MDDC - 1356

UNITED STATES ATOMIC ENERGY COMMISSION

QUANTUM CORRECTIONS TO THE THERMODYNAMIC PROPERTIES
OF LIQUIDS, WITH APPLICATION TO NEON

by

O. K. Rice

Oak Ridge National Laboratory

Date Declassified: October 8, 1947

Technical Information Branch, Oak Ridge, Tennessee
AEC, Oak Ridge, Tenn., 4-25-49--850-A1507

Printed in USA.
PRICE 10 CENTS

QUANTUM CORRECTIONS TO THE THERMODYNAMIC PROPERTIES
OF LIQUIDS, WITH APPLICATION TO NEON

By O. K. Rice*

ABSTRACT

The quantum correction has been expressed as a deviation η from RT ln Q_c, where Q_c is the classical partition function. Changes in volume, energy, specific heat, etc., caused by quantization can be expressed in terms of η and certain thermodynamic quantities. η itself is expressed in terms of thermodynamic quantities. The equations obtained give for solid neon the same results, within the limits of error, as the usual treatment of a Debye solid with the aid of the Grüneisen equation. To apply the equation to liquid neon, various thermodynamic quantities have been obtained from known values for argon by use of the law of corresponding states. The difference in volume and specific heat of liquid neon from the values expected from the law of corresponding states has been computed and found to agree reasonably well with the observations. However, the melting point and the ΔE and ΔS of fusion are found experimentally to be much closer to the classical values than one would expect from the theory. No explanation of this discrepancy is apparent.

* * * * *

It has frequently been noted that the properties of neon are somewhat out of line with those of the other condensed rare gases. These deviations have been ascribed to quantum effects in neon,[1] which, it is believed, would otherwise obey the law of corresponding states. Quantum effects in the solid are easily taken care of with the help of the Debye theory; the liquid presents more of a problem.

The quantum corrections for a liquid have recently been given in a general form by Mayer and Band.[2] Their results, however, involve some multiple integrals containing distribution functions and second derivatives of the interatomic potential function. Therefore, they are difficult to evaluate, and it seems desirable to derive some rougher equations which will be more easily handled. It will be the purpose of this paper to express the magnitude of the quantum effects in terms of thermodynamic quantities which have either been measured or may be approximated from the law of corresponding states, and apply the results to neon.

1. EQUATION FOR A ONE-PHASE ISOTHERMAL AND ISOBARIC SYSTEM

We shall express the quantum deviation by means of a quantity η defined by the equation†

$$\ln Q = \ln Q_c + \eta \tag{1}$$

Here Q is the actual partition function, and Q_c is the classical partition function of the system, at the given temperature T and molal volume V. Q_c is found by taking the limiting form of Q for high temperatures, and inserting the actual value of T in this limiting form. In calculating Q, only the thermal part of the energy E_t and the zero-point energy E_z are considered. The Helmholtz free energy is therefore given by

$$A = -RT \ln Q + E_p \tag{2}$$

---

*On leave 1946-47 from the University of North Carolina, Chapel Hill, North Carolina.

† If η is very small we may write equation 1 in the form $Q = Q_c(1 + \eta)$, which brings out the significance of η. However, to actually define η by this equation would be less convenient for purposes of computation than to use equation 1.

where E_p is the potential energy (excluding any potential energy involved in E_t and E_z); that is, E_p is the value the energy would have at absolute zero with all the atoms at their positions of equilibrium. For a solid, the positions of equilibrium form a regular lattice, but this is of course not true for a liquid. From equation 1 this may be written

$$A = -RT \ln Q_c - RT \eta + E_p \tag{3}$$

$$= A_c - RT\eta$$

In this equation we assume either that E_p is the same for the classical and quantum case if the volume remains fixed, or better, that any change is included in η. Since E_p is the energy after subtracting out all thermal and zero-point energy, it would appear that any change in it which could be caused by quantization could be referred to a change in the average coordination number caused by quantization. Such a change could occur in the liquid, but may be included in η. This, then, eventually becomes merged with the assumptions regarding η which are later made, in order to estimate it for the liquid.

The Gibbs free energy F is equal to the Helmholtz free energy if the pressure p = 0, as is essentially the case for condensed systems around atmospheric pressure. It is to be noted, however, that in equation 3 A_c is to be evaluated at the same molal volume as A, not the same pressure. If A is evaluated at zero pressure, A_c must be evaluated at that pressure, δp, at which the system would have the same volume if the classical statistics held.

Since the pressure is given by

$$p = -(\partial A / \partial V)_T \tag{4}$$

and since δp is the pressure the system would have if Q_c were the correct partition function, we may write

$$\delta p = -(\partial A_c / \partial V)_T \tag{5}$$

The true pressure being zero, we obtain from equations 3, 4, and 5

$$\delta p = -RT(\partial \eta / \partial V)_T \tag{6}$$

If we let $A_{c,0}$ be the classical value of A at zero pressure, we have*

$$A_c = A_{c,0} + \int_0^{\delta p} (\partial A_c / \partial p)_T \, dp = A_{c,0} + \int_0^{\delta p} (\partial A_c / \partial V)_T \, (\partial V / \partial p)_{T,c} \, dp$$

Using equation 5, and integrating, assuming $(\partial V / \partial p)_{T,c}$ to be constant,

$$A_c = A_{c,0} - (\delta p / 2)^2 \, (\partial V / \partial p)_{T,c}$$

Aside from the assumption that $(\partial V / \partial p)_{T,c}$ is constant, this equation is exact. If η and hence δp is a small quantity, it shows that $A_c - A_{c,0}$ is a small quantity of the second order. Such quantities may in general be neglected in the case of the liquid, but may not be entirely negligible for the solid. The form of the dependence of $A_c - A_{c,0}$ on δp is that which is to be expected from the fact that for p = 0, the condition of equilibrium is that A be a minimum.

There will be a first-order effect on the volume of the system. Let V_c be the volume the system would have at zero pressure if the classical statistics held, and let V be its actual volume. A classical system at volume V would have the pressure δp. To go to zero pressure its volume must change by $-(\partial V / \partial p)_{T,c} \delta p$. We therefore have

$$V - V_c = (\partial V / \partial p)_{T,c}\delta p = -RT(\partial \eta / \partial V)_T \, (\partial V / \partial p)_{T,c} \tag{7}$$

There will also be a first-order effect on the energy. We have, in general, for the sum of the thermal energy and zero-point energy

$$E_t + E_z = RT^2 \, d \ln Q/dT \tag{8}$$

_____

*In general, we use a subscript c to designate the classical value of any quantity.

At a given volume **V** therefore

$$E_t + E_z - E_{t,c} = RT^2\left[(\partial \ln Q/dT)_V - (\partial \ln Q_c/\partial T)_V\right] = RT^2(\partial \eta/\partial T)_V \tag{9}$$

where $E_{t,c}$ is the classical thermal energy at the volume **V**. As noted above, quantization causes no change in E_p, since any effect is taken care of by η. However, at volume **V** the pressure of a classical system would, as we have seen, be δp. Going back to zero pressure, the energy would change by $-(\partial E/\partial V)_{T,c}(\partial V/\partial p)_{T,c}\,\delta p$. Further, at zero pressure we may write $(\partial E/\partial V)_{T,c} = T(\partial S/\partial V)_{T,c} = T(\partial p/\partial T)_{V,c}$. Therefore, for fixed zero pressure we may write

$$E - E_c = RT^2(\partial \eta/\partial T)_V - RT^2(\partial \eta/\partial V)_T\,(\partial p/\partial T)_{V,c}\,(\partial V/\partial p)_{T,c}$$

$$= RT^2\left[(\partial \eta/\partial T)_V + (\partial \eta/\partial V)_T\,(\partial V/\partial T)_{p,c}\right] \tag{10}$$

Provided the differential coefficients are constant, both equations 7 and 10 are exact.

The quantum contribution to the specific heat, δC_p, can be obtained by differentiating equation 10. We note that $(\partial/\partial T)_p = (\partial/\partial T)_V + (\partial V/\partial T)_p\,(\partial/\partial V)_T$. This expression is to be applied to the true quantized system rather than a hypothetical classical one, so the $(\partial V/\partial T)_p$, which appears here (without subscript c) is the actual, rather than a classical value. However, the operator, $(\partial/\partial T)_p$, or $(\partial/\partial T)_V$ and $(\partial/\partial V)_T$, applied to a classical expression gives a classical expression. We therefore obtain

$$\delta C_p = 2RT[(\partial \eta/\partial T)_V + (\partial \eta/\partial V)_T\,(\partial V/\partial T)_{p,c}]$$
$$+ RT^2\Big\{(\partial \eta^2/\partial T^2)_V + (\partial^2\eta/\partial T\,\partial V)\,[(\partial V/\partial T)_p + (\partial V/\partial T)_{p,c}]$$
$$+ (\partial^2\eta/\partial V^2)_T\,(\partial V/\partial T)_p\,(\partial V/\partial T)_{p,c} + (\partial \eta/\partial V)_T\,(\partial^2 V/\partial T^2)_{p,c}\Big\} \tag{11}$$

In the case of liquid neon, $(\partial V/\partial T)_p$ and $(\partial V/\partial T)_{p,c}$ will be nearly enough alike so it will not be necessary to distinguish between them.

2. THE EVALUATION OF THE QUANTUM CORRECTION

The evaluation of the quantum correction for the solid is very easy if we assume that it obeys the Debye specific heat law. In this case we can write the expression for ln Q in the form[3]

$$\ln Q = \ln[(T/\Theta)^3 e] - (3/40)(\Theta/T)^2 + (3/6720)(\Theta/T)^4 - \ldots \tag{12}$$

where Θ is the Debye characteristic temperature. If we break off equation 12 at the second term and compare with equation 1, we see that this gives

$$\eta = -(3/40)e^{2/3}\,Q_c^{-2/3} = -0.1464\,Q_c^{-2/3} \tag{13}$$

In many respects the liquid resembles the solid, and we shall assume that equation 13 holds for the liquid as well as the solid. It is true that there is a translational, as well as a vibrational, contribution to the partition function of the liquid, and there may be some complications arising from the possibility of a change in coordination number in the liquid, as indicated in the discussion following equation 3. However, the quantum correction will, in general, be expected to decrease as the partition function increases, and in view of the reasonably close similarity between liquid and solid, it would appear that equation 13 cannot be too greatly incorrect for the liquid.

We may now refer to equation 2 to get η in terms of thermodynamic quantities. Since $A_c - E_p = E_c - TS_c - E_p = E_{t,c} - TS_c$, where $E_{t,c}$ is the classical thermal energy, we may write from equation 13

$$\eta = -0.146\,e^{2E_{t,c}/3RT}e^{-2S_c/3R} \tag{14}$$

Since $(\partial E_{t,c}/\partial T)_V = C_{v,c}$ and $(\partial S_c/\partial T)_V = C_{v,c}/T$ we have

$$(\partial \eta/\partial T)_V = -(2/3)\eta E_{t,c}/RT^2 \tag{15}$$

We also have

$$(\partial\eta/\partial V)_T = (2/3)\eta \left\{ [(\partial E_{t,c}/\partial V)_T/RT] - [(\partial S_c/\partial V)_T/R] \right\} \tag{16}$$

We note that $T(\partial S_c/\partial V)_T = (\partial E_c/\partial V)_T + p$. Substituting this into equation 16, and remembering that $E_c = E_{t,c} + E_p$ (the zero-point energy does not occur in the classical case) we get

$$(\partial\eta/\partial V)_T = -(2/3)\eta \left[(dE_p/dV)/RT \right] - (2/3)\eta \left[p/RT \right] \tag{17}$$

We will, in general, apply this with $p = 0$.

To apply equation 11 we also need the second derivatives. In the final expressions for the second derivatives we set $p = 0$.

$$(\partial^2\eta/\partial T^2)_V = (4/9)\eta \left(E_{t,c}^2/R^2 T^4 \right) - (2/3)\eta \left(C_{v,c}/RT^2 \right)$$
$$+ (4/3)\eta \left(E_{t,c}/RT^3 \right) \tag{18}$$

$$d^2\eta/\partial V \partial T = (4/9)\eta \left[E_{t,c}(dE_p/dV)/R^2 T^3 \right]$$
$$- (2/3)\eta \left[(\partial E_{t,c}/\partial V)_T/RT^2 \right] \tag{19}$$

$$(\partial^2\eta/\partial V^2)_T = (4/9)\eta \left[(dE_p/dV)^2/R^2 T^2 \right]$$
$$- (2/3)\eta \left[(d^2 E_p/dV^2)/RT \right]$$
$$- (2/3)\eta \left[(\partial p/\partial V)_T/RT \right] \tag{20}$$

equation 19 can be somewhat transformed. Using the relation at zero pressure,

$$(\partial E_c/\partial V)_T = (\partial E_{t,c}/\partial V)_T + (dE_p/dV) = T(\partial S_c/\partial V)_T = T(\partial p/\partial T)_{V,c}$$

we have

$$\partial^2\eta/\partial V \partial T = (4/9)\eta \left[E_{t,c}(dE_p/dV)/R^2 T^3 \right] + (2/3)\eta \left[(dE_p/dV)/RT^2 \right] - (2/3)\eta \left[(\partial p/\partial T)_V/RT \right] \tag{21}$$

3. APPLICATION TO SOLID NEON

Application of the above results to a Debye solid should yield nothing essentially different from application of the Gruneisen equation,[4]

$$p = \Gamma(E_t + E_z) - (dE_p/dV), \tag{22}$$

where

$$\Gamma = -\Theta^{-1} \, d\Theta/dV \tag{23}$$

However, by way of illustration, it will be of some interest to apply equations 7 and 11 to solid neon. In this case, we shall not use equations 15 or 17 but will go directly to the relation which follows from equation 12.

$$\eta = -(3/40)(\Theta/T)^2 + (3/6720)(\Theta/T)^4 \tag{24}$$

From this we obtain

$$(\partial\eta/\partial V)_T = \Gamma \left[(6/40)(\Theta/T)^2 - (12/6720)(\Theta/T)^4 \right] \tag{25}$$
$$\cong -2\Gamma\eta \left[1 - 0.0060 \, (\Theta/T)^2 \right]$$

We may also write

$$(\partial V/\partial p)_{T,c} = -(\partial V/\partial T)_{T,c}/(\partial p/\partial T)_{V,c} \tag{26}$$

$(\partial p/\partial T)_{V,c}$ is readily obtained by differentiating equation 22, taken for the classical case. Since Γ and dE_p/dV are independent of T, this gives

$$(\partial p/\partial T)_{V,c} = C_{v,c} \, \Gamma = 3R\Gamma \tag{27}$$

$(\partial V/\partial T)_{p,c}$ may be written in the form

$$(\partial V/\partial T)_{p,c} = -\Gamma^{-1}T^{-1}(\partial \ln \Theta / \partial \ln T)_{p,c} \tag{28}$$

Using equations 25 to 28 in equation 7 we obtain

$$\Gamma(V - V_c) = (2/3)(\partial \ln \Theta / \partial \ln T)_{p,c}\eta\left[1 - 0.0060(\Theta/T)^2\right] \tag{29}$$

If we have a series of substances which obey the law of corresponding states, the value of $(\partial \ln \Theta / \partial \ln T)_{p,c}$ will be the same for all of them.[5] In the case of the rare gases, xenon may be considered as practically classical at its melting point. The melting points are very near to corresponding states; hence we may take the value of $(\partial \ln \Theta / \partial \ln T)_p$ given by Murphy and Rice for xenon at its melting point* as the $(\partial \ln \Theta / \partial \ln T)_{p,c}$ for neon at its melting point.

If we set Θ_c equal to the value of Θ at V_c, then it is seen that the left-hand side of equation 29 will be $(\Theta - \Theta_c)/\Theta_{av}$, where Θ_{av} may be taken as the mean of Θ and Θ_c. Θ at the melting point of Ne (or rather the temperature of the corresponding point, based on the melting point of xenon, which differs by only a few tenths of a degree) may be found by a slight extrapolation in Table V of Murphy and Rice, while Θ_c may be estimated from the results with xenon. We find

$$(\Theta - \Theta_c)/\Theta_{av} = (59.2 - 65.8)/62.5 = -0.106 \tag{30}$$

Evaluating the right-hand side of equation 29, using $\Theta = 59.2$ and $T = 24.9$ to calculate η, we obtain

$$-(2/3)(\partial \ln \Theta / \partial \ln T)_{p,c}\eta[1 - 0.0060(\Theta/T)^2] = -0.667 \times 0.385 \times 0.410 \times 0.965 = -0.101 \tag{31}$$

This is an excellent check, especially since $(\partial V/\partial p)_{T,c}$ will actually vary with volume, but is evaluated at V_c.

The value of Γ for argon has been taken as 0.18 moles/cc. For neon it can be calculated by multiplying by the inverse ratio of the critical volumes[6] according to the law of corresponding states; it therefore is 0.325 moles/cc. This gives $V - V_c = 0.33$ cc/mole. The actual volume of solid neon given by Clusius[7] is 13.98 cc/mole. If we multiply the volume of solid krypton[8] at its melting point by the ratio of the critical volumes we get 13.42 cc/mole for V_c. Similarly, from argon[9] we get 13.59 cc/mole for V_c. The calculated value of $V - V_c$ seems to agree about as well as one might expect.

We have also evaluated equation 11 for the solid. This requires some further differentiation, including differentiation of equation 28, which brings in the quantity $(\partial^2 \ln \Theta / \partial \ln T \Theta T)_{p,c}$, which has been estimated as $-0.00405 \times (289.8/44.8)$ from Table II, Murphy and Rice (the ratio in parentheses is the ratio of critical temperatures of xenon and neon, taken from Guggenheim). We also have to evaluate $(\partial V/\partial T)_p$ (nonclassical) which is done with the aid of Table V of Murphy and Rice. We have obtained for δC_p at the melting point 2.0 cal/mole/deg. Comparison of Tables II and V of Murphy and Rice shows that this is about right.

4. APPLICATION TO LIQUID NEON

The checks obtained in Section 3 merely confirm the consistency of the present calculation with that of Murphy and Rice. The comparison of experimental and calculated $V - V_c$ may have some significance, but again the calculation may be handled equally well by either method. For the case of the liquid, however, only the equations of the present paper are available.

To calculate $V - V_c$, or better $(V - V_c)/V_c$, we clearly need, from equations 7, 17, and 26, values of V_c, dE_p/dV, $(\partial V/\partial T)_{p,c}$ and $(\partial p/\partial T)_{V,c}$. To get δC_p we need also $E_{t,c}$, $C_{v,c}$, $(\partial^2 V/\partial T^2)_{p,c}$ and d^2E/dV^2. These quantities are not known for neon; but they are known or may be readily calculated for argon from related quantities.[10] Since the quantities appearing in the expressions for $(V - V_c)/V_c$ and δC_p are, except for η, in a combination which is independent of the substance if the law of corresponding states holds, the values for argon should be sufficiently good. The values for the second derivatives show a rather sudden change at a molar volume equal to the molar volume at the normal melting point of argon. However, the volumes we are interested in are equal to or greater than the normal melting volume, so no ambiguity occurs here. The second derivatives can be obtained by differences from the first derivatives; the values are necessarily rough, but they fortunately do not contribute greatly to δC_p. d^2E_p/dV^2

---

*We will use the calculations based on Murphy's and Rice's Curve II. These calculations do not fit the experimental data on neon and xenon perfectly, but they are reasonably good, and they do exactly fit the law of corresponding states as extended by Murphy and Rice.

is sufficiently small and the terms containing it are sufficiently unimportant that they can be neglected.

We have yet to consider η for neon. This is to be obtained from equation 13. Q_c can be obtained by comparison with argon. We have previously shown that Q_c can be expressed approximately in the form[10]

$$Q_c = Q_0^3 = \left[(2e)^{1/3}(T/\Theta) + (2\pi mkT/h^2)^{1/2} 2^{-1/6} e(a - a_0) \right]^3 \tag{32}$$

On going from one substance to another which obeys the law of corresponding states, the two terms in the bracket transform in the same way. (For the transformation of Θ see Murphy and Rice.[5] To convert Θ from argon to neon, we use f_Θ (argon) = 1.530 and f_Θ (neon) = 1.405.) Q_0 has been calculated for argon in connection with the calculations of the article cited, whence Q_0 for neon and η for neon can be obtained as indicated. The various thermodynamic quantities required and η are listed in Table 1.

Table 1. Thermodynamic Quantities for Argon; η for Argon and Neon.

$$\overline{V} = 28.02 \text{ cc/mole}$$

$$T(\text{fusion}) = 83.78°K$$

$$dE_p/dV = 50.5 \text{ cal/cc}$$

$$E_t/3RT = 0.7961$$

$$C_\nu/3R = 0.856$$

$$(\partial V/\partial T)_p = 0.1178 \text{ cc/mole/deg}$$

$$(\partial p/\partial T)_V = 0.556 \text{ cal/cc/deg}$$

$$(\partial^2 V/\partial T^2)_p = 0.00165 \text{ cc/mole/deg}^2$$

$$Q_0(\text{argon}) = 3.681$$

$$\eta(\text{argon}) = 0.01080$$

$$\eta(\text{neon}) = 0.1030$$

This table gives the values of the various quantities at the melting temperature and melting volume of argon, or, in the case of η, at the corresponding point for neon. Neon at its melting point (24.55°K), or at its corresponding temperature (24.9°K, which is the temperature we have actually used), is slightly expanded beyond its corresponding volume. The errors which will be caused by this discrepancy are not sufficient to make it worthwhile to perform further calculations. It is easy to find from Reference 10 how the various quantities involved change with volume at constant pressure. This should give the order of magnitude of the errors involved, and it is found to be of the order of 20% in $(V - V_c)/V_c$ and 20% in δC_p. However, these are probably exaggerations, since the most-affected quantity is η, and it will be affected considerably less at constant temperature than at constant pressure.

Use of Table 1 enables us to estimate $(V - V_c)/V_c$ as 0.026. Figure 2 of Guggenheim's article[6] enables one to estimate $(V - V_c)/V_c$ by comparing the ratio of density to critical density for neon and other gases. It appears that neon is about 4 to 5% expanded over what one might expect from the law of corresponding states. However, just the points near the melting points near the melting point for neon are a little out of line, so 4% expansion is probably the better estimate. Pitzer states that liquid neon has a density of about 3% less than that of the "perfect liquid."[11] So it appears that the theoretical estimate of $(V - V_c)/V_c$ cannot be far out of line.

δC_p is calculated as 1.53 cal/mole. The specific heat of liquid neon is given[7] as 8.64 near the melting point, that of argon[7] as 10.05 or[12] 10.5, that of krypton[13] as 10.6, and that of xenon[14] as 10.7.

Therefore, it is obvious that there is reasonably good agreement between the calculated and experimental values.

5. TWO-PHASE SYSTEMS

We will now consider the effect of the quantum correction on the equilibrium between the solid and the liquid. We shall first consider the change in the temperature of melting at zero pressure. At zero pressure the Gibbs free energy F is equal to the Helmholtz free energy A. We can consequently use equation 3, substituting F for A and F_c for A_c. F_c really corresponds to $A_{c,0}$, since we should compare classical and quantum F's at the same pressure. The difference between A_c and $A_{c,0}$ is, as we have shown following equation 6, a second-order quantity. It is not entirely negligible for the solid, but is not important and may be neglected for our purposes.

The condition for equilibrium between two phases may be written

$$\Delta F = \Delta F_c - RT \, \Delta \eta = 0 \tag{33}$$

If there were no quantization, equilibrium would occur at a temperature T_c with $\Delta F_c = 0$, while equation 33 holds at a temperature T where $\Delta F_c = 0 + (\partial \Delta F_c / \partial T)_p \, (T - T_c) = -\Delta S_c (T - T_c)$. Substituting this into equation 33 we obtain

$$T - T_c = -RT \, \Delta \eta / \Delta S_c \tag{34}$$

Using the values of η for solid and liquid given in Sections 3 and 4, and taking for ΔS_c the entropy of melting of argon, 3.35, we obtain $T - T_c = -4.4°$. The observed value of $T - T_c$ is about $24.55 - 24.9 = -0.35°$. The discrepancy is very large and quite surprising, considering the the apparently good results obtained with solid and liquid separately.

We can analyze the situation further by considering $\Delta E - \Delta E_c$ and $\Delta S - \Delta S_c$ for the fusion process. Since the melting temperature is so nearly a corresponding temperature with respect to the melting temperature of xenon, say, we can neglect any effect of change in temperature on these quantities. This means that we can calculate $\Delta E - \Delta E_c$ by applying equation 10 directly to both solid and liquid at 24.9°K. For the solid, we apply the equations of Section 3. For the liquid, we apply the equations of Section 2 and the data of Section 4, and convert from argon to neon. We obtain $E - E_c = -54.3$ cal/mole for solid argon and $E - E_c = 18.3$ for liquid argon. Thus,

$$\Delta E - \Delta E_c = -36.0 \text{ cal/mole, calc.}$$

From the heat of krypton,[13] we get for the corresponding heat of fusion of neon 83.2 cal/mole, while actual heat of fusion is about 80.1 cal/mole. Thus,

$$\Delta E - \Delta E_c = -3.1 \text{ cal/mole, obs.}$$

A similar discrepancy occurs for the entropy. We can write

$$\Delta S - \Delta S_c = (\Delta E - \Delta E_c - \Delta A + \Delta A_c)/T$$
$$= \left[(\Delta E - \Delta E_c)/T \right] + R \Delta \eta$$
$$= -1.45 + 0.61 = -0.84 \text{ cal/mole/deg}$$

The actual value of $\Delta S - \Delta S_c$ is around -0.1 cal/mole/deg.

The results, with $\Delta E - \Delta E_c$ and $\Delta S - \Delta S_c$, appear to indicate that the quantum correction for the liquid is nearly as great as for the solid. This would seem very strange in itself, but it is still more puzzling in the light of the results of Section 5. The calculation for δC_p may indeed indicate that equation 13 gives something of an underestimate of η; if it were increased by perhaps 30%, a better value of C_p would result. On the other hand, it must also be noted that the derivatives of η in equation 11 involve the quantity dE_p/dV, which is somewhat indirectly calculated from the data. It does not appear likely, however, that this can cause appreciable error. We have

$$dE_p/dV = (\partial E/\partial V)_T - (\partial E_t/\partial V)_T.$$

$(\partial E_t/\partial V)_T$ is certainly negative; therefore dE_p/dV should be slightly larger than $(\partial E/\partial V)_T$ which at zero pressure is equal to $T(\partial p/\partial T)_V$. Now the value of dE_p/dV used is only slightly larger than $T(\partial p/\partial T)_V$; it seems likely that dE_p/dV should be increased rather than decreased, and this would actually increase

$|\delta C_p|$, so that $|\eta|$ would have to be increased less. The use of values at the normal melting temperatures and volumes gives a slight overestimate for $|\delta C_p|$, which might mean that $|\eta|$ should be increased by a little more than 30%, but this effect is not very great.

Another quantity that occurs in the derivatives of η that is not entirely directly determined experimentally is $E_{t,c}$. We have also used the calculated, rather than the experimentally determined, value of $C_{v,c}$. However, it does not appear that any possible change in these quantities could clear up the discrepancy.

On the other hand, it appears likely that the discrepancy is too great to be accounted for on the basis of deviations from the law of corresponding states.

Therefore, we are forced to leave the question of the quantum correction for neon in a somewhat unsatisfactory state.

REFERENCES

1. Pitzer, K. S., J. Chem. Phys. 7:583 (1939).
2. Mayer, J. E. and W. Band, J. Chem. Phys. 15:3 (1947).
3. Mayer, J. E. and M. G. Mayer, Statistical Mechanics p. 255, John Wiley and Sons, Inc., 1940.
4. Rice, O. K., J. Chem. Phys. 12:289 (1944).
5. Murphy, G. W. and O. K. Rice, J. Chem. Phys. 14:518 (1946).
6. Guggenheim, E. A., J. Chem. Phys. 13:253 (1945).
7. Clusius, K., Zeits. physik. Chem. B31:459 (1936).
8. Clusius, K. and K. Weigand, Zeits. physik. Chem. B46:1 (1940).
9. Rice, O. K., J. Chem. Phys. 14:321 (1946).
10. Rice, O. K., J. Chem. Phys. 14:324 (1946); see especially Tables V and VI.
11. Pitzer, K. S., J. Chem. Phys. 7:588 (1939).
12. Eucken, A. and H. Hanck, Zeits f. physik. Chemie 134:161 (1928).
13. Clusius, K., A. Krius, and F. Konnertz, Ann. d. Physik. 33:642 (1938).
14. Clusius, K. and L. Riccoboni, Zeits. f. physik. Chemie B38:81 (1937).

END OF DOCUMENT