$$C_{s(l)}=\left(\frac{\partial H_{(l)}}{\partial\theta}\right)_s\frac{d\theta}{dT}-V_{(l)}\left(\frac{\partial P}{\partial\theta}\right)_s\frac{d\theta}{dT}. \tag{7}$$

For mercury below 500° C the last term is small and therefore may be approximated with sufficient accuracy by replacing $d\theta/dT$ by 1 and by substituting for $V_{(l)}$ the constant value 15.9 cm^3 g-atom^{-1}, equal to the volume of the saturated liquid at 400° C [6]. A simple vapor pressure equation, sufficiently accurate for the present purpose, is

$$P=6.345(10^7)e^{-7136.5/\theta}. \tag{8}$$

(This was derived from the values of P and $dP/d\theta$ given at the normal boiling point by eq 19, and provides on differentiation an equivalent of $(\partial P/\partial\theta)_s$). With these substitutions, together with the equivalent of $(\partial H/\partial\theta)_s$ obtained by differentiating eq 6, eq 7 becomes

$$\left.\begin{aligned}C_{s(l)}=7.25939-2.73302(10^{-3})\theta+2.42718(10^{-6})\theta^2\\-\frac{2.294(10^8)}{\theta^2}e^{-\frac{7136.5}{\theta}}+6.55(d\theta/dT-1).\end{aligned}\right\} \tag{9}$$

The heat capacity at constant pressure may be found from the thermodynamic relation

$$C_p=C_s+T(\partial V/\partial T)_p(\partial P/\partial T)_s. \tag{10}$$

The last term is small in this case and need not be highly accurate. In fact, it will be used with T replaced by θ. Deriving $(\partial P/\partial\theta)_s$ from eq 8 as before, and substituting as a constant value for the slowly changing $(\partial V_{(l)}/\partial\theta)_p$ the value at 400° C [6], $3.09(10^{-3})$ cm^3 g-atom^{-1} deg^{-1}, eq 10 becomes

$$C_{p(l)}=C_{s(l)}+\frac{44585}{\theta}e^{-\frac{7136.5}{\theta}} \tag{11}$$

The heat capacity at constant volume may in turn be calculated from the thermodynamic relation

$$C_v=C_p-\frac{\alpha^2VT}{\beta}, \tag{12}$$

where α and β are the coefficients of isobaric thermal expansion and isothermal compressibility, respectively.

In the use of eq 12 to calculate C_v, use was made of the following equation for the liquid (t being in deg. C):

$$\begin{aligned}V_{(l)}=14.756+2.678(10^{-3})\,t+1.36(10^{-7})\,t^2\\+9.8(10^{-11})t^3+9.93(10^{-13})t^4.\end{aligned} \tag{13}$$

This equation was derived from the equation of Sears [6,7] for the relative volume and from the mean experimental value of the density of the liquid at 0° C. Sears' equation seems to be based on data covering the range 0° to 300° C only. However, it fits well the available data for temperatures below 0° C. Its use in this paper between 300° and 500° does not introduce an appreciably increased uncertainty to any of the thermal properties calculated, as the affected terms in the equations are relatively small.

For the isothermal compressibility, the values of Smith and Keyes [8], extrapolated to zero pressure (the approximate vapor pressure up to 200° C), were used. The values of C_v tabulated in this paper extend only up to 200° C, because reliable values of the compressibility above this temperature are not now available.

4. Entropies of Liquid and Vapor

The entropy of the saturated liquid is

$$S_{(l)}=\int_{T_0}^{T}\frac{C_{s\,(l)}}{T}dT+S_{0\,(l)}, \tag{14}$$

where T_0 is the thermodynamic temperature of the normal boiling point ($\theta=629.74$), $S_{0\,(l)}$ is the absolute entropy of the saturated liquid at that temperature, and C_s is the heat capacity given by eq 9. Of the terms in the second member of eq 9, the sum of all except $6.55000\ d\theta/dT$ is always relatively small, as discussed in the preceding section and may thus, without appreciable error, be conveniently divided by and integrated with respect to θ instead of T. The remaining term must be divided by and integrated with respect to T, giving

$$6.55000\int_{629.74}^{\theta}\frac{d\theta}{T},$$

and this will be replaced by

$$6.55000\ \ln\frac{\theta}{629.74}+6.55\int_{629.74}^{\theta}\left(\frac{1}{T}-\frac{1}{\theta}\right)d\theta,$$

in order that again the term including the correction will be small. Upon integrating, it is found that

$$\left.\begin{aligned}S_{(l)}=&16.71536\ \log\ \theta-2.73302(10^{-3})\theta\\&+1.21359(10^{-6})\theta^2\\&-4.511\left(\frac{7136.5}{\theta}+1\right)e^{-\frac{7136.5}{\theta}}\\&+6.55\int_{629.74}^{\theta}\left(\frac{1}{T}-\frac{1}{\theta}\right)d\theta\\&-45.548507+S_{0\,(l)}.\end{aligned}\right\} \tag{15}$$

The value of the entropy of the liquid at the normal boiling point, $S_{0\,(l)}$, will now be evaluated as a function of the corrections for gas imperfection and temperature-scale divergence. The result is eq 24.

The entropy of the ideal vapor (S^0), with ideality assumed to imply monatomicity as well, is given by the well-known statistical mechanical (so-called Sackur-Tetrode) equation. (The ground state of the mercury atom is singlet. As for all values of entropy in this paper, nuclear-spin and isotopic contributions are omitted.) The equation is as follows:

$$S^0=Rln\left(\frac{2\pi m}{h^2}\right)^{3/2}\frac{(kT)^{5/2}}{P}+\frac{5}{2}R, \tag{16}$$

where R is the gas constant, m is the mass of the atom, h is Planck's constant, k is Boltzmann's constant, and P is the pressure. The entropy of the real gas at the same pressure can be shown thermodynamically to be less by PB' (see eq 5). Subtracting this and adding the temperature-scale correction lead to

$$S_{(g)}=Rln\left(\frac{2\pi m}{h^2}\right)^{3/2}\frac{(k\theta)^{5/2}}{P}+\frac{5}{2}R+\frac{5}{2}Rln\frac{T}{\theta}-PB'. \tag{17}$$

Making the substitutions $R=1.98719$ cal g-atom^{-1}, $m=3.3308(10^{-22})$[2] g-molecule^{-1}, $h=6.624(10^{-27})$ erg-sec, $k=1.38047(10^{-16})$ erg molecule^{-1} deg^{-1}, and 1 cm^3-mm (of mercury)$=3.186484(10^{-5})$ cal, eq 17 becomes, for any pressure P,

$$\left.\begin{aligned}S_{(g)}=&11.439185\log\theta-4.575674\log P+26.6702\\&+11.44\log\frac{T}{\theta}-3.186(10^{-5})PB'.\end{aligned}\right\} \tag{18}$$

Beattie, Blaisdell, and Kaminsky [9] have accurately measured the vapor pressure of mercury from 349° to 362° C. They have given the normal boiling point ($P=760$) as 356.58° C, and in this temperature range the vapor pressure equation (t=deg C International),

$$\left.\begin{aligned}t=&356.580+7.30951(10^{-2})(P-760)\\&-3.9866(10^{-5})(P-760)^2\\&+3.191(10^{-8})(P-760)^3\end{aligned}\right\}, \tag{19}$$

from which their individual determinations vary by only 0.001 deg on the average. Equation 19, which will be adopted in what follows, gives a value of 13.6808 (mm deg^{-1}) for $dP/d\theta$ at the normal boiling point. This value will be substituted into the Clapeyron equation to obtain a value for the entropy of vaporization at this temperature. Substituting for the vapor volume its equivalent from eq 5, the Clapeyron equation may be written

$$S_{(g)}-S_{(l)}=\frac{RT}{P}\left(\frac{\partial P}{\partial T}\right)_s+(B-V_{(l)})\left(\frac{\partial P}{\partial T}\right)_s. \tag{20}$$

If T be replaced by θ, only the first term of the second member is large enough at the boiling point to require the addition of a correction term, which is obviously

$$\frac{R}{P}\left(\frac{\partial P}{\partial\theta}\right)_s\left(T\frac{d\theta}{dT}-\theta\right).$$

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[2] Mean molecular mass for the naturally occurring isotopic mixture. The strictly correct procedure of using in eq 17 the weighted mean of the logarithms of the isotopic masses would have resulted, in the case of mercury, in a value of the entropy of the vapor that is only 0.00005 cal g-atom deg^{-1} different.

Equation 20 then becomes

$$S_{(g)}-S_{(l)}=\left(\frac{R\theta}{P}+B-V_{(l)}\right)\left(\frac{\partial P}{\partial\theta}\right)_s+\frac{R}{P}\left(\frac{\partial P}{\partial\theta}\right)_s\left(T\frac{d\theta}{dT}-\theta\right). \qquad (21)$$

Letting $\theta=629.74$, at which temperature $V_{(l)}=15.748$ [6], applying the subscript "0" to designate this temperature, and substituting the above value 13.6808 mm deg^{-1} for $(\partial P/\partial\theta)_s$, eq 21 gives

$$\left.\begin{aligned}S_{0(g)}-S_{0(l)}&=22.519887+4.359(10^{-4})B_0\\&+0.03577(T-\theta)_0\left(\frac{d\theta}{dT}\right)_0\\&+22.53\left(\frac{d\theta}{dT}-1\right)_0.\end{aligned}\right\}\qquad (22)$$

At $\theta=629.74$, eq 18 gives

$$S_{0(g)}=45.508660+11.44\log\left(\frac{T}{\theta}\right)_0-0.02422\,B_0'. \qquad (23)$$

Substituting for $S_{0(g)}$ from eq 23 into 22 gives

$$\left.\begin{aligned}S_{0(l)}&=22.988773-0.02422\,B_0'-4.359(10^{-4})\,B_0\\&+11.44\log\left(\frac{T}{\theta}\right)_0-0.03577\,(T-\theta)_0\left(\frac{d\theta}{dT}\right)_0\\&-22.53\left(\frac{d\theta}{dT}-1\right)_0.\end{aligned}\right\}\qquad (24)$$

And finally, the value of $S_{0(l)}$ may be substituted into eq 15 to give an equation for the absolute entropy of the "saturated" liquid at any temperature in the range covered:

$$\left.\begin{aligned}S_{(l)}&=16.71536\log\theta-2.73302(10^{-3})\theta\\&+1.21359(10^{-6})\theta^2-4.511\left(\frac{7136.5}{\theta}+1\right)e^{-\frac{7136.5}{\theta}}\\&-22.559734-0.02422B_0'-4.359(10^{-4})B_0\\&+6.55\int_{629.74}^{\theta}\left(\frac{1}{T}-\frac{1}{\theta}\right)d\theta+11.44\log\left(\frac{T}{\theta}\right)_0\\&-0.03577(T-\theta)_0\left(\frac{d\theta}{dT}\right)_0-22.53\left(\frac{d\theta}{dT}-1\right)_0.\end{aligned}\right\}\qquad (25)$$

5. Enthalpy of the Vapor; Free Energy; General Vapor Pressure Equation

The relative Gibbs free energy of the liquid may next be found from the entropy and the relative enthalpy, by using the thermodynamic definition

$$F=H-TS. \qquad (26)$$

For this purpose eq 26 may be written in the form

$$-(F_{(l)}-H_{TP(l)})=\theta S_{(l)}-(H_{(l)}-H_{TP(l)})+(T-\theta)S_{(l)} \qquad (27)$$

From the thermodynamic relation

$$C_P=T\left(\frac{\partial S}{\partial T}\right)_p \qquad (28)$$

and eq 18, there is obtained for the heat capacity of the gas at constant pressure

$$C_{p(g)}=4.96797-3.186(10^{-5})P\theta B''. \qquad (29)$$

Integration of eq 29 with respect to T at constant pressure yields the enthalpy of the gas at pressure P,

$$\begin{aligned}H_{(g)}&=4.96797\theta+3.186(10^{-5})[B-\theta B']P\\&+4.97(T-\theta)+A.\end{aligned}\qquad (30)$$

The integration constant A may be expressed in terms of $H_{TP(l)}$ the constant used in the case of the liquid, by utilizing the value obtained from eq 22 for the enthalpy of vaporization at the boiling point. Multiplying eq 22 by the temperature $T_0(=629.74+(T-\theta)_0)$ and neglecting the very small terms as before, there results:

$$\left.\begin{aligned}H_{0(g)}-H_{0(l)}&=14181.674+0.2745B_0\\&+22.53(T-\theta)_0\left(\frac{d\theta}{dT}+1\right)_0\\&+1.419(10^4)\left(\frac{d\theta}{dT}-1\right)_0.\end{aligned}\right\}\qquad (31)$$

Evaluating eq 6 at $\theta=629.74$ gives

$$H_{0(l)}-H_{TP(l)}=2595.531. \qquad (32)$$

By evaluating eq 30 at $\theta=629.74$ and substituting the resulting equivalent of $H_{0(g)}$ into the sum of eq 31 and eq 32, an equivalent of the constant A in terms of $H_{TP(l)}$ is provided that when substituted for A into eq 30 gives

$$\left.\begin{aligned}H_{(g)}-H_{TP(l)}&=13648.676+4.967970\theta\\&+2022e^{-7136.5/\theta}[B-\theta B']+0.2503B_0\\&+15.25B_0'+22.53(T-\theta)_0\left(\frac{d\theta}{dT}+1\right)_0\\&+1.419(10^4)\left(\frac{d\theta}{dT}-1\right)_0\\&+4.97[(T-\theta)-(T-\theta)_0].\end{aligned}\right\}\qquad (33)$$

In this equation, the vapor pressure has been evaluated (with sufficient accuracy, for the correction term, from eq 8) and has been substituted for P. Subtraction of eq 6 from eq 33 will give the heat of vaporization at any temperature in the range studied.

The relative Gibbs free energy of the gas, as does that for the liquid, now follows by the use of eq 26, which may now be written in the form

$$-(F_{(g)}-H_{TP(l)})=\theta S_{(g)}-(H_{(g)}-H_{TP(l)})+(T-\theta)S_{(g)}. \tag{34}$$

By equating the free energies of saturated liquid and gas from eq 27 and 34; substituting for the enthalpy and entropy of vapor and liquid from eq 33, 18, 6, and 25; and solving for log P contained in S_g, the following vapor pressure equation is obtained:

$$\left.\begin{aligned}
\log P=&11.259839-\frac{3340.449}{\theta}-1.153092\log\theta \\
&+2.98647(10^{-4})\theta-8.8409(10^{-8})\theta^2 \\
&+9.526(10^{-5})\left(\frac{\theta-629.74}{\theta}\right)(B_0+55.56B_0') \\
&-\frac{6.963(10^{-6})}{\theta}(PB-760B_0) \\
&+0.9860\left(\frac{7136.5}{\theta}+1\right)e^{-\frac{7136.5}{\theta}} \\
&+2.500\log\frac{T/\theta}{(T/\theta)_0}-1.431\int_{629.74}^{\theta}\left(\frac{1}{T}-\frac{1}{\theta}\right)d\theta \\
&+7.817(10^{-3})\left(\frac{\theta-629.74}{\theta}\right) \\
&\quad\left[629.74\left(\frac{d\theta}{dT}-1\right)_0+(T-\theta)_0\left(\frac{d\theta}{dT}\right)_0\right] \\
&+\frac{1}{\theta}\left[\left\{1.8705-1.1531\log\theta+\frac{3099.3}{\theta}\right.\right. \\
&+5.973(10^{-4})\theta \\
&\left.\left.-2.652(10^{-7})\theta^2\right\}(T-\theta)-3.838(T-\theta)_0\right].
\end{aligned}\right\} \tag{35}$$

(In the part of the last bracketed term which represents the entropy of vaporization, all minor terms have been omitted, since they would be multiplied by the very small factor $(T-\theta)$. In this bracketed term, P (contained in the equivalent of $S_{(g)}$) has been replaced by its equivalent in terms of θ, by using eq 8.)

If the specific corrections for gas imperfection and temperature-scale differences described in the next two sections be adopted, eq 35 may be approximated by the following more readily applicable vapor pressure equation:

$$\left.\begin{aligned}
\log P=&11.257555-\frac{3339.202}{\theta}-1.153092\log\theta \\
&+2.95697(10^{-4})\theta-7.4588(10^{-8})\theta^2 \\
&-1.5605(10^{-11})\theta^3+3.600e^{-5360/\theta}.
\end{aligned}\right\} \tag{36}$$

Between 100° and 500° C, this equation reproduces the vapor pressures of eq 35 to within 0.01 percent. Below 100°, however, it gives lower values, the discrepancy amounting to 0.1 percent at 25° and 0.6 percent at −39°, the triple point.

6. Calculation of the Second Virial Coefficient; Corrections for Gas Imperfection

Smith and Menzies [10] found the density of mercury vapor to be ideal between 360° and 400° C to within their probable experimental error, about 2 percent. Apparently no one has measured such densities with much greater accuracy.

Approximate values for the degrees of gas imperfection at various temperatures have been calculated for many gases by the use of some equation of state, such as Berthelot's. To employ the last equation, the critical constants must be known. In the case of mercury, however, the values that have been reported for the critical temperature (around 1,500° C) and critical pressure (from 1,000 to 3,500 atm) show such wide variations that this method is hardly applicable.

There is abundant spectroscopic evidence that mercury vapor contains appreciable amounts of the dimer Hg_2, which is known to possess a singlet ground state. Adopting suitable constants for this molecule as described below, values of the second virial coefficient B of mercury vapor, treated as an imperfect monatomic gas in which only binary collisions are important below 500° C, were calculated from the following statistical mechanical equation [11]:

$$B(T)=-2\pi N\int_0^\infty(e^{-U(r)/RT}-1)r^2dr, \tag{37}$$

where N is Avogadro's number, and $U(r)$ is the potential energy of a mole of Hg_2 molecules, all at an interatomic separation of r. $U(r)$ was calculated from a Morse potential function in which it was assumed that the equilibrium separation is $3.2(10^{-8})$ cm, and that the first vibrational constant ω_e is 36 cm^{-1}. The former figure, derived from data on liquid mercury, has been generally accepted as approximately correct. The latter figure, considered by Kuhn [12] to be the most likely choice among alternative multiples for which there is spectroscopic evidence, is supported by the theoretical calculation of a value of 35 cm^{-1} by Heller [13], whose values for a number of other diatomic molecules are in good agreement with well-established experimental values.

The third parameter needed in the use of the Morse function is the molar dissociation energy of the Hg_2 molecule in its ground state. Evidence for various values has been described in the literature. London [14] made a theoretical calculation of the polarization force and arrived at 2.0 kcal mole^{-1}; however, Kuhn [12] points out that this is undoubtedly too high because of the neglect of repulsion forces. Kuhn measured the total absorption in the discrete band system (2,540 A) at 175° C and calculated a value for the concentration of Hg_2. He claims that the extrapolation to 0° K (giving a dissociation energy of 2.1 kcal) yields too high a value because of the neglect of vibrational anharmonicity. If this be true, then, as he claims, the values obtained by measuring the decrease in absorption with rising temperature are too low. By the latter method and with the assumption of vibrational harmonicity, Koernicke [15] found a dissociation energy of 1.4 kcal, Kuhn and Freudenberg [16] found 1.6 kcal, and Winans and Heitz [17] found 1.38 ±0.07 kcal. Gaydon [18] recommends the latter value for the dissociation energy, whereas Herzberg [19] lists 1.84 kcal.

Equation 37 was solved graphically by the authors for values of B at the temperatures $T=430$, 530, 630, and 730, by using for each temperature values of 1.4, 1.5, 1.6, and 1.7 kcal for the molar dissociation energy of Hg_2. In these ranges the calculated value of B for a given temperature varies almost linearly with the value of the dissociation energy used. The thermodynamic properties of mercury listed in this paper were calculated assuming a value of 1.5 kcal as a reasonable weighted mean of the above values of the dissociation energy. This particular value was adopted partly because of the support it receives in figure 4, where calculated and experimental vapor pressures are compared. The following empirical equation represents the corresponding values of the second virial coefficient B, in cm^3 g-atom^{-1}, in this temperature range:

$$B=56.4-43.82e^{\frac{655}{\theta}}, \tag{38}$$

which agrees with the directly calculated values to within 0.5 percent from $\theta=430$ to $\theta=730$. On differentiation with respect to temperature, eq. 38 gives:

$$B'=\frac{655}{\theta^2}(56.4-B). \tag{39}$$

Values calculated from eq 38 and 39 are listed in table 2.

TABLE 2. *Second virial coefficient (B) and its temperature derivative (B′) for mercury vapor*

Temperature	B	B'	Temperature	B	B'
°C	*cm³ g-atom⁻¹*	*cm³ g-atom⁻¹ deg⁻¹*	*°C*	*cm³ g-atom⁻¹*	*cm³ g-atom⁻¹ deg⁻¹*
100	−197	+1.19	320	−76	+0.25
120	−175	0.98	340	−71	.22
140	−158	.82	356.58(bp)	−68	.20
160	−142	.69	360	−67	.20
180	−130	.59	380	−63	.18
200	−118	.51	400	−60	.17
220	−109	.45	420	−56	.15
240	−101	.39	440	−53	.14
260	−93	.34	460	−51	.13
280	−87	.31	480	−48	.12
300	−81	.27	500	−46	.11

7. Corrections to Basis of Thermodynamic Temperature Scale

The results of recent investigations [20] of the differences between the thermodynamic and International temperature scales have been formulated by an equation [21] equivalent to the following:

$$T-\theta=0.6381-4.809(10^{-3})\theta+1.1096(10^{-5})\theta^2 -7.481(10^{-9})\theta^3 \tag{40}$$

(The value of $(T-\theta)$ is so small and changes so slowly with temperature that when desirable, θ may be replaced by T in the second member of eq 40 without appreciably changing the corrections calculated.)

It is believed that the differences given by eq 40 are the most probable values in the light of the evidence now available, and that their uncertainties may be considered to correspond to probable errors of about half their respective values. All thermodynamic properties given in this paper have been corrected by this equation to units involving deg K thermodynamic, though for convenience of usage the tabulated values of these properties have been calculated for rounded temperatures on the International scale of 1948.

By use of eq 40 it may be shown that the integral appearing in eq 25 and 35 is approximately as follows

$$\left.\begin{aligned}\int_{629.74}^{\theta}\left(\frac{1}{T}-\frac{1}{\theta}\right)d\theta=0.01107\ \log\ \theta+\frac{0.6381}{\theta}\\ -1.1096(10^{-5})\theta\\ +3.7405(10^{-9})\theta^2-0.0264958\end{aligned}\right\} \tag{41}$$

V. Tables

1. Thermodynamic Properties

In tables 3, 4, and 5, values calculated from preceding equations are given for saturated liquid and gaseous mercury at temperatures from the triple point, −38.88° C [22], to 500° C. The numbers in parentheses given under the symbols heading the various columns indicate the particular equations from which the values were calculated.

Though the tabulated values of the heat capacities of the liquid were calculated to apply at the vapor pressures, the corresponding values of $C_{p(l)}$ at any small fixed pressure are practically identical. For it may be readily shown by using eq 13 that $C_{p(l)}$ varies by not more than 0.001 percent in this temperature range when the pressure varies by 1 atm.

It will be noted that the free-energy values calculated from eq 27 and listed in table 5 apply to either the saturated liquid or vapor.

TABLE 3. *Relative enthalpy; heat of vaporization; compressibility factor*

Temperature	Relative enthalpy		Heat of vaporization, $H_{(g)}-H_{(l)}$ (6, 33)	Compressibility factor of vapor, $pV_{(g)}/RT$ (5)
	Liquid, $H_{(l)}-H_{TP(l)}$ (6)	Vapor, $H_{(g)}-H_{TP(l)}$ (33)		
°*C Int*	*cal g-atom*$^{-1}$	*cal g-atom*$^{-1}$	*cal g-atom*$^{-1}$	
−38.88[a] (tp)	0.00	14800.8	14800.8	1.0000
−20	127.20	14894.5	14767.3	1.0000
0	261.37	14993.8	14732.4	1.0000
20	394.98	15093.1	14698.1	1.0000
25	428.29	15118.0	14689.7	1.0000
40	528.06	15192.5	14664.4	1.0000
60	660.65	15291.8	14631.2	1.0000
80	792.80	15391.2	14598.4	1.0000
100	924.54	15490.6	14566.1	1.0000
120	1055.91	15590.0	14534.1	1.0000
140	1186.96	15689.4	14502.4	1.0000
160	1317.71	15788.8	14471.1	1.0000
180	1448.21	15888.1	14439.9	1.0000
200	1578.49	15987.5	14409.0	0.9999
220	1708.60	16086.8	14378.2	.9999
240	1838.58	16186.0	14347.4	.9998
260	1968.46	16285.1	14316.6	.9997
280	2098.28	16384.1	14285.8	.9996
300	2228.08	16482.9	14254.8	.9994
320	2357.90	16581.6	14223.7	.9992
340	2487.78	16679.9	14192.1	.9990
356.58 (bp)	2595.53	16761.2	14165.7	.9987
360	2617.76	16778.0	14160.2	.9986
380	2747.88	16875.7	14127.8	.9982
400	2878.17	16973.1	14094.9	.9978
420	3008.67	17070.0	14061.3	.9972
440	3139.42	17166.4	14027.0	.9966
460	3270.47	17262.3	13991.8	.9959
480	3401.85	17357.7	13955.8	.9950
500	3533.59	17452.4	13918.8	.9942

TABLE 4. *Heat capacity*

Temperature	Heat capacity			
	Liquid			Vapor
	$C_{s(l)}$ (9)	$C_{p(l)}$ (11)	$C_{v(l)}$ (12)	$C_{p(g)}$ (29)
°*C Int*	*cal g-atom*$^{-1}$ *deg*$^{-1}$	*cal g-atom*$^{-1}$ *deg*$^{-1}$	*cal g-atom*$^{-1}$ *deg*$^{-1}$	*cal g-atom*$^{-1}$ *deg*$^{-1}$
−38.88[a] (tp)	6.7578	6.7578	5.969	4.968
−20	6.7272	6.7272	5.900	4.968
0	6.6967	6.6967	5.831	4.968
20	6.6683	6.6683	5.769	4.968
25	6.6615	6.6615	5.752	4.968
40	6.6419	6.6419	5.708	4.968
60	6.6176	6.6176	5.650	4.968
80	6.5954	6.5954	5.594	4.968
100	6.5752	6.5752	5.544	4.968
120	6.5571	6.5571	5.494	4.968
140	6.5410	6.5410	5.449	4.968
160	6.5270	6.5270	5.403	4.968
180	6.5150	6.5150	5.364	4.969
200	6.5050	6.5050	5.335	4.969
220	6.4970	6.4970	------------	4.970
240	6.4909	6.4910	------------	4.970
260	6.4867	6.4869	------------	4.971
280	6.4845	6.4847	------------	4.973
300	6.4840	6.4843	------------	4.975
320	6.4853	6.4858	------------	4.977
340	6.4884	6.4890	------------	4.980
356.58 (bp)	6.4922	6.4930	------------	4.983
360	6.4931	6.4940	------------	4.984
380	6.4993	6.5005	------------	4.988
400	6.5071	6.5087	------------	4.993
420	6.5164	6.5186	------------	4.999
440	6.5270	6.5298	------------	5.005
460	6.5390	6.5426	------------	5.013
480	6.5522	6.5567	------------	5.021
500	6.5666	6.5723	------------	5.030

[a] Triple point.

TABLE 5. *Entropy; relative free energy; vapor pressure*

Temperature	Absolute entropy		Relative free energy (liquid or vapor), $-(F-H_{TP(l)})$ (27)	Vapor pressure, P (35)
	Liquid, $S(l)$ (25)	Vapor, $S(g)$ (18)		
°*C Int.*	*cal g-atom*$^{-1}$ *deg*$^{-1}$	*cal g-atom*$^{-1}$ *deg*$^{-1}$	*cal g-atom*$^{-1}$	*mm* Hg
−38.88 [a] (tp)	16.5045	79.6736	3867.1	2.191(10^{-6})
−20	17.0267	75.3563	4183.4	2.336(10^{-5})
0	17.5367	71.4701	4529.0	1.996(10^{-4})
20	18.0088	68.1470	4884.4	1.268(10^{-3})
25	18.1215	67.3906	4974.7	1.935(10^{-3})
40	18.4480	65.2766	5248.9	6.340(10^{-3})
60	18.8584	62.7760	5622.0	0.026048
80	19.2436	60.5809	6003.2	.090954
100	19.6065	58.6409	6391.8	.27710
120	19.9494	56.9161	6787.6	.75213
140	20.2745	55.3742	7190.0	1.8499
160	20.5836	53.9894	7598.9	4.1795
180	20.8781	52.7401	8013.8	8.7734
200	21.1594	51.6086	8434.4	17.273
220	21.4286	50.5798	8860.6	32.147
240	21.6870	49.6414	9292.1	56.931
260	21.9351	48.7828	9728.6	96.481
280	22.1741	47.9949	10169.9	157.234
300	22.4045	47.2699	10615.9	247.413
320	22.6270	46.6013	11066.4	377.27
340	22.8421	45.9828	11521.2	559.22
356.58 (bp)	23.0153	45.5047	11901.4	760.00
360	23.0505	45.4098	11980.2	808.00
380	23.2525	44.8776	12443.1	1140.65
400	23.4486	44.3824	12909.9	1576.64
420	23.6391	43.9207	13380.4	2137.76
440	23.8246	43.4895	13854.6	2848.09
460	24.0051	43.0861	14332.2	3733.8
480	24.1812	42.7080	14813.2	4822.9
500	24.3529	42.3531	15297.5	6145.4

[a] Triple point.

2. Effects of Gas Imperfection and Temperature Scale

The values listed in tables 3, 4, and 5 contain contributions from the small terms (in the equations) that contain B, or its derivatives, or T and that thus correct for gas imperfection of mercury vapor and for the deviations between the thermodynamic and International temperature scales. When these contributions for a given property vary appreciably with temperature, they are listed separately in tables 6 and 7 for a number of temperatures. (Except for vapor pressure these are listed in the same units as the values in tables 3, 4, and 5.) The magnitudes of these contributions depend in most cases on the particular way in which the properties have been calculated in this paper, as well as on what basic data have been used. Consequently, they are not intrinsically characteristic of the properties themselves.

Table 3. There are no contributions to the relative enthalpy of the liquid, as the values used are those measured essentially directly. The contributions are hence identical for the relative enthalpy of the vapor and for the heat of vaporization. These are listed in tables 6 and 7.

Table 4. The three calculated heat capacities of the liquid have no contribution from gas imperfection. At a given temperature they have identical contributions from the temperature-scale correction, as listed in table 7. The contribution to $C_{p\,(g)}$ from gas imperfection is the deviation from 5/2 R (i. e., from 4.968 cal g-atom^{-1}deg^{-1}).

TABLE 6. *Contributions to thermodynamic properties from gas imperfection of mercury vapor*

Temperature	To $H_{(g)}-H_{TP(l)}$ and $H_{(g)}-H_{(l)}$	To $S_{(g)}$	To $-(F-H_{TP(l)})$	To vapor pressure
°*C*	*Cal g-atom*$^{-1}$	*cal g-atom*$^{-1}$ *deg*$^{-1}$	*cal g-atom*$^{-1}$	*Percent*
−38. 88	−13. 8	0. 0000	+5. 7	+1. 73
0	−13. 8	. 0000	+6. 7	+1. 31
40	−13. 8	. 0000	+7. 7	+0. 98
80	−13. 8	. 0000	+8. 6	+. 73
120	−13. 8	. 0000	+9. 6	+. 53
160	−13. 9	−. 0001	+10. 6	+. 37
200	−14. 0	−. 0003	+11. 6	+. 24
240	−14. 3	−. 0007	+12. 6	+. 14
280	−15. 1	−. 0015	+13. 5	+. 061
320	−16. 5	−. 0030	+14. 5	+. 015
356. 58	−18. 6	−. 0049	+15. 4	. 000
360	−18. 8	−. 0052	+15. 5	. 000
400	−22. 4	−. 0085	+16. 5	+. 021
440	−27. 8	−. 0129	+17. 4	+. 082
480	−35. 1	−. 0186	+18. 4	+. 18
500	−39. 7	−. 0218	+18. 9	+. 25

TABLE 7. *Contributions to thermodynamic properties from correction to thermodynamic temperature scale*

Temperature	To $H_{(g)}-H_{TP(l)}$ and $H_{(g)}-H_{(l)}$	To $C_{s(l)}$, $C_{p(l)}$, $C_{v(l)}$	To $-(F-H_{TP(l)})$	To vapor pressure
°*C*	*cal g-atom*$^{-1}$	*cal g-atom*$^{-1}$ *deg*$^{-1}$	*cal g-atom*$^{-1}$	*Percent*
−38. 88	+2. 0	+0. 0055	+1. 0	−0. 20
0	+1. 9	+. 0028	+0. 7	−. 47
49	+1. 8	+. 0004	+0. 6	−. 49
80	+1. 8	−. 0015	+0. 8	−. 43
120	+1. 9	−. 0029	+1. 1	−. 33
160	+2. 0	−. 0039	+1. 7	−. 23
200	+2. 2	−. 0044	+2. 3	−. 14
240	+2. 3	−. 0044	+3. 0	−. 077
280	+2. 4	−. 0039	+3. 6	−. 031
320	+2. 5	−. 0030	+4. 2	−. 006
356. 58	+2. 6	−. 0017	+4. 6	. 000
360	+2. 6	−. 0016	+4. 6	+. 002
400	+2. 6	+. 0003	+4. 8	−. 009
440	+2. 6	+. 0026	+4. 6	−. 035
480	+2. 4	+. 0054	+4. 1	−. 075
500	+2. 4	+. 0070	+3. 7	−. 100

Table 5. To the entropy of the liquid the contribution from gas imperfection is the same at all temperatures, +0.0245 cal g-atom^{-1}deg^{-1}. The contribution to the entropy from the temperature-scale correction is practically constant, being equal to +0.002 cal g-atom^{-1}deg^{-1} at all temperatures in the case of the liquid and not lying outside the range 0.000 to +0.001 in the case of the vapor. The other contributions to the entropy of the vapor, the free energy, and the vapor pressure are listed in tables 6 and 7.

VI. Discussion of Results

1. Reliability

An index to the reproducibility, or "precision", of the enthalpy measurements on liquid mercury is afforded by the deviations from the means, as shown by the results of the individual measurements, which are recorded in table 1. Another index is provided by the deviations (also listed in table 1) from the smoothed values as represented by the empirical equation adopted. All the results lead to an average probable error of the mean of about 0.02 percent on enthalpy, and a corresponding magnitude of about 0.1 percent on the derived heat capacity values ($C_{s(l)}$ or $C_{p(l)}$).

One check on the over-all accuracy of the apparatus in measuring enthalpy was made by measuring the heat delivered to the ice calorimeter by a Monel capsule containing water and dropping from 250° C. By thus determining in several measurements the difference in heats for two amounts of water differing by about 6 g, a mean value of 1042.05 abs j g^{-1} for $\alpha]_0^{250}$ of water, an enthalpy function defined elsewhere [23], was obtained. This figure differs by only 0.02 percent from the value of 1041.85 published in the latest report [24] on the thermal properties of water as accurately measured earlier in this laboratory by an adiabatic calorimeter.

The various sources of appreciable systematic error were examined in order to estimate their likely contributions. As measurements by the General Electric Co. [24a] of Nitralloy and of Swedish iron in mercury at various temperatures indicate a solubility of less than 1 part in 100,000,000 at 500° C, no error in the enthalpy should be caused by the dissolving of the container. Considering the uncertainty in each possible error, the authors believe that the values of the enthalpy of the liquid given in table 3 are accurate to 0.1 percent, except below 100° C, where small errors in measurement become relatively more important as 0° C is approached. As a consequence, it is believed that the corresponding uncertainties in the heat capacity values $C_{s(l)}$ and $C_{p(l)}$ (table 4) may be as large as 0.3 percent between 25° and 425° C. Outside this temperature range the values given should be considered much more uncertain, as they resulted from the extrapolation of an empirical function beyond the range of experimental measurements.

The calculated properties other than the enthalpy and heat capacity of the liquid are, as pointed out earlier in this paper, subject to varying uncertainties caused by uncertainties in the corrections for gas imperfection and temperature scale. The values in tables 6 and 7 should aid in estimating such uncertainties in specific cases. In many cases the difference between the values at two temperatures for a given property will be much more accurate than the listed absolute magnitude of the property itself.

The value of the absolute entropy as calculated here may be compared with that arrived at through use of low-temperature heat-capacity data for solid mercury. For liquid mercury at the triple point, for example, table 5 gives a value of 16.50 cal g-atom^{-1}deg^{-1}, based principally on vaporization data. If eq 19, representing the vapor pressure data of Beattie, Blaisdell, and Kaminsky [9], can be accepted as having an accuracy comparable to that which they claim, the entropy value just quoted should not be uncertain beyond a very few hundredths of a cal g-atom^{-1}deg^{-1}. This estimate includes the consideration of the aforementioned uncertainty in the extrapolated heat capacity of the liquid between 0° C and the triple point.

Pickard and Simon [25] have recently measured the heat capacity of solid mercury down to 3° K.

By using their data and those of others, the authors have computed a value of 14.34 cal g-atom^{-1}deg^{-1} for the entropy of solid mercury at the triple point. Addition of the entropy of fusion, 2.38 cal g-atom^{-1}-deg^{-1} [26, 27], gives a value of 16.72 for the liquid at the same temperature. This is 0.2 cal g-atom^{-1}-deg^{-1} higher than the value in table 5. The discrepancy seems to the authors as more likely due to errors in the low-temperature heat-capacity data than to any other source.

The effect of certain possible errors on the accuracy of vapor pressures as calculated by eq 35 will now be examined. As stated earlier, this equation has been adjusted to agree with the empirical eq 19 at, and in the immediate vicinity of, the normal boiling point, which both equations give as 356.58° C. (However, according to the experimental results on which eq 19 is based, there may be an absolute error of 0.01 deg in this temperature, corresponding to an error of 0.02 percent in the vapor pressure at any neighboring temperature.) Equation 19 gives values of vapor pressure at 350° and 362° C (temperatures near the extremes of the range of claimed validity of the equation) that are higher by 0.004 and 0.001 percent, respectively, than those given by eq 35. These divergences are within the precision of the data on which eq 19 is based.

The small uncertainty in the temperature assumed for the normal boiling point will affect all vapor pressures calculated from eq 35 by the same percentage. There are four other factors contributing significant uncertainty to these calculated pressures, and as the temperature becomes increasingly higher or lower than the boiling point, the effect of each of these four factors becomes acceleratingly greater. These factors are (1) degree of gas imperfection, (2) thermodynamic temperature scale, (3) heat of vaporization at the normal boiling point, and (4) average heat capacity of the liquid between the boiling point and the temperature in question. Taking the uncertainty in the last factor to be 0.3 percent, as estimated above, it was computed that the resulting uncertainties in the calculated vapor pressures would be as follows: At −39° C, 0.7 percent; at 100°, 0.15 percent; and at 250° or 500°, 0.02 percent. The assumption of these and reasonable uncertainties in each of the other factors has led to the assignment of the following uncertainties in individual values of vapor pressure calculated from eq 35 and listed in table 5: At −39° C, 1.5 percent; at 100°, 0.5 percent; at 250° or 500°, 0.2 percent; and at 357° (the boiling point), 0.03 percent. These figures were arrived at without consideration of agreement of the calculated vapor pressures with any direct measurements, except those represented by eq 19.

A number of investigators [28 to 33] have directly measured the vapor pressure of mercury in this temperature range. The deviations of most of the more precise of these experimental values from those given by eq 35 are shown in figure 1. In most of these measurements there was an average variation of several times the uncertainties just stated.

2. Comparison of Liquid Heat Capacity Values With Those of Other Experimental Investigations

A number of other investigators [34 to 47] have measured the heat capacity of mercury above 0° C. Most of these results are shown in figure 2 for comparison with the results reported in this paper. The experimental points labeled NBS were calculated by dividing by the temperature interval the differences in the mean unsmoothed experimental heats for pairs of successive furnace temperatures. A very small correction for curvature was applied.

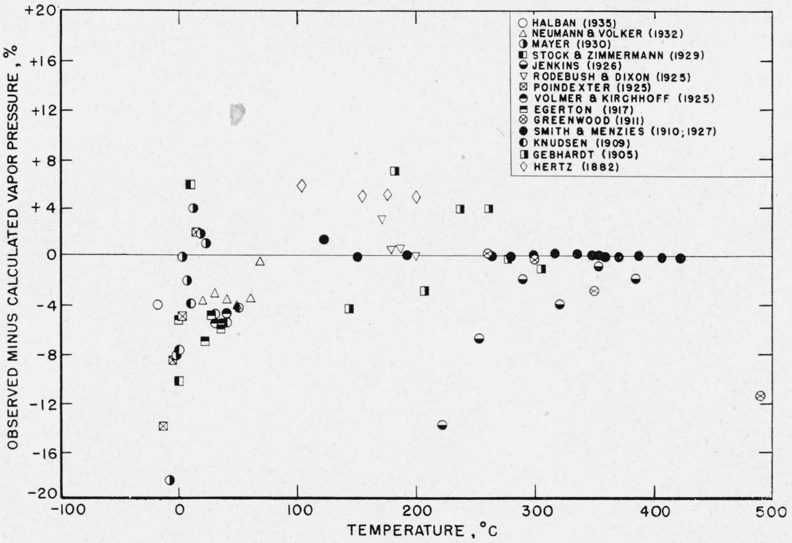

FIGURE 1. *Comparison between values of vapor pressure of mercury observed by various workers and values calculated from eq 35.*

To avoid confusion, only representative data of each worker are shown. The temperatures of Smith and Menzies have been corrected by table 8.

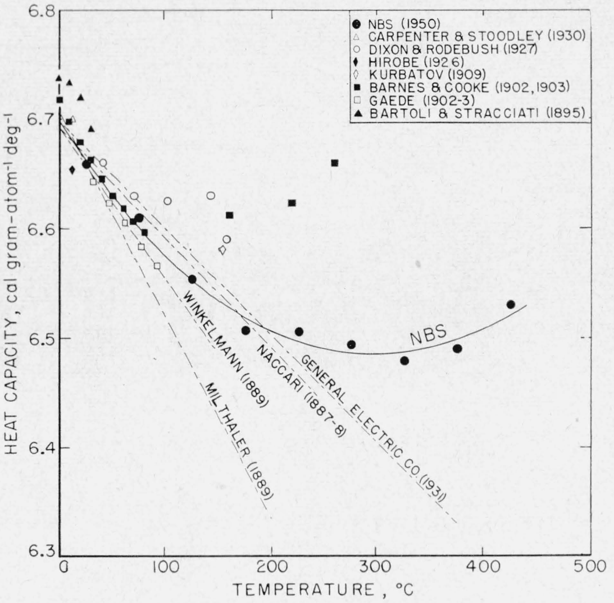

FIGURE 2. *Saturation heat capacity (C_s) of liquid mercury, as found by various investigators.*

Most observers are in substantial agreement below 100° C, but those who extended their measurements to higher temperatures show considerable disagreement. Gaede [42] employed an essentially adiabatic calorimeter; Hirobe [46] used an isothermal one; and Dixon and Rodebush [41], claiming an accuracy of approximately 1 percent, resorted to adiabatic compression. The observations of Milthaler [39], Naccari [37], and Winkelmann [38], all of whom employed the method of mixtures, agree approximately, as to a value of the negative temperature coefficient, with the later measurements of the General Electric Co. [45]. The measurements of Barnes and of Barnes and Cooke [34] were made, apparently, with considerable care by using a continuous flow method previously employed in measuring the specific heat of water. They considered their measurements below 100° to be accurate to 0.1 percent. However, above 150° their values differ markedly from those of all other observers, including the present authors. In spite of this difference, their values have often been considered by some in the past to have a reliability superior to the heat-capacity values of mercury of the other observers.

Recently Kleppa [48] has used an electronic pulse-circuit technique to measure ultrasonic velocities in mercury at 50° and 150° C, obtaining a precision of about 1 percent. When these velocities were combined with the coefficients of thermal expansion given by eq 13 and with the values of $C_{p\,(l)}$ interpolated from table 4, they gave values of $C_{v\,(l)}$ of 5.72 ±0.01 and 5.49 ±0.01 cal g-atom^{-1}-deg^{-1}, respectively, at these two temperatures. The corresponding values of $C_{v\,(l)}$ interpolated from table 4, based on the directly measured compressibilities of Smith and Keyes [8], are 5.68 and 5.43, respectively.

3. Isobaric and Isochoric Heat Capacities of the Liquid

The values of the heat capacities of the liquid C_p and C_v that are given in table 4 are represented graphically in figure 3 as multiples of the gas constant R. It is of interest that the curve for C_p shows a minimum at a temperature somewhat below the boiling point. This is analogous to the results obtained by the authors for two other liquid metals, sodium [3] and potassium [49], whose values of C_p were found to exhibit even deeper minima than mercury, and at temperatures somewhat below their respective normal boiling points.

It is well known that the theoretical interpretation of C_v is simpler than that of C_p. The curve for C_v of liquid mercury in figure 3, in contrast to that for C_p, shows no definite evidence of extrapolating to a minimum below the critical temperature, indicating that the distinct minimum in C_p is caused by the increasing difference between C_p and C_v as the temperature rises. (Though Smith and Keyes [8] measured the compressibility of mercury up to 300° C, their values above 200° show a very rapid and unexpected increase, which would lead to a minimum in the calculated curve for C_v above this temperature. However, they discredited their results above 200° because of invalidating experimental circumstances.)

It is of interest that the value of C_v calculated in this paper (table 4) for liquid mercury at its triple point is only 0.1 percent different from $3R$, which is the value predicted at this temperature by a recent fairly successful theoretical treatment of liquid mercury [50]. According to some recently published theories [51], a liquid exhibits a fairly continuous transition from the crystalline to the gaseous state as the temperature rises. The heat capacity C_v of a monatomic liquid, taken at small pressures, may be expected to vary from approximately $3R$ at the triple point and approach $\frac{3}{2}R$ near the critical point. The decrease in C_v as the temperature rises may be interpreted as being due to a decreasing contribution to disorderliness in the liquid. The curve for C_v of mercury shown in figure 3 is consistent with this picture.

4. Vapor Pressure

Near the normal boiling point, 357° C, the terms for gas imperfection have very little influence on the values calculated for the vapor pressure from eq 35. However, as pointed out in an earlier section, the effect is many times as great at much higher or lower temperatures. If the calculated vapor pressures at such temperatures agree with corresponding measured values, there is thus afforded an independent experimental check on the adopted value of the principal parameter determining the gas-imperfection corrections in the various equations for thermodynamic properties. This assumes, of course, that the experimental values of vapor pressure have sufficient accuracy and precision.

The vapor pressure of mercury has been measured by various workers [52] from the triple point to 1400° C. Though at very low and very high temperatures in this range the percentage accuracy of the vapor pressure measurements need not be very great, the precision of most of these results is so relatively poor as to exclude their use for this test.

In 1910 Smith and Menzies [53] carefully measured the vapor pressure of mercury from about 250° to 435° C with a precision of about ±0.1 percent. The temperatures were recalculated by Menzies [52] in 1927 on the basis of the new value for the sulfur boiling point. Menzies added three more experimental points between 120° and 200° C and derived the following equation to represent the data:

$$\log P = 9.957094 - \frac{3283.92}{\theta'} - 0.665240 \log \theta', \quad (42)$$

where

$$\theta' = t' + 273.1, \quad (43)$$

t' being deg C Int as measured by the platinum thermometer of Smith and Menzies.

The authors have recalculated Menzies' centigrade temperatures, as given by eq 43, in accordance with the present knowledge of the platinum-thermometer scale. Smith and Menzies [54] had reported for their thermometer a δ value of 1.6147, on the basis of their assumed sulfur boiling point of 445° C. Correcting this to the basis of the temperature assumed by Menzies in 1927, 444.6°, yields a value of δ of 1.5919. Equation 42 gives a mercury normal boiling point of 356.711° C, which is 0.13 deg higher than reported by Beattie, Blaisdell, and Kaminsky [9]. Waidner and Burgess [55] and Beattie, Blaisdell, and Kaye [56] have found independent evidence that a platinum thermometer accurately calibrated at the ice, steam, and sulfur points indicates for the mercury boiling point a temperature depending fairly systematically on the δ value of the thermometer. In fact, Beattie et al. have argued that by adding the mercury boiling point as a fourth calibration point and using a cubic temperature-resistance relation, the platinum-thermometer scale will be approximately independent of the thermometer constants.

This recommendation has been followed here. A cubic temperature-resistance equation has been derived that gives the same temperatures for the ice, steam, and sulfur points but a value of 356.58° C. for the mercury boiling point when there are substituted the resistances given for these four temperatures by a Callendar equation with $\delta = 1.5919$, and with the mercury boiling point taken as 356.711° C. Equating the resistances given by the two equations indicates that the Centigrade temperatures given by eq 42 should be changed by the amounts shown in table 8 to accord with a four-point calibration. Though a fourth calibration point is obviously, in itself, an asset toward greater accuracy, it is believed that considerably more uncertainty should be attached to the interpolations of temperature provided by a thermometer with such a high δ value than to those by thermometers meeting present-day standards.

After correcting the Centigrade temperatures of eq 42 by the values of table 8, figure 4 was obtained for the differences between the experimental vapor pressures of Smith and Menzies and those calculated from eq 35. The four curves represent the differences obtained depending on what dissociation energy is made the basis of calculating the gas-imperfection terms in the latter equation. This equation has been derived to give the experimentally measured normal boiling point regardless of the magnitudes of the gas imperfections assumed. For a range of 200 deg below the boiling point, the best agreement between experimental and calculated vapor pressures is seen to correspond to a gas imperfection equivalent to a dissociation energy of 1.5 kcal mole^{-1} of Hg$_2$. This value was claimed earlier in this paper to be a reasonable weighted mean of those indicated by independent spectroscopic evidence. However, in view of the smallness of the

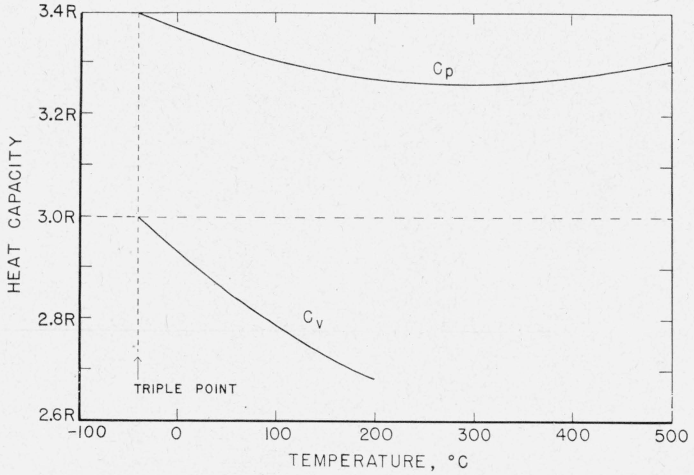

FIGURE 3. *Heat capacities of liquid mercury at constant pressure and constant volume.*

deviations of figure 4 and the uncertainties in some of the small corrections applied to both experimental and calculated vapor pressures, the agreement may be somewhat fortuitous.

Table 8. *Correction of temperature values of a platinum thermometer with $\delta = 1.5919$ to accord with a four-point calibration in which the mercury boiling point is changed from 356.711° to 356.58° C*

Temperature	Correction
°C Int.	*°C Int.*
100	0.000
150	−.033
200	−.076
250	−.115
300	−.138
330	−.140
356.58	−.131
400	−.089
430	−.034
444.6	.000

It will be noted that above the boiling point all four curves indicate lower experimental than calculated vapor pressures. This may be attributed quantitatively, in large part, to the fact that as the temperature rises the saturated vapor becomes denser, and as a result the empirical eq 42, derived to fit the data well near the boiling point and at lower temperatures, is too simple to represent the increasing importance of gas imperfection and liquid volume.

The ordinate differences in figure 4 are of the same order of magnitude as the absolute uncertainties assigned in an earlier section to the vapor pressures calculated from eq 35. However, the several factors named there as affecting the accuracy of this equation have effects that vary in roughly comparable ways with temperature. Therefore, errors in the adopted magnitudes of their effects on the calculated vapor pressures at various temperatures would be capable of being compensated considerably by the choice of a single somewhat erroneous value for the dissociation energy of Hg_2 for calculating the effects of gas imperfection. It is thus possible that the choice of 1.5 kcal per mole (made partly on the basis of the apparent agreement in fig. 4 between observed and calculated vapor pressures when this value is selected) is of this nature.

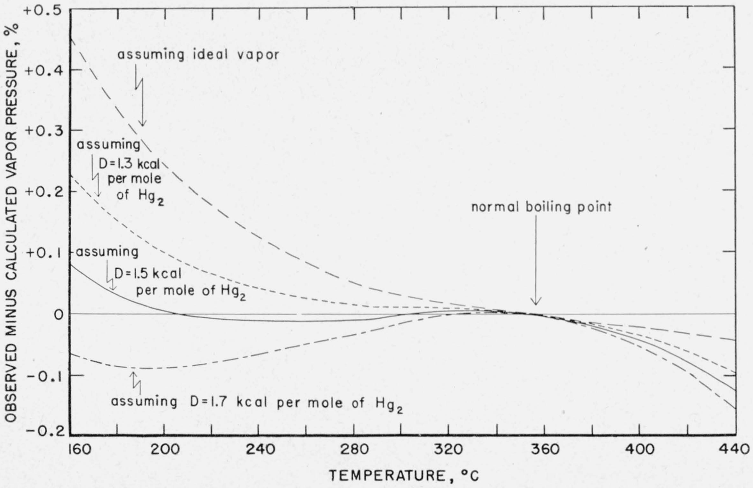

Figure 4. *Comparison between observed vapor-pressure values of Smith and Menzies (corrected to present temperature scale) and values calculated from eq 35, taking as a parameter several degrees of gas imperfection.*

Nevertheless, it is believed that the comparison afforded by figure 4 provides confirmatory evidence that the values of dissociation energy and second virial coefficient of mercury that were selected in this paper are not far from the correct ones. That this comparison between observed and calculated vapor pressures has such significance is due in no small degree to the accuracy of the experimental values of liquid heat capacity recently measured and reported in this paper. For a given temperature, an error in the heat capacity produces an approximately proportional error in the vapor pressure calculated in this manner. The previously available heat capacity values, because of their disagreement in the region above and below the boiling point, would no doubt have been considered up to 10 times as uncertain. Therefore had it been necessary to rely on these previous values, the relatively small differences of such a comparison graph as figure 4 would have had very much less significance.

The heat-capacity measurements were greatly expedited by the commendable cooperation of Leo F. Epstein and his associates, of the Knolls Atomic Power Laboratory, Schenectady, N. Y. Under his direction the mercury samples were painstakingly prepared and supplied in a state of very high purity and ready for the thermal measurements. Collaborating with him in this work were L. W. Hibbs, Jr., who purified the mercury, filled and sealed the containers, and tested them; George Strichman, who tested the containers for tightness; and R. E. Schofield, who performed the mass-spectrometer analyses.

The authors express their special indebtedness also to certain members of this Bureau. B. F. Scribner and his associates performed a spectrochemical

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