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## A Partition Function for Liquid Mercury

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From a model for liquid mercury we have formulated a partition function of sufficient generality to give by means of the usual statistical mechanical equations the vapor pressure, the equation of state, the entropy of melting and the specific heats. The partition function involves four parameters characterizing the particular substance concerned. Having chosen these parameters for mercury it is possible to calculate all the above properties from the melting point to the boiling point within experimental

error except for a slight divergence of about 2 percent (0.1 cal./mole/degree) in the specific heat at the melting point. The van der Waals' constants follow from the theory and when employed in his equation give satisfactory agreement between calculated and observed critical properties. The long liquid range, low melting point, and low viscosity of metals are all in agreement with our model in which it is assumed that in the liquid the kernels move independently of their valence electrons.

### INTRODUCTION

WE are here concerned with developing and applying a simple model for liquids which will lead to a partition function sufficiently general for all the thermodynamic properties to be derived from it. We use the conception of a free volume, in which liquid molecules move, developed in earlier papers from this laboratory,<sup>1-3</sup> but suitably modified to take account of the temperature coefficient of the volume available to the molecules. This makes an important addition to the free volume, and is of even greater importance in calculations of the specific heats. We have chosen mercury as our test liquid for two reasons. First because there is adequate experimental data and second because it appeared anomalous in the earlier treatment of Eyring and Hirschfelder.

The partition function derived below may be expected to apply to close-packed monatomic liquids, e.g., many of the liquid metals and perhaps the rare gases near their melting points. The essential postulates may be stated as follows. The total energy (in excess of the zero-point energy) may be divided into two parts: first, the kinetic and potential energy of displacements from the equilibrium positions, and second the potential energy that the liquid would have if the atoms remained static in their mean positions. For lack of better names we will call the first the

dynamic and the second the static energy. The static energy is assumed to be a function of volume only, while the dynamic energy is chiefly a function of temperature, but also has volume dependence.

The dynamic energy at sufficiently low temperatures is assumed for simplicity to be that of a simple harmonic vibrator. As the temperature is raised and the liquid expands a flat space of zero potential energy is introduced into the curve, the extent of which is governed by the amount of expansion. This behavior may be seen in Fig. 1. It may be observed that the extent of the flat space in the curve determines the ratio of kinetic to potential energy, and that thus this ratio is unity at low temperatures and increases as the temperature is raised at any particular pressure. Both the characteristic frequency of vibration, and the flat space in the potential curve are functions of pressure of course, but in what follows the variation of the frequency with pressure has been assumed to be sufficiently small to be neglected.

### Fusion

Hirschfelder, Stevenson and Eyring<sup>3</sup> have discussed the process of fusion and the entropy of melting from essentially this point of view. On their picture of melting the volume of the liquid at the melting point is just great enough so that if a hole appears in the liquid a molecule in a neighboring position can slip into the hole without appreciable activation energy. That this is not true for the solid is indicated by its high viscosity. Thus a body-centered solid lattice

<sup>1</sup> Roy F. Newton and Henry Eyring, *Trans. Faraday Soc.* **33**, 73 (1937).

<sup>2</sup> Henry Eyring and J. O. Hirschfelder, *J. Phys. Chem.* **41**, 249 (1937).

<sup>3</sup> J. O. Hirschfelder, D. P. Stevenson and Henry Eyring (To be submitted).

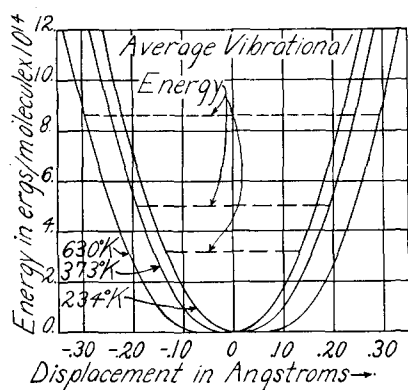


FIG. 1. Potential energy function for displacements from equilibrium position.

composed of incompressible atoms should melt to a liquid of somewhat similar structure having a volume about 20 percent greater than that of the solid at the absolute zero. Since the atoms are compressible, and liquids at the melting point are only quasicrystalline, the observed volume will generally be somewhat smaller than this. The most important term arising in the calculation of the entropy of melting of mercury is the contribution,  $R$ , arising from the fact that in the liquid the entire volume is jointly used by the molecules whereas in the solid each molecule is restricted to its own small region in the lattice.

We may think of this mechanism of melting in the following way. Thus we think of a perfect crystal as a single supermolecule whereas the perfect liquid at the melting point results from its complete dissociation. This complete dissociation with its resultant communal sharing of the total free volume among the molecules increases the entropy by  $R$ . This we call the communal entropy. This communal entropy of melting of the perfect solid into the perfect liquid may be further modified by volume changes accompanying melting as well as by changes in the rotation of individual molecules. Another not unusual situation is that the process of melting leads to double molecules so that the increase due to communal entropy is only  $(\frac{1}{2})R$  with more or less complete compensation of this lowered value arising from the new rotational degrees of freedom of the double molecules. Melting into other types of liquid molecules leads to still other obvious modifications. The breaking of these structures above the melting point provides an expla-

nation for the frequently observed slightly large specific heats we discuss later.

Supercooling, on the other hand, results in the appearance of molecular aggregates which do not readily rearrange into the perfect crystal. Inside the aggregates the communal entropy has been lost, whereas the aggregates themselves still share their free volume and so retain a portion of the communal entropy which, however, gradually disappears with further aggregation. The interior of these aggregates when acted upon by a shearing stress will suffer the characteristic plastic deformation of crystals whereas the aggregates themselves will obey the usual laws of viscous flow and will show the usual high viscosity always associated with large molecules. The energy of activation for viscous flow for the non-metals is usually about one-third the heat of vaporization.<sup>4</sup> Since any rate process always proceeds simultaneously by all possible mechanisms and therefore principally by the faster ones we expect a glass to exhibit both entropies and viscosities, which depending on the state of aggregation, take all the intermediate values, between the perfect liquid and the perfect solid.

We now consider the peculiarly low activation energy for viscous flow of metals. Since the activation energy has been related by Hirschfelder, Stevenson and Eyring<sup>3</sup> to a hole approximately one-third the size of the molecule we immediately suspect that the particle which flows must be smaller than the atom which vaporizes. This seems highly reasonable from several points of view. First, since the high electrical conductivity of metals indicates that the conducting electrons can flow without the atomic kernels it seems clear that the kernels can undergo the slight displacements necessary to provide the small holes for viscous flow or diffusion without disturbing the electrons. Secondly, since the small kernels do the diffusing (into holes when they appear) the liquid will not need to be nearly as expanded at the melting point as if the whole atom moved as a unit. Thus because of the abnormally small expansion of the metals we should expect abnormally low melting points. This will then lead to an abnormally long liquid range since the vapor, being composed not of kernels but of

<sup>4</sup> H. Eyring, J. Chem. Phys. **4**, 283 (1936).

normal atoms, will possess a normal boiling point. Stated more tersely, the abnormally long liquid range for metals is explained if we assume that the kernels melt while the atoms vaporize. This is exemplified by gallium which, although it melts at a temperature just above room temperature has a liquid range of about 2000° whereas the typical nonmetal melting in the same range will in general have a liquid range of 100° or less.

Our model for the metals is thus consistent with the considerations on cohesion presented by Mott and Jones<sup>5</sup> who, "picture these metals as composed of hard spheres (the ions) held together by the Coulomb attraction between the ions and the valence electrons." Simon,<sup>6</sup> Schubert<sup>7</sup> and Mott<sup>8</sup> have considered the problem of conductivity in liquid metals. Mott gives the equation

$$\frac{\sigma_L}{\sigma_S} = \exp \left( -\frac{2}{3} \frac{\Delta S}{R} \right), \quad (1)$$

which agrees with experiment for a number of the metals;  $\sigma_L$  and  $\sigma_S$  are the conductivity of liquid, conductivity of solid, and entropy of melting respectively. Although this relationship has been derived by assuming that the entire change in entropy arises from the greater amplitude of the characteristic frequency of the liquid, we expect an increase in randomness arising from the communal entropy to have a similar effect in that it too provides a larger electronic target area. A model essentially of the type used in this paper seems necessary from the other considerations developed below.

### The partition function

We may now formulate the partition function based on the qualitative arguments given above. The partition function for a monatomic molecule may be written as

$$f(T) = \frac{(2\pi mkT)^{\frac{1}{2}} V_f}{h^3} \exp(E(V)/RT),$$

where  $E(V)$  denotes the expression for the static energy as a function of volume, a function to be discussed later, and  $V_f$  is the total free volume available to the molecule. Now since we picture the liquid as being composed of vibrating particles which are not necessarily confined to particular lattice positions,  $V_f$  is equal to  $Nv_f$ ,  $v_f$  being defined in terms of the potential curve, illustrated in Fig. 1, for displacements of a single molecule from its equilibrium position.

In order to secure the free volume per molecule,  $v_f$ , an explicit expression for the magnitude of the space of zero potential energy must be obtained. Following Hirschfelder and Eyring<sup>2</sup> we have

$$2(V/N)^{\frac{1}{3}} - 2(V_0/N)^{\frac{1}{3}}$$

where  $V_0$  is the volume of the liquid at some reference temperature and  $V$  is its volume at a point where it has expanded somewhat thus, introducing the flat space into the curve shown in Fig. 1. Both  $V_0$  and  $V$  are considered at the same pressure. The complete expression for  $V_f$  is then

$$V_f = Nv_f = N \left[ 2 \int_0^\infty \exp(-1/2fx^2/kT) dx + 2(V/N)^{\frac{1}{3}} - 2(V_0/N)^{\frac{1}{3}} \right]^3, \quad (2)$$

where  $f$  is defined by,  $\nu = 1/2\pi(f/m)^{\frac{1}{2}}$ . On carrying out the integration and rearranging,  $V_f$  becomes

$$V_f = N \left[ \frac{kT/h\nu}{(2\pi mkT)^{\frac{1}{2}}/h} + 2(V/N)^{\frac{1}{3}} - 2(V_0/N)^{\frac{1}{3}} \right]^3 \quad (3)$$

accordingly,

$$f(T) = N \left[ \frac{kT}{h\nu} + \frac{(2\pi mkT)^{\frac{1}{2}}}{h} 2((V/N)^{\frac{1}{3}} - (V_0/N)^{\frac{1}{3}}) \right]^3 \exp(E(V)/RT). \quad (4)$$

<sup>5</sup> Mott and Jones, *Properties of Metals and Alloys* (Oxford Press), p. 144.

<sup>6</sup> Simon, *Zeits. f. Physik* **27**, 157 (1924).

<sup>7</sup> Schubert, *Physik. Zeits. Sowjetunion* **5**, 83 (1934).

<sup>8</sup> N. F. Mott, *Proc. Roy. Soc. A* **146**, 465 (1934).

We are now in a position to discuss the entropy of fusion, and the closely allied subjects, the specific heats at constant volume and pressure,  $C_V$  and  $C_P$ . We have for the liquid

$$S - S_0 = k[\ln(f(T)/N)^N + N] + \bar{E}/T \quad (5)$$

and for the solid

$$S - S_0 = k \ln \kappa(T) + \bar{E}_s/T, \quad (6)$$

where  $\kappa(T)$  is defined by

$$\kappa(T) = (kT/h\nu_s)^{3N} \exp(E_s(V)/kT) \quad (7)$$

and

$$\bar{E} = NkT^2(d/dT) \ln f(T), \quad (8)$$

$$\bar{E}_s = kT^2(d/dT) \ln \kappa(T). \quad (9)$$

Then if we define the characteristic temperature,  $\Theta$ , in the usual way,

$$\Theta = h\nu/k \quad (10)$$

we have

$$\Delta S_f = -1/2R + 3R \ln \left[ \frac{\Theta_s}{\Theta_l} + 2 \left( \frac{2\pi mk}{h^2 T} \right)^{1/2} \frac{\Theta_s}{(N)^{1/2}} (V^{1/3} - V_0^{1/3}) \right] \\ + 3RT \frac{1 + 4/3(1/N)^{1/2}((2\pi mkT)/h^2)^{1/2} \Theta_l (\alpha_l V^{1/3} - \alpha_s V_s^{1/3})}{2T + 4((2\pi mkT)/h^2)^{1/2} \Theta_l (1/N)^{1/2} (V^{1/3} - V_0^{1/3})}, \quad (11)$$

where  $\alpha \equiv (1/V)(\partial V/\partial T)_P$ .

Of the many methods of securing characteristic temperatures for solids Debye's specific heat formula provides the most consistent values. It is justifiable to use Debye's characteristic temperature in the classical vibrational partition function given above since his partition function reduces to the classical form at temperatures high compared to  $\Theta$ . Since for mercury,  $T_m$  is 234°K while  $\Theta$  is only 84°K, the value of Debye's  $\Theta$  chosen so as to give the correct thermodynamic properties for the solid at the melting point is the proper quantity to use in the classical vibrational partition function.

Given the value for the characteristic temperature for the solid at the melting point several alternative methods are open for the computation of entropies of fusion. Since we wish to find as nearly the correct model as possible these will be inspected and the one most consistent with experiment will be chosen as most nearly representing the true state of affairs. Hirschfelder, Stevenson and Eyring<sup>3</sup> have taken  $\Theta_l$  equal to  $\Theta_s$  and  $V_0$  equal to the volume of the solid at the melting point. Calculations for the monatomic metals where the data were available gave values for  $\Delta S_f$  consistently too high by about half an entropy unit. The model may be changed to take care of this discrepancy in a number of ways. A better

approximation to the dynamic energy function might be secured by allowing the characteristic temperature for the liquid to be an adjustable parameter to be fixed by the entropy of fusion. Thus they found that if  $\Theta_l$  were taken as 1.1  $\Theta_s$  excellent agreement was obtained for the metals considered. Agreement might also be secured by taking  $\Theta_l = \Theta_s$  and making  $V_0$  a parameter. Finally  $V_0$  might be taken equal to the volume of the liquid at the melting point, the necessary flexibility being secured by again making  $\Theta_l$  adjustable. A decision between these alternatives was made by considering the specific heat at constant volume at the melting point. The observed value is 6.06 cal./mole/degree. The first alternative gives 5.39, the second 5.56, and the third 3R or 5.96 cal./mole/degree. Obviously, only the last mechanism can be consistent with both the entropy of fusion and the specific heat. It should be noted that it is also the most consistent with our picture of the melting process since we have assumed a quasicrystalline structure for the liquid at the melting point. The value for  $\Theta_l$  of 79 as compared to 84 for the solid gives the experimental entropy of fusion of 2.38 E.U.<sup>9</sup> A decrease in  $\Theta$  on going from solid to liquid is

<sup>9</sup> K. K. Kelley, Bulletin 393, Bur. Mines, 1936.

also more reasonable than an increase since one would expect the vibrations in the liquid to be less stiff than those in the solid.

### Specific heats

An independent check of the assumptions we have made is afforded by the variation of the specific heats with temperature.  $C_V$  is given by—

$$C_V = \left( \frac{\partial E}{\partial T} \right)_V = 3R \frac{[T^{1/2}/\theta + \frac{1}{2} 1.9281(V^{\frac{1}{3}} - V_0^{\frac{1}{3}})]}{[T^{1/2}/\theta + 1.9281(V^{\frac{1}{3}} - V_0^{\frac{1}{3}})]^2} + \frac{3R[T^{1/2}/\theta 1.9281(V^{\frac{1}{3}} - V_0^{\frac{1}{3}})]}{8[T^{1/2}/\theta + 1.9281(V^{\frac{1}{3}} - V_0^{\frac{1}{3}})]^2} \quad (12)$$

where  $2(2\pi mk)^{1/2}/hN^{5/6}$  has been replaced by its numerical value of 1.9281.  $C_p$  was secured from the thermodynamic formula:

$$C_p = C_V + (T\alpha^2 V)/\beta, \quad (13)$$

where values of  $\beta$ , defined by  $-(1/V)(\partial V/\partial P)_T$ , were secured as outlined below and  $\alpha$  was evaluated from the equation given in the *International Critical Tables*.  $C_p$  rather than  $C_V$  was selected for direct comparison with experiment because the  $\beta$  values for temperatures above room temperature used in formula (13) were evaluated with the aid of the theory outlined below. It is believed, however, that the error introduced in the computation of the term,  $T\alpha^2 V/\beta$ , is quite small. The calculated results are compared with experiment in Table I and in Fig. 2. It may be noted that the minimum in the calculated curve comes at just the same place as that in the observed one.

The agreement is all that could be expected, the region near the melting point being the only one where the discrepancy is definitely greater than the experimental error. That fact in itself is of some interest. It will be recalled that the observed value for  $C_V$  of the liquid at the melting point was 6.06. Now  $3R (= 5.96)$  is the highest value

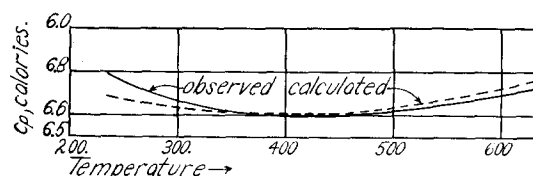


FIG. 2. Calculated and observed molal specific heats of mercury.

that can be secured by using simple harmonic potential curves. Since it is not likely that 0.10 cal./mole/degree is contributed to  $C_V$  by electronic terms the discrepancy must be due to a more complicated structure in the liquid than the homogeneous form we have assumed for it here. Any association of the liquid will change with temperature in such a way as to absorb more heat near the melting point than the simple structure assumed. This effect has been considered by Simon,<sup>10</sup> by Bernal<sup>11</sup> and by Hirschfelder, Stevenson and Eyring.<sup>3</sup>

It is interesting to note that even though the treatment we are using can be expected to hold best at temperatures below the boiling point the general form of the  $C_V$  against  $T$  curve is very similar to that given by Bauer, Magot, Surdin<sup>12</sup> for a number of monatomic liquids. Also by taking a reasonable value for the volume at the critical point a value for  $C_V$  of about 3.7 is obtained at that temperature. Although the specific heat at constant volume at the critical temperature is not known for mercury this value is in agreement with the values for the few monatomic liquids for which this experimental value is available.

This method gives a means of computing specific heats at constant volume from a knowledge of the entropy of fusion, and the volume of the liquid, the results being, for mercury at least, in excellent agreement with experiment. Specific heats under pressure may also be obtained provided the volume is known. Although the change of  $C_V$  with pressure may be obtained thermodynamically a second derivative is necessary, and pressure data are rarely of sufficient accuracy to make this procedure possible. Bridgman<sup>13</sup> has,

<sup>10</sup> *Ergebn. exakt. Naturwiss.* **9**, 248 (1930); *Zeits. f. anorg. allgem. Chemie* **203**, 219 (1931).

<sup>11</sup> *Trans. Faraday Soc.* **33**, 27 (1937).

<sup>12</sup> E. Bauer, M. Magot and M. Surdin, *Trans. Faraday Soc.* **33**, 81 (1937).

<sup>13</sup> P. W. Bridgman, *Proc. Am. Acad.* **47**, 347 (1912).

TABLE I. Observed and calculated specific heats.

| $T^\circ$ | $C_V$ (calc.) | $C_p$ (calc.) | $C_p$ (obs.) |
|-----------|---------------|---------------|--------------|
| 234       | 5.96          | 6.69          | 6.79         |
| 273       | 5.84          | 6.65          | 6.72         |
| 293       | 5.78          | 6.63          | 6.67         |
| 373       | 5.63          | 6.62          | 6.60         |
| 473       | 5.47          | 6.61          | 6.60         |
| 573       | 5.36          | 6.70          | 6.67         |
| 630       | 5.32          | 6.76          | 6.72         |

however, estimated  $C_V$  for liquid mercury at 0° and 7000 atmos. He finds that over this pressure range  $C_V$  increases by 0.121 cal./mole/degree. Substitution of the volumes into Eq. (12) gives 0.114 cal./mole/degree, a value which is probably within the error of the thermodynamic computation.

### Compressibilities and vapor pressures

In order to consider compressibilities and vapor pressures a form must be chosen for the function,  $E(V)$ , giving the static energy of the liquid as a function of volume. Since there is as yet no complete theoretical basis for choosing any particular form, the decision must finally be made on an empirical basis. However, quantum mechanics shows that the repulsive potential terms arising from exchange forces for pairs of molecules fall off exponentially with the distance between the nuclei. Further, Gibson<sup>14</sup> has used an exponential equation to accurately represent the volume of water and aqueous solutions as a function of pressure. Since an exponential term in the equation of state can arise only if such a term occurs in the form for the static energy an expression of

the kind  $E(V)=f(V)+d \exp (-c V^{\frac{1}{3}})$  is indicated where  $d$  and  $c$  are constants and  $f(V)$  is the attractive part of the static potential. Reasoning again from the case for a pair of molecules the attractive part of the energy,  $f(V)$ , was assumed to be given by  $1/V^m$ .

Hildebrand<sup>15</sup> has found that when  $m$  is set equal to one the expression gives a good representation of the energy of liquids that are not sufficiently close packed for the repulsive forces to be important. Further it will be recalled that the partition function corresponding to van der Waals' equation is

$$f(T)=(2\pi mkT)^{\frac{1}{2}}/h^3(V-b) \exp (a/VRT), \quad (14)$$

in which the static energy term is of the form  $a/V$ . These two considerations, we believe, justify the use of the form  $a/V$  for the attractive part of the static energy. A check is provided by the fact that if the considerations given above are valid the numerical value for the constant,  $a$ , as determined for the liquid should be essentially the same as that for van der Waals'  $a$ . This point will be discussed in detail later. The complete form for  $E(V)$  is then:

$$E(V)=a/V-d \exp (-CV^{\frac{1}{3}}) \quad (15)$$

and the partition function becomes

$$f(T)=(2\pi mkT)^{\frac{1}{2}}/h^3 N[(kT/h\nu)/(2\pi mkT)^{\frac{1}{2}}/h+2(V/N)^{\frac{1}{3}}-2(V_0/N)^{\frac{1}{3}}]^3 \exp (E(V)/RT). \quad (16)$$

The vapor pressure follows from free energy considerations. The free energy of the liquid is given by

$$A(\text{liquid})=kT \ln \frac{[(2\pi mkT)^{\frac{1}{2}}/h^3 N((kT/h\nu)/(2\pi mkT)^{\frac{1}{2}}/h+2(V/N)^{\frac{1}{3}}-(V_0/N)^{\frac{1}{3}})]^{3N}}{N^N \exp (-N)} +E(V), \quad (17)$$

while that of the gas is

$$A(\text{gas})=kT \ln \frac{[(2\pi mkT)^{\frac{1}{2}}V_g]^N}{N^N \exp (-N)}. \quad (18)$$

$$\text{But} \quad A(\text{gas})-A(\text{liquid})=RT. \quad (19)$$

These relations lead to an explicit expression for the vapor pressure if  $V_g$  is replaced by the ideal gas expression,  $RT/P$ . We have

$$\frac{1}{P(\text{mm})}=\frac{4.8679}{T} \left[ \frac{T^{\frac{1}{3}}}{\theta}+1.9281(V^{\frac{1}{3}}-V_0^{\frac{1}{3}}) \right]^3 \times \exp (E(V)/RT). \quad (20)$$

<sup>14</sup> R. E. Gibson, J. Am. Chem. Soc. **56**, 4 (1934).

In assuming mercury vapor to be ideal and monatomic we are not in agreement with some

TABLE II. *Compressibilities and vapor pressures for mercury at atmospheric pressure.*

| $T^\circ$ | $P$ (calc.)              | $P$ (obs.)               | $\beta$ (calc.)       | $\beta$ (obs.)        | $dV_0/dP$             |
|-----------|--------------------------|--------------------------|-----------------------|-----------------------|-----------------------|
| 234       | $2.01 \times 10^{-8}$ mm | $1.99 \times 10^{-8}$ mm | $3.79 \times 10^{-8}$ |                       | $56.0 \times 10^{-6}$ |
| 273       | $1.89 \times 10^{-4}$    | $1.88 \times 10^{-4}$    | 4.01                  | $3.93 \times 10^{-8}$ | 56.2                  |
| 293       |                          |                          | 4.11                  | 4.08                  | 56.0                  |
| 373       | 0.269                    | 0.269                    | 4.54                  |                       | 55.9                  |
| 473       | 17.00                    | 17.02                    | 5.09                  |                       | 56.0                  |
| 573       | 244.8                    | 245.4                    | 5.72                  |                       | 56.8                  |
| 630       | 760.0                    | 760.0                    | 6.13                  |                       | 57.5                  |

<sup>15</sup> J. H. Hildebrand, *Solubility*, second edition (Reinhold Publishing Corporation, 1936).

investigators. Thus, Kelley<sup>16</sup> from free energy considerations concludes that 7 percent of the vapor pressure of mercury at its boiling point is due to diatomic mercury molecules. It should be noted, however, that the vapor pressure calculated from Kelley's free energy data are not consistent with his recommended best values even in the range where no diatomic mercury molecules are supposed to exist. Further, Smith and Menzies<sup>17</sup> have found the density of mercury vapor to be ideal in the range of vapor pressures from one to two atmospheres to within the probable experimental error, about 2 percent.

Two of the three arbitrary constants in  $E(V)$  were adjusted to fit the observed vapor pressures, and the third was determined from the compressibilities by a process to be described below.

The resulting expression for the static energy in cc atmospheres is

$$E = (11.173 \times 10^6) / V - 2.346 \times 10^{13} \exp(-7.80 V^{1/3}).$$

The observed and calculated values are shown in Table II, the observed values being those recommended by Kelley.<sup>16</sup> The agreement is well within the probable experimental error of the observed values and is unusually good for a two constant equation.

The equation of state is given by the relation

$$P = RT \left( \frac{\partial \ln f(T)}{\partial V} \right)_T \quad (21)$$

and we find

$$PV^{1/3} - \frac{RT \cdot 1.9281 [1 - (V/V_0)^{1/3} (\partial V_0 / \partial P)_T / (\partial V / \partial P)_T]}{T^{1/3} \Theta + 1.9281 (V^{1/3} - V_0^{1/3})} + \frac{a}{V^{4/3}} = \frac{cd}{3} \exp(-cV^{1/3}) \quad (22)$$

and if  $[1 - (V/V_0)^{1/3} (\partial V_0 / \partial P)_T / (\partial V / \partial P)_T]$  is considered independent of  $P$ ,

$$\beta = V^{1/3} \left\{ (4/3) \frac{a}{V^{5/3}} - \frac{c^2 d}{9} \exp(-cV^{1/3}) - \frac{RT(1.9281)^2 [1 - (V/V_0)^{1/3} (\partial V_0 / \partial P)_T / (\partial V / \partial P)_T]^2}{3[T^{1/3} \Theta + 1.9281 (V^{1/3} - V_0^{1/3})]^2} \right\}^{-1} \quad (23)$$

We have also neglected  $(\partial \Theta / \partial P)_T$  since from the behavior of this quantity for the solid we expect it to be small. At low volumes and temperatures, i.e., for the supercooled liquid the term becomes important but since mercury does not form a glass we need not consider this point further at this time.

TABLE III. Compressions of liquid mercury at 0° and 20°.

| P        | 0°        |          | 20°       |          |
|----------|-----------|----------|-----------|----------|
|          | V (calc.) | V (obs.) | V (calc.) | V (obs.) |
| 1 atmos. | 14.755    | 14.755   | 14.808    | 14.808   |
| 1,000    | 14.698    | 14.698   | 14.748    | 14.749   |
| 2,000    | 14.643    | 14.643   | 14.689    | 14.691   |
| 3,000    | 14.588    | 14.588   |           |          |
| 4,000    | 14.535    | 14.536   | 14.579    | 14.583   |
| 5,000    | 14.485    | 14.486   |           |          |
| 6,000    | 14.437    | 14.438   | 14.479    | 14.483   |
| 7,000    | 14.392    | 14.392   |           |          |
| 8,000    |           |          | 14.392    | 14.391   |
| 10,000   |           |          | 14.314    | 14.309   |

<sup>16</sup> K. K. Kelley, Bull. 383, Bur. of Mines (1935).

<sup>17</sup> A. Smith and A. W. C. Menzies, J. Am. Chem. Soc. **32**, 1541 (1910).

The term,  $(\partial V_0 / \partial P)_T / (\partial V / \partial P)_T$ , arising in Eqs. (22) and (23) merits some discussion.  $V_0$ , it will be remembered, is the volume of the liquid at the melting point, and is thus a function of pressure. Since the derivative to obtain the equation of state is taken at constant temperature, the term,  $(\partial V_0 / \partial V)_T$  which arises is interpreted as being the ratio,  $(\partial V_0 / \partial P)_T / (\partial V / \partial P)_T$ .

Eqs. (22) and (23) were used as follows. For any arbitrary value of the constant,  $c$ , the constants  $a$  and  $d$  were determined from the vapor pressures.<sup>18</sup> Then Eq. (22) was used to determine the value of the term

$$[1 - (V/V_0)^{1/3} (\partial V_0 / \partial P)_T / (\partial V / \partial P)_T],$$

the value being adjusted so as to give the correct volume at atmospheric pressure. This gave the necessary data for the calculation of volumes under pressure, provided neither  $\Theta$  nor the term  $1 - (V/V_0)^{1/3} (\partial V_0 / \partial P)_T / (\partial V / \partial P)_T$  were considered

<sup>18</sup> Precise vapor pressures are not available over a sufficient range of volumes to make it possible to get accurate values for all three constants from vapor pressure measurements alone.



to be functions of the pressure, an assumption which is probably quite valid for the relatively small pressure ranges considered here. The method of successive approximations may then be used to secure values of  $a$ ,  $c$  and  $d$  consistent with both the compressions and vapor pressures.

Since compressions at one temperature serve to fix the value of the parameter, compressions at other temperature, will serve as an independent check. Bridgman<sup>13</sup> has determined volumes of mercury under pressure at 0° and at 20°. The agreement of the calculated values with his observed ones is shown in Table III. Such small discrepancies as exist are probably within experimental error.

A further test of the theory is provided by calculating values for  $\beta$  as a function of temperature. Again the term

$$[1 - (V/V_0)^{\frac{1}{3}}(\partial V_0/\partial P)_T/(\partial V/\partial P)_T]$$

is determined from values for the volume at atmospheric pressure, and the values so obtained are used to calculate the compressibility. With the values for the compressibility,  $V$ ,  $V_0$  and  $[1 - (V/V_0)^{\frac{1}{3}}(\partial V_0/\partial P)_T/(\partial V/\partial P)_T]$  available it becomes possible to compute  $(\partial V_0/\partial P)_T$  as a function of temperature. If the interpretation we have given this quantity is correct it should be a constant, independent of temperature, and equal to the value of  $V\beta$  for the liquid at the melting point. Table II shows how nearly this is true. The value of  $V\beta$  at the melting point is  $55.5 \times 10^{-6}$  ml/mole/atmos. while the average value of the same quantity as computed indirectly is  $56.3 \times 10^{-6}$  ml/mole/atmos. and the average deviation from this mean value is only 0.7 per cent. It may also be pointed out that at least for mercury it is not necessary to utilize compression results directly in order to obtain good values for the constants in the partition function, since at the melting point the term

$$[1 - (V/V_0)(\partial V_0/\partial P)_T/(\partial V/\partial P)_T]$$

becomes equal to zero and we are left with

$$PV^{\frac{1}{3}} + a/V^{\frac{1}{3}} = (cd/3) \exp(-cV^{\frac{1}{3}}), \quad (24)$$

an expression which may be used to determine the constant,  $c$ , from the volume of the liquid at the melting point. This makes possible the calculation of compressions and compressibilities from

vapor pressures and volumes at atmospheric pressure with a considerable degree of accuracy.

### Calculation of heats of vaporization and vapor pressures from compressions alone

We have shown how it is possible to put vapor pressures and compressions into one self-consistent scheme and a method for calculating pressure results from vapor pressures has been indicated. The converse calculation of vapor pressures from compressions is quite possible, and indeed may prove to be a fruitful method for substances of very low vapor pressures, e.g., gallium. In order to get an estimate of the accuracy to be expected from such a procedure the constants in an equation of the form

$$V^{\frac{1}{3}} = A \log (P + (B + CT)/V^2) + D \quad (25)$$

were evaluated from Bridgman's data at 0° and at 20°. The constants  $A$ ,  $B$ ,  $C$  and  $D$  were then related to those in the static energy equation (15) by analogy to Eq. (22). Since the depth of the minimum in the potential curve,  $E(V)$ , plus the zero point energy should represent the heat of vaporization at  $T=0$  this is one check that may be used. It was found that the compression results gave a value of 16.6 kcal. for this value. Kelley<sup>16</sup> gives 15.0 for  $\Delta H$  of evaporation extrapolated to  $T=0$  and 15.3 for  $\Delta E_0^0$ , the discrepancy between these two results being an indication of the probable accuracy of the experimental values. The value 16.6 may also be compared with the more accurate value of 15.30 for the same quantity obtained by using both the vapor pressure and the compressions. The static energy constants obtained by Eq. (25) may also be applied to the calculation of vapor pressures. Thus a value for the vapor pressure of mercury at the melting point is obtained which is too small by a factor of about 5, this discrepancy in the vapor pressure being considerably greater than that in the energy of vaporization since the energy of vaporization occurs as a large exponential term in the expression for the vapor pressure. It is thought that the agreement between the observed heat of vaporization and vapor pressures, and those calculated from the compressions alone is quite satisfactory and indicates that the method may be usefully applied in certain cases. The differences are thought to be entirely due to

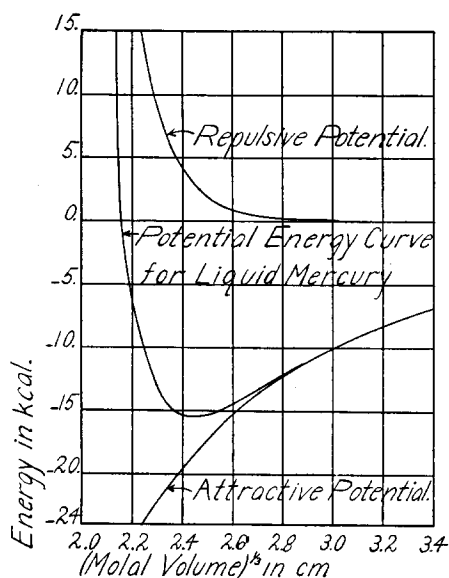


FIG. 3. Potential energy function at zero absolute for liquid mercury minus  $3/2 h\nu$  (0.24 kcal. at minimum).

the roughness of the method of calculation employed, and to the lack of sensitivity of the constants to the data.

#### Comparison of metals and nonmetals

Hildebrand<sup>15</sup> has pointed out that the difference in the thermodynamic behavior of metals and nonmetals may be attributed to the strong repulsive forces operating in the liquid metals. In agreement with this view we note by inspection of Fig. 3 that at the volume equal to that of the liquid at its melting point at atmospheric pressure the repulsive energy is 19 percent of the total static energy and 16 percent of the attractive energy. At the volume the liquid occupies at its boiling point these figures have dropped to 12 percent and 10 percent, respectively. It is only at a volume of about 20 cc corresponding to a temperature of about 1500°K, 900° above the boiling point, that these figures have dropped to a value as low as 3 percent. The contribution of the repulsive energy to the total energy of typical nonmetallic liquids at low pressures and temperatures is probably even below this low value.

#### Generalization to include high temperatures and large volumes. Critical properties

It is of interest to inquire if the static energy as found here for mercury may be applied without

change to the equation of state developed by Hirschfelder, Stevenson and Eyring.<sup>3</sup> The equation is

$$P + \frac{\partial E(V)}{\partial V} = \frac{RT}{V} \left[ 1 + b/V + 5/3(b/V)^2 + 0.2869(b/V)^3 + 0.1928(b/V)^4 \right], \quad (26)$$

where  $b$  is related to that in van der Waals' equation of state and is given by using the equation

$$b = 4N\lambda^3/3\pi d^3/8 \quad (27)$$

and identifying our Eq. (16) for the partition function of a liquid with Eq. (1) and (8) of Eyring and Hirschfelder<sup>2</sup>

$$F_l = N8 \left[ \left( \frac{V}{N} \right)^{\frac{1}{3}} - d \right]^3 \frac{(2\pi mkT)^{\frac{1}{2}}}{h^3} \exp \left( \frac{\Delta E}{RT} \right). \quad (28)$$

For the two expressions to be consistent we must have:

$$2 \left( \frac{V}{N} \right)^{\frac{1}{3}} - 2d = \frac{kT/h\nu}{(2\pi mkT)^{\frac{1}{2}}/h} + 2 \left( \frac{V}{N} \right)^{\frac{1}{3}} - 2 \left( \frac{V_0}{N} \right)^{\frac{1}{3}}, \quad (29)$$

from which it follows that

$$\left( \frac{b}{2} \right)^{\frac{1}{3}} = \left( \frac{\pi}{3} \right)^{\frac{1}{3}} \left[ V_0^{\frac{1}{3}} - \frac{N^{\frac{1}{3}}}{2\nu} \left( \frac{kT}{2\pi m} \right)^{\frac{1}{2}} \right]. \quad (30)$$

Values of  $b$  were obtained from this formula and substituted into Eq. (26). The observed and calculated volumes are shown in Table IV.

It will be noted that the calculated curve almost exactly parallels the observed one, but is displaced from it by about 0.65 cc. Inspection of Eq. (26) shows that both the left and right-hand

TABLE IV. Comparison of observed orthobaric volumes with those calculated by Eq. (26).

| $T^\circ$ | $b$<br>cc | $V$ (calc.)<br>cc | $V$ (exp.)<br>cc | $V$ (obs. - calc.)<br>cc |
|-----------|-----------|-------------------|------------------|--------------------------|
| 234       | 26.0      | 15.33             | 14.65            | -.68                     |
| 373       | 25.0      | 15.7              | 15.03            | -.67                     |
| 630       | 24.0      | 16.4              | 15.75            | -.65                     |
| 903       | 23.2      | 17.2              | (16.6)*          | (-.6)                    |
| 1273      | 22.2      | 18.2              | —                | —                        |

\* Extrapolated.

sides will disappear together at low pressures only if the minimum in the function  $E(V)$  comes at a volume corresponding to that of the liquid at  $T=0$ . However, the condition that we have previously imposed that

$$P + a/V^2 = (cd/3V^{1/3}) \exp(-cV^{1/3})$$

fixes the minimum in the curve at a volume equal to that of the liquid at the melting point at low pressures, since

$$a/V^2 - (cd/3V^{1/3}) \exp(-cV^{1/3})$$

is simply  $\partial E(V)/\partial V$ . Thus we expect Eq. (26) to be inconsistent by an amount about equal to the expansion from  $T=0$  to the melting point, which is just what we observe. It is expected that further work will eliminate the difficulty.

Since we have a means available for getting van der Waals' constants  $a$  and  $b$ , it should be possible to compute approximate values for the critical constants by using the relations

$$T_c = 8a/27Rb \quad \text{and} \quad P_c = a/27b^2.$$

On substitution of the values  $11.172 \times 10^6$  and 21.0 cc for  $a$  and  $b$ , respectively, the values, 1900°K and 950 atmos. are obtained for the critical temperature and pressure to be compared to the experimental values of 1800°K and 1000 atmos.<sup>19</sup> Conversely the value  $9.0 \times 10^6$  is obtained for  $a$  from the critical temperature and pressure. The agreement between the  $a$  value ob-

tained from the critical constants and that from the vapor pressure gives us added confidence in the validity of the form chosen for  $E(V)$ . This agreement is particularly interesting since the bonding in metallic solids and liquids is usually thought of as quite different from the van der Waals forces acting between a pair of molecules. Although we expect Eq. (26) to give better values than van der Waals' equation for the critical phenomena we have not carried through the rather laborious calculations.

### Further applications

If vapor pressures are available it seems a procedure somewhat similar to that outlined for liquids might be used to get empirical information about the lattice energy of solids. Hitherto<sup>20</sup> a scheme based on compressions alone has been used to get the variation of lattice energy with volume, but our results for liquid mercury indicate that more accurate results may be obtained if other thermodynamic properties are considered as well. A further improvement in the results obtained would no doubt follow any improvement in the form for representing static energy as a function of volume. Our present form certainly yields remarkably satisfactory results, however.

Further applications of the method developed here are being made in this laboratory and the results will be reported at an early date along with some more theoretical aspects of the subject.

<sup>19</sup> Landolt-Börnstein, *Tabellen*.

<sup>20</sup> Reference 5, p. 23.