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Corresponding States in the Frozen Rare Gases

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A method is presented for extending the principle of corresponding states to solids at comparatively low temperatures, where quantum effects are appreciable. The method has been applied to solid neon, argon, krypton, and xenon. The principle of corresponding states, as applied to the liquid and vapor states, is used for calculation of the potential energies and interatomic distances of three of the substances in terms of the other. The quantum contribution to the energy is taken into account by assuming the Debye theory for all the solids, and this is related to the potential energy by means of a modified Grüneisen equation. The Debye Θ's for three of the solids are determined from that of the other by a dimensional analysis of the mechanical system. Using this information, C_p for neon, argon, and krypton have been calculated from the experimental data for xenon. Agreement of the calculated values with experiment is reasonably good; small deviations may be caused by breakdown of the Debye theory, or may be indications of inexactitude in the law of corresponding states.

1. INTRODUCTION

THE principle of corresponding states has been the subject of two recent papers. Pitzer[1] has given a list of assumptions required for a substance to behave as a "perfect liquid." All such substances will obey the law of corresponding states. He pointed out that the rare gas liquids argon, krypton, and xenon conform closely to this behavior with respect to a number of their properties, while neon shows appreciable deviations caused by quantum effects. More recently Guggenheim[2] has undertaken a critical analysis of Pitzer's assumptions and has called attention to several additional properties of argon, krypton, and xenon in conformity with the principle.

Aside from the comparison of the entropy of fusion and the expansion on fusion of these substances, no attempts have yet been made to extend the principle to the solid state. We shall show in this article that Pitzer's assumptions, when due account is taken of the quantum effects, lead to what may be considered to be an extension of the principle of corresponding states, which should be valid for the solid rare gases even at low temperatures. Furthermore, we shall show that neon may be included in the comparison as effectively as the others.

[1] K. S. Pitzer, J. Chem. Phys. **7**, 583 (1939).

[2] E. A. Guggenheim, J. Chem. Phys. **13**, 253 (1945).

2. THEORY

By setting up a phase integral for substances conforming to his five assumptions, Pitzer has shown that the behavior of these substances will be the same when they are compared at equal values of T/A and V/r_0^3, where T is the absolute temperature, V the molar volume, and A and r_0^3 are constants characteristic of a given substance taken at some corresponding point. Since the critical point is a corresponding point, A may be taken as proportional to the critical temperature T_c and r_0^3 as proportional to the critical volume V_c.

We shall not consider all of Pitzer's assumptions in detail, but will comment on assumptions I and V, which are pertinent to our investigation. The former states that "classical statistical mechanics will be used." In this case we certainly do not have classical statistics alone operative, but we shall take into account quantum effects separately by assuming that they are taken care of by the Debye theory. Assumption V states: "The potential energy for a pair of molecules can be written $A\varphi(r/r_0)$, where r is the intermolecular distance, A and r_0 are characteristic constants, and φ is a universal function." If the potential energy of pairs is additive, as Pitzer has assumed, then a similar relation must hold for the total potential energy E_p of the solid. The A and r_0 of this assumption are the same as the A and r_0 of the preceding paragraph. Pitzer's and Guggenheim's

discussions of the rare gas liquids indicate that assumption V is justified. We will use it as one of the principal bases of our development. Since the Debye Θ will also depend on r_0, this assumption can also eventually be used to obtain a relation between E_p and Θ. (For a closer definition of E_p see page 290 of reference 4 below.)

The total energy E of a simple solid may be separated into three parts:

$$E = E_z + E_t + E_p,$$

where E_z is the zero point energy and E_t the "thermal energy." In the Debye theory $E_z = (9/8)R\Theta$, where $\Theta = h\nu_{max}/k$ is the characteristic temperature. E_t/T is given in the Debye tables as a function of Θ/T.

We shall apply the principle of corresponding states to our case in the following manner: we select one of the four solids, xenon, as a standard, calculating E_p as a function of Θ by means of the experimental specific heat data and the Debye theory; since, for a given solid, both E_p and Θ are functions of r or the volume only, one can express E_p as a function of Θ only. We then calculate suitable factors for the conversion of the energy and interatomic distance of xenon to those of neon, argon, and krypton by using data at some corresponding point at a sufficiently high temperature so that all of Pitzer's assumptions, including the first, are fulfilled. We then extend the principle of corresponding states to low temperatures, where assumption I no longer holds, by keeping these same factors for E_p and r, and take into account quantum effects separately by calculating E_z and E_t from the Debye theory. This is done with the help of a factor to convert Θ of Xe to that of Ne, A, or Kr, which we obtain by a dimensional analysis of the mechanical system, using the energy and distance factors calculated above.

Following Pitzer, we take the critical point as a corresponding point. The energy factor f_e is then just $T_c(S)/T_c(Xe)$, where S stands for one of the solids other than xenon. The melting temperatures are found to be in the same ratio as the critical temperatures for argon and krypton, but not for neon. We can therefore take the melting points as corresponding points for the first two cases, and obtain the energy factor as the ratio of the heats of vaporization at the melting point.

TABLE I. Conversion factors.[a]

	f_e from T_c	f_e from L_v at M. P.	f_r	f_Θ
Ne	0.155	0.140	0.714	1.405
A	0.520	0.518	0.872	1.496
Kr	0.722	0.716	0.928	1.145
Xe	1.000	1.000	1.000	1.000

[a] For data see reference 2.

The energy factors calculated in both ways are shown in Table I. They agree very well; we have actually used 0.155 for Ne, 0.520 for A, and 0.720 for Kr.

The "volume factor" was obtained as the ratio of the critical volumes for neon, and the ratio of the volumes of the solid at the triple point for the other substances (the result in no case differs greatly from that obtained from the critical-volume ratio). The "distance factor" f_r is the cube root of the volume factor.

The "Θ-factor" is calculated as follows: Θ varies as the (limiting) frequency ν of vibration, which in turn varies as (force constant/mass)$^{\frac{1}{2}}$. A force constant has the dimensions of energy/distance,[2] whereas the mass is proportional to the molecular weight. Since we have already calculated the energy and distance factors, the Θ factor f_Θ reduces to

$$f_\Theta = \frac{1}{f_r}\left(\frac{f_e M(Xe)}{M(S)}\right)^{\frac{1}{2}}, \quad (1)$$

the M's representing the molecular weights.

The various calculated factors have been collected and appear in Table I.

The specific heat at constant pressure for xenon[3] has been measured from 10°K up to temperatures near the melting point, 161.3°K. Following the procedure that Rice used in the case of argon[4] we can obtain the entropy as a function of T by integrating under the C_p/T curve, and, from this, Θ as a function of T from the Debye tables.[5]

We now make use of the Grüneisen equation,[6]

[3] K. Clusius and L. Riccoboni, Zeits. f. physik. Chemie B38, 81 (1937).
[4] O. K. Rice, J. Chem. Phys. 12, 289 (1944).
[5] Landolt-Börnstein Tabellen, Supplement 1, pp. 702–707 (1927).
[6] E. Grüneisen, Handbuch der Physik (1926), Vol. X. See also below, reference 9, Appendix I.
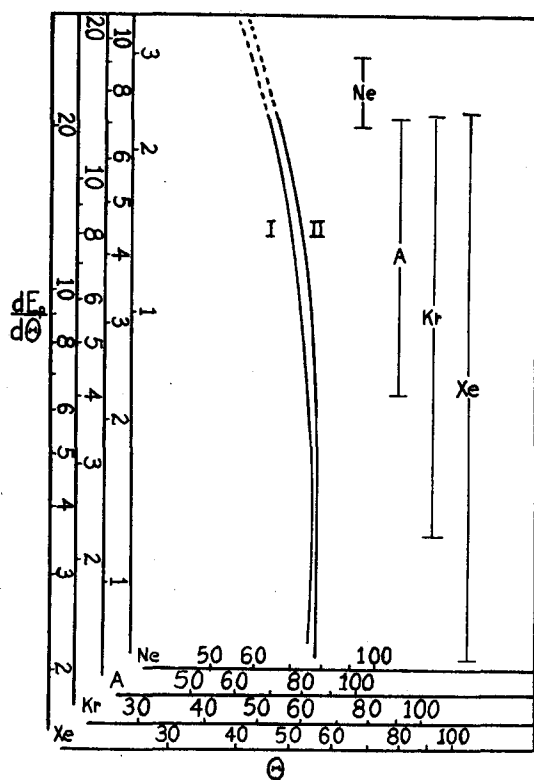
FIG. 1. $dE_p/d\Theta$ as a function of Θ. Θ in degrees, energy in cal./mole. Vertical lines indicate range of $dE_p/d\Theta$ values for each substance from 0°K to melting point. Curve I from xenon experimental specific heat data; Curve II is the assumed curve.

valid for the Debye solid, setting the pressure equal to zero for our process.

$$\frac{dE_p}{dV} = -\frac{E_t}{\Theta}\frac{d\Theta}{dV} - \frac{dE_z}{dV}. \qquad (2)$$

Multiplying through by $dV/d\Theta$ and substituting $dE_z/d\Theta = E_z/\Theta$, we obtain

$$\frac{dE_p}{d\Theta} = -\frac{E_t + E_z}{\Theta} = -\left(\frac{E_t}{\Theta} + \frac{9}{8}R\right). \qquad (3)$$

The right-hand side of this expression is a function only of Θ/T, and its values are obtainable from the Debye tables. This relation thus enables us to determine $dE_p/d\Theta$ as a function of Θ for xenon, and by means of our energy and Θ-factors, likewise for the other rare gas solids. However, in the latter case, we do not know to what temperature these values correspond, and we must reverse the procedure by substituting

$dE_p/d\Theta = -(E_t/\Theta + 9R/8)$ for each substance back into the Debye tables to obtain the proper Θ/T, and hence T.

We may test our procedure by means of the experimentally determined specific heats of neon, argon, and krypton.[3] To do this we make use of a relation of Grüneisen,[6] relating C_p, C_v, and the variation of Θ with T,

$$C_p = C_v\left(1 - \frac{d\ln\Theta}{d\ln T}\right), \qquad (4)$$

which holds for any Debye solid. This relation permits a direct calculation of C_p from the data we have obtained.

3. PROCEDURE

A graphical method was used to obtain $dE_p/d\Theta$ as a function of Θ/T for neon, argon, and krypton, from the xenon data. $E_t/\Theta + 9R/8$ was obtained from the Debye tables and plotted as a function of Θ/T on log-log paper. The particular values of $dE_p/d\Theta$ for xenon were plotted as a function of Θ on another sheet of log-log paper. On superposition of the sheets, a shifting of the ordinate of the latter by $\log f_e/f_\Theta$ (for a given substance) corresponds to a multiplication of $dE_p/d\Theta$ by that factor; and a changing of the zero of the abscissa by $\log f_\Theta$ amounts to multiplication of Θ by that factor. Intersection of the two curves then gives Θ/T at the particular Θ or T desired. After one has obtained several intersection points at different temperatures, obtained by horizontal displacement of the two curves relative to each other, he has Θ/T and hence Θ as a function of T. The derivative $d\ln\Theta/d\ln T$ was obtained by

TABLE II. Xenon. [Units: temperature in °K; C_p in cal. mole^{-1} deg.$^{-1}$; α in deg.$^{-1}$.]

	Curve I (graphical)		Curve II				
T	Θ	C_p	Θ	$\dfrac{d\ln\Theta}{d\ln T}$	$\alpha\cdot10^3$	C_p	C_p (expt)
10	53.6	1.95	56.0g	0.00	—	1.81	1.98
20	54.8	4.06	56.0g	0.00	—	4.15	4.06
40	54.9	5.69	56.0g	0.015	0.085	5.50	5.72
60	53.1	6.19	55.95	0.068	0.26	6.10	6.16
80	51.6	6.46	54.57	0.112	0.32	6.46	6.41
100	50.4	6.75	52.95	0.166	0.38	6.86	6.76
120	48.7	7.10	51.13	0.234	0.46	7.29	7.23
140	47.1	7.75	49.19	0.303	0.49	7.73	7.73
160	44.4	8.55	46.95	0.380	0.54	8.18	8.5

Melting point at 161.3°K.

plotting Θ vs. T on log-log paper and determining the slope graphically.

The results were later checked and extended by direct numerical calculation. A series of Θ and $dE_p/d\Theta$ values for one of the solids were calculated from the standard, and tabulated according to integral values of Θ. E_t/Θ was then obtained from $dE_p/d\Theta$ by the subtraction of $9R/8$, and from this Θ/T and hence T from the Debye tables. The difference in successive tabular values of T is just $dT/d\Theta$ for an intermediate Θ value, and by interpolation we get $dT/d\Theta$ for each integral value of Θ. $d \ln \Theta/d \ln T$ is the reciprocal of $(\Theta/T)dT/d\Theta$.

4. RESULTS OF CALCULATIONS

It was found that the results obtained with neon, argon, and krypton from the $dE_p/d\Theta$ curve for xenon (Curve I of Fig. 1) calculated from Clusius' and Riccoboni's experimental specific heat data, left much to be desired, especially in the case of argon. There is an apparent discrepancy in the data, however, which might account for the unsatisfactory agreement. The entropy at the melting point which Clusius and Riccoboni obtained by integrating under the C_p/T curve is 14.93 e.u., checking within 0.1 e.u. with the value calculated statistically. Using the same data we get 15.64 e.u., the percentage deviation from Clusius and Riccoboni's results being far outside the possible errors of computation. We are unable to explain this discrepancy. Furthermore, Curve I leads to an impossible trend in Θ at low temperatures (see Table II).

We decided to seek a $dE_p/d\Theta$ curve for xenon so adjusted as to give the best results for all the solids. The curve chosen is shown as Curve II in Fig. 1. The empirical equation which fits our assumed curve is

$$dE_p/d\Theta = 18.75 - 1.51(\Theta - 48)$$
$$+0.0245(\Theta - 48)^2 - 0.00338(\Theta - 48)^3. \quad (5)$$

This equation fits less accurately at high values of Θ, or low temperatures, where we have purposely given an infinite slope to the $dE_p/d\Theta$ curve over a considerable range.

The effect of assuming this particular curve is to reduce our calculated entropy for xenon, though it still does not reach the value of 14.93 given by Clusius. In Table II are given the values

TABLE III. Krypton.

T	Θ	C_p (calc)	C_p (expt)	$\dfrac{d \ln \Theta}{d \ln T}$	$\alpha \cdot 10^3$
10	63.9g	1.39	1.36	0.00	—
20	64.0g	3.75	3.72	0.00	—
30	63.6g	4.92	5.00	0.02	0.15
40	64.02	5.55	5.65	0.056	0.32
60	61.95	6.30	6.30	0.114	0.43
80	59.31	6.92	6.81	0.194	0.55
100	56.17	7.60	7.53	0.296	0.67
110	54.48	7.96	8.10	0.352	0.73

Melting point at 116.0°K.

TABLE IV. Argon.

	$f_\Theta = 1.496$ (graphical)		$f_\Theta = 1.530$				
				$\dfrac{d \ln \Theta}{d \ln T}$			
T	Θ	C_p	Θ		$\alpha \cdot 10^3$	C_p	C_p (expt)
10	82.9	0.75	85.1g	0.00	—	0.70	0.82
20	82.5	2.89	84.7g	0.01	0.11	2.82	2.84
30	81.6	4.40	83.89	0.053	0.40	4.38	4.40
40	80.2	5.35	82.20	0.092	0.52	5.30	5.28
50	78.3	5.97	80.12	0.140	0.64	6.00	5.90
60	75.9	6.60	77.68	0.202	0.76	6.60	6.40
70	73.0	7.27	74.90	0.276	0.90	7.18	7.00
80	69.7	7.79	71.87	0.342	0.97	7.70	7.70

Melting point at 83.8°K.

TABLE V. Neon (graphical).

T	Θ	C_p (calc)	C_p (expt)	$\dfrac{d \ln \Theta}{d \ln T}$	$\alpha \cdot 10^3$
10	65.9	1.36	1.43	0.045	1.02
14	64.7	2.64	2.58	0.070	1.14
18	63.2	3.86	3.69	0.120	1.52
21	61.7	4.79	4.62	0.195	2.11
23	60.5	5.35	5.46	0.240	2.37

Melting point at 24.5°K.

of C_p calculated from each of these curves and compared with the experimental values. As we would expect, Curve I checks the specific heats almost exactly throughout the temperature range, while with Curve II we get deviations as great as 0.3 cal. per degree.

The calculated specific heats obtained from Curve II are given in Tables II–V. The two methods of calculation checked closely, except at the lowest temperatures, where the empirical Eq. (5) deviates somewhat from the curve as drawn. The numerical calculations are given in the tables over most of the temperature range, unless otherwise indicated, since they are the more accurate. At low temperatures graphical
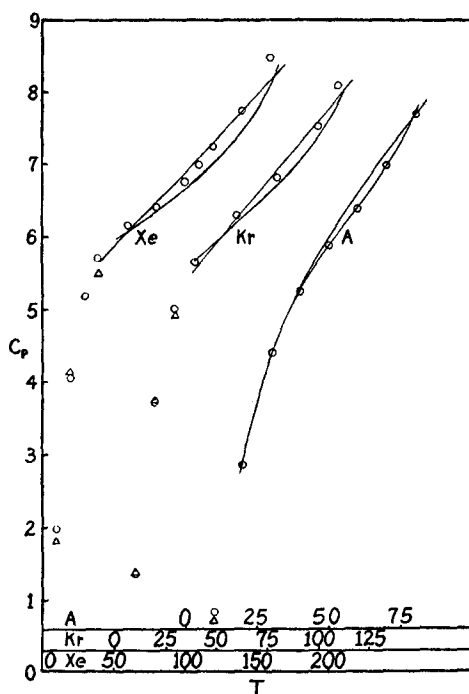
FIG. 2. Specific heats of the rare gas solids. Upper curves from Curve II, lower curves from argon $dE_p/d\Theta$ curve. ○ experimental points. △ calculated by graphical method from Curve II.

calculations are given and are denoted by the letter g.

It is seen that our attempt to find a $dE_p/d\Theta$ curve capable of explaining the experimental facts for the various substances is reasonably successful. Nevertheless, certain not entirely negligible differences remain, especially in the case of argon. Setting $f_\Theta = 1.530$ instead of 1.496 (without changing f_e), improves the results somewhat. This corresponds to an approximately 2 percent error in f_r, or a 6 percent error in the critical volume. This seems rather large; however, some such adjustment does seem to be necessary, since it brings the Θ's at the higher temperatures into agreement with those of Rice's earlier calculations.[4] Θ in Table IV, however, changes more rapidly with temperature than his calculations indicated. In view of the still remaining discrepancies, it seemed desirable, simply for comparison, to make some calculations based on the $dE_p/d\Theta$ curve for argon obtained from Rice's calculations. Actually the curve given by Rice in his latest paper[7] was very slightly modi-

[7] O. K. Rice, J. Chem. Phys. **14**, 321 (1946).

fied, starting at about $\Theta = 74$. At $\Theta = 71$ the value of $dE_p/d\Theta$ has become a little over one-half percent, lower than that given by Eq. (7) of reference 7, thus increasing C_p at $\Theta = 71$ by about 1 percent. This was done to effect a better fit with the values of C_p at the highest temperatures. That such a slight change in $dE_p/d\Theta$ can produce this much change in C_p indicates that C_p is sensitive to small errors in calculation in this region of temperatures just below the melting point, and cannot be obtained with high accuracy in this region. It should be stated, however, that if all the values of $dE_p/d\Theta$ were changed uniformly only a small change in C_p would be caused; it is $d^2E_p/d\Theta^2$ which affects C_p.

The curve for xenon was obtained by reverse use of the f_e and f_Θ factors ($f_\Theta = 1.530$), and that for krypton then obtained from xenon in the standard way. This $dE_p/d\Theta$ curve, referred to xenon, is given by the empirical equation,

$$dE_p/d\Theta = 18.50 - 1.68(\Theta - 48)$$
$$- 0.0125(\Theta - 48)^2 - 0.0014(\Theta - 48)^3. \quad (6)$$

We have not tabulated the results of the last mentioned calculation, but the results of both calculations are summarized in Fig. 2.

The experimental C_p values for krypton lie about midway between the values calculated from the assumed xenon $dE_p/d\Theta$ curve and the argon $dE_p/d\Theta$ curve. In the case of xenon a better fit is obtained with the assumed $dE_p/d\Theta$ curve. The experimental specific heats appear to show a gradual transition from one curve to the other as we go from argon to xenon.

Neon has not been included in this comparison, since most of the calculated C_p values must be obtained from an extrapolation of the $dE_p/d\Theta$ curve to higher values. It should be remarked, however, that the assumed $dE_p/d\Theta$ curve lends itself more readily to an extrapolation, which reproduces the experimental data for neon, than does the argon $dE_p/d\Theta$ curve. This will be discussed further in Section 6.

The quantity $-d\ln\Theta/d\ln T$ is a measure of the contribution of the thermal expansion to the specific heat. It can also be written

$$-\frac{d\ln\Theta}{d\ln T} = -\frac{d\ln\Theta}{d\ln V}\frac{T}{V}\frac{dV}{dT} = \gamma T\alpha, \quad (7)$$

where $\gamma = -d \ln \Theta / d \ln V$, and α is the coefficient of thermal expansion. γ has been assumed by Grüneisen to be constant. Rice[7] has shown that $\Theta^{-1} d\Theta / dV = 0.18$ is consistent with the experimental data for argon. Using the molal volume for argon at the melting point, 24.5 cc/mole, we find the corresponding value of γ to be 4.40. Since the volume does not change much over the temperature range, γ as calculated by assuming $\Theta^{-1} d\Theta / dV$ to be constant will not vary by more than a few percent. Since the thermal expansion goes to zero in any event at low temperatures, we should get reasonably accurate results by the use of $\gamma = 4.40$ at all temperatures. This same value of γ will be used for the other solids; in effect we have already assumed this in the main part of the paper.

The coefficients of expansion for the four solids calculated in this manner appear along with the other data from Curve II in Tables II–V. The values are accurate to the extent that the Debye theory holds for the rare gas solids and to the extent that Curve II approximates the true $dE_p / d\Theta$ curve for each substance. The available experimental data on α are at present too scanty to make a useful comparison.

$d \ln \Theta / d \ln T$ should always be either zero or have a negative value, in order that α always remain positive. The values shown in this table correspond to this behavior. However, we must remember that at low temperatures these result from an assumed $dE_p / d\Theta$ curve, and at the lowest temperature our calculated C_p is generally less than the experimental value. This means that $d \ln \Theta / d \ln T$ would appear to become positive at very low temperatures, if the experimental data were followed exactly. This is connected with the Θ anomalies in argon at low temperatures already noted by Clusius,[8] and by Rice.[4,9] The available evidence does not enable us to decide between the various possible explanations for this anomaly.

5. EFFECT OF QUANTIZATION

The range of $dE_p / d\Theta$ values for the four solids indicated by the vertical lines of Fig. 1 provides an interesting study. The lower limit of these lines represents a temperature of absolute zero for that particular solid, and the upper limit the melting point. Xenon is seen to have a very wide
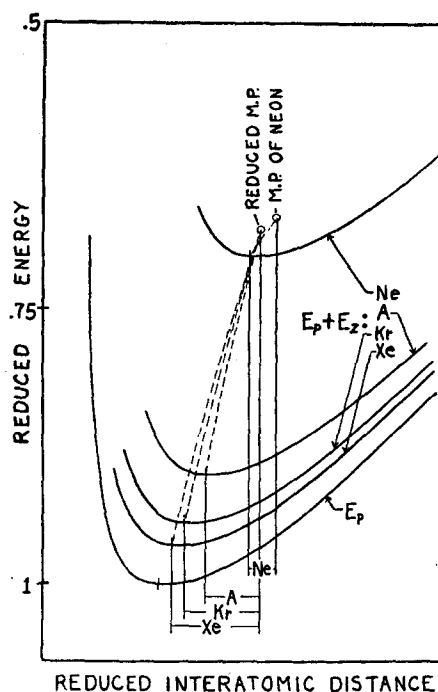
[8] K. Clusius, Zeits. f. physik. Chemie B31, 459 (1936).
[9] O. K. Rice, J. Am. Chem. Soc. 63, 3 (1941).

FIG. 3. Effect of zero point energy.

range of $dE_p / d\Theta$ values, the range gradually decreasing as we go from xenon to krypton to argon to neon. Furthermore, the point on the $dE_p / d\Theta$ curve where melting occurs is about the same for argon, krypton, and xenon, but is considerably higher for neon.

The difference in location of the absolute zero for the four solids is undoubtedly caused by the relative importance of the zero point energy. The situation can be visualized by considering the series of energy curves shown schematically in Fig. 3. The lowest curve is the "reduced" E_p curve for the four solids plotted against "reduced" interatomic distance. The other curves are the corresponding "reduced" $E_p + E_z$ curves for xenon, krypton, argon, and neon. At the absolute zero the state of equilibrium is at the minimum of these $E_p + E_z$ curves, not the E_p curve itself. As the relative importance of zero point energy becomes greater, this position of equilibrium is shifted more to the right of the E_p minimum. On heating the solid from absolute zero to the melting point the total energy will rise along some such path as is shown by the dotted lines.

We also see in Fig. 3 why the melting point is

not a corresponding point for neon. The large relative effect of the zero point energy has shifted the minimum of the $E_p + E_z$ curve so far to the right that neon has expanded beyond the "reduced" interatomic distance of melting before enough quantum levels have become excited to cause a breakdown of the lattice. Thus it must go to greater interatomic distances and consequently greater values of E_p before melting occurs.

6. DEVIATIONS BETWEEN CALCULATION AND EXPERIMENT

Although fairly good agreement is obtained in general between calculated and experimental values of C_p, one must try to explain the deviations which do occur. The deviations are of three types. (1) While there is a tendency for the C_p values of all the substances to rise rather sharply at temperatures near the melting point, there is difficulty in accounting for all the cases by the same curve. (2) We have noted that a change of 2 percent in f_Θ for argon improves the agreement, and indeed, appears to be required, though this corresponds to a 6 percent error in the critical volume. (3) There seems to be a definite difference in the character of the curvature of the experimental C_p vs. T curves of the different substances (see Fig. 2). To explain these deviations we may consider three possibilities, (A) experimental error, (B) failure of the Debye theory, and (C) failure of Pitzer's assumption V.

Let us first consider deviation (1). Near the melting point the experimental specific heats show a sharp rise for all four solids that is reproduced qualitatively, though not very exactly, for xenon, krypton, and argon, by calculation from the argon $dE_p/d\Theta$ curve, but not from Curve II. This rise in specific heat near the melting point is reflected in the $dE_p/d\Theta$ curve by a rapid change of slope, i.e., by a large $d^2E_p/d\Theta^2$ near the melting point. The calculated C_p's are very sensitive to the slope of the $dE_p/d\Theta$ curve. In the case of neon, we must pass through these high values of $d^2E_p/d\Theta^2$ long before melting occurs, and we must extrapolate the curve until the melting point is reached. The extrapolation on the assumed $dE_p/d\Theta$ curve is shown in Fig. 1. The specific heat calculated from this is higher than the experimental over most of the temperature range. If we make the straightest possible extrapolation of the

argon $dE_p/d\Theta$ curve, the calculated C_p for neon is still higher, and an extrapolation with a uniform rate of change of the slope would be even worse. The situation could not be improved much by altering the energy and Θ factors for neon. It would be necessary to make a definite inflection in the $dE_p/d\Theta$ curve in the upper regions, giving an unreasonable appearance to the over-all curve, and it could be done only at the expense of the other solids, which require a high $d^2E_p/d\Theta^2$ near the melting point.

(A) In order to advance an explanation for these difficulties, we must ask why the sharply rising specific heats near the melting point occur. It may be caused, at least in part, by a pre-melting phenomenon, i.e., to a setting in of disorder before the melting temperature is reached, a rather special case of breakdown of the Debye theory. Rice[4] has concluded that the experimental data on solid argon are best explained by the assumption of no disorder in the solid, but a small amount may appear very close to the melting point. It may be possible, on the other hand, that the rise in experimental specific heat is greater than it should be because of experimental difficulties incident to specific heat measurements in this region. The fact that Clusius' experimental specific heats tended to be slightly erratic near the melting point lends some credence to this view. An experimental error could occur because melting was taking place on the faces of the crystals because of non-equilibrium temperature conditions. Disorder in the solid would mean that premelting was occurring throughout the interior of the crystal.

In general we hesitate to claim that deviations of type (2) or (3) are caused by errors in the specific heats, though the errors required would be of the order of only a few percent, and, as we have noted, some difficulties are apparent in the case of xenon (in fact the percentage difference between the two sets of Θ's shown in Table II is greater than the percentage difference between the two f_Θ's used in Table IV). It seems quite possible that explanations of the type (B) or (C) may hold the answer in these cases.

(B) The Debye theory itself rests on the theory of small vibrations in a molecular lattice; small vibrations are also implied in our method of calculating the Θ factor. Rice[4] has presented a

discussion of the failure of the theory of small vibrations in the case of argon, pointing out that the relatively large amplitudes deducible from experimental data should give rise to appreciable anharmonicities in the vibration. With this in view, it is not surprising that small changes are necessary in the Θ-factor; in fact the surprising thing is that our bold assumption that the Θ's can be obtained by a dimensional analysis of the mechanical system works as well as it does. This difficulty might also conceivably cause deviations of type (3).

(C) Pitzer's assumption V that the four substances have the same reduced E_p curve may not be strictly true. Guggenheim[2] noted that this assumption should be accurate for large values of r, where the intermolecular potential energy ϵ is proportional to $-r^{-6}$, but that there was good reason to suppose that it does not hold accurately in general. He further stated that many macroscopic properties were insensitive to the precise form of the relation between ϵ and r for small r. The fact that argon, krypton, and xenon obey the principle of corresponding states as liquids is consistent with these considerations. In the solid state, however, it seems likely that the properties are considerably more sensitive to the shape of the potential energy curve.

On the Ultraviolet Absorption Spectrum of Ozone†

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The absorption spectrum of ozone has been investigated in the near ultraviolet from λ3439 to 3850A at two temperatures. The bands observed have been interpreted as arising in part from transitions from the vibrationless ground electronic state and in part from transitions from excited vibrational levels of the ground electronic state. The distinction between the two groups is based primarily on the relatively large temperature sensitivity of the intensity of the bands ascribed to transitions from excited vibrational states. A partial analysis gives strong support to the assignment of the frequency 1043 cm⁻¹ to a fundamental vibration of the molecule. Moreover, it appears quite unlikely that the frequency 710 cm⁻¹ can be eliminated as one of the fundamental frequencies. No information concerning the third fundamental frequency was obtained.

THE spectroscopic evidence on the structure of ozone has recently been critically examined by Simpson,[1] who gives a new assignment of the fundamental vibration frequencies of the ozone molecule. This assignment leads to a configuration in which the oxygen atoms are arranged in the form of an obtuse isosceles triangle with apical angle 125° and bond length 1.17A, in fair agreement with the electron diffraction results[2] which give an apical angle of 127° and bond length 1.26A. However, the infra-red absorption spectrum of ozone has not been examined in sufficient detail under high enough dispersion to permit an unambiguous assignment of the three fundamental frequencies from among the four possibilities which seem most likely in view of the experimental data, namely, 710, 1043, 1740, and 2105 cm⁻¹.[3–6]

An analysis of the effect of temperature on the vibrational structure of the band system in the ozone spectrum lying in the region λ3000–3850A offers hope of affording additional information as to the fundamental vibrational frequencies of the normal state of the molecule. Such analysis

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