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On the Theory of Fusion

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Although equilibrium between two phases is in general determined by both phases, fusion stands somewhat apart in that a crystal cannot be overheated. As a type of the simplest possible crystal, the exact equation of state of frozen argon has been developed here. It has been found that the pressure as function of the volume at a given temperature has a minimum, which means the breakdown of the crystal under these conditions. The temperature at which this minimum occurs at zero pressure is interpreted as the melting point. It has been found in accordance with experiment that a positive pressure is necessary for the existence of crystalline helium but the numerical agreement is bad.

Introduction

Some time ago, we attempted[1] to get a better understanding of the liquid state through investigation of a simplified one-dimensional model but succeeded only in recognizing the conditions for the existence of definite phases. Here the same problem is attacked in a different manner. The equation of state of simple crystals (e.g., frozen rare gases) is calculated from the forces according to lattice theory. We find that the isotherms in which p is plotted against V have a minimum. Now a state in which the pressure increases with volume is unstable. Accordingly the crystal breaks down at the minimum pressure. Above the temperature at which this pressure minimum lies at zero pressure, the crystal cannot exist without external pressure. This temperature we interpret as the melting point.

In general, equilibrium between two phases is not defined by any particular happening in one of the two but by the equality of the free energies of the two at given pressure and temperature. For example, the equilibrium between liquid and vapor being given by the equality of their free energies, one can undercool the vapor or overheat the liquid without any discontinuous change in the properties of either. The same is even true for equilibria between allotropic crystals. It is possible to overheat grey tin or undercool white tin without any discontinuity appearing anywhere. The only known exception is the fact that no crystal can be heated above the melting point at the given pressure. It seems therefore reasonable to assume that fusion is conditioned by something happening in the crystal alone and to identify the point of instability of the crystal, which was described above, with the melting point. But then another question arises. At the melting point, the melt is in equilibrium with the crystal, i.e. the pressure, temperature and free energy of the melt must have values which are prescribed completely by the crystal (while in other equilibria, as stated above, the pressure is *selected* so as to give the equality of free energies). The only variables that seem to be left to the liquid to adjust its free energy are the values of the constants that appear in the potential energy and frequency and these are again determined by the arrangement of the molecules. Accordingly, the arrangement of the molecules in the liquid has to adjust itself so as to give the correct free energy.[1a] What this arrangement has to be is not investigated here but is reserved for later consideration.

If this view of fusion is correct, one would expect, for all normal substances, the volume of the liquid to be greater than that of the solid for the same temperature. It is then clear why, in the process of melting, the crystal does not melt in different small regions inside. A small molten region inside would have to contain the liquid in a highly compressed state, which would have a considerably higher free energy than the surrounding solid. It is, however, quite possible for the fusion to occur in channels communicating with the outside.

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[1] K. F. Herzfeld and M. Goeppert Mayer, J. Chem. Phys. 2, 38 (1934).

[1a] However it seems that this arrangement should be the one to give the smallest free energy of the liquid. How that is possible is not yet clear.

On the other hand, it seems not impossible for small crystals to persist in a liquid, a fact for which there appear to be experimental indications.[2] Up to now three other theories of fusion exist.

Lindemann[3] made the assumption that melting takes place if the amplitude of the vibrations is a certain fraction of the distance between nearest neighbors. Upon determining this fraction from the data for one crystal of each type and applying it to all crystals of the same type, one gets very good agreement.

Braunbeck[4] considers the mutual vibrations of two parts of the lattice, taken as rigid, assumes a suitable form of the mutual potential curve and finds positions of minimum energy. One of these he interprets as belonging to the solid, the other to the liquid state. The melting point is then determined as the temperature at which the free energies corresponding to these two states are equal.

Raschevsky[5] has come close to the ideas followed in this paper by pointing out that the heat of fusion is of the same order of magnitude as the elastic energy necessary to expand the lattice to the breaking point, i.e., the point where the tension has a maximum.

THE ENERGY AND THE ELASTIC CONSTANTS FOR A FACE-CENTERED LATTICE

Argon has a face centered lattice.[6] Call r the distance to the nearest neighbor, which is at the center of the face, so that the side of the cube is $r\sqrt{2}$. The volume per atom is

$$(r\sqrt{2})^3/4 = r^3/\sqrt{2}. \tag{1}$$

As potential energy φ_1 of attraction between two atoms we use a van der Waals expression (A, a constant)

$$-\varphi_1 = A/r^6, \tag{2}$$

which, summed up over the lattice, gives[7]

$$\Phi_1 = -14.4539A/r^6 \tag{3}$$

with $\Phi_1 = \Sigma\varphi_1$. The repulsive potential is written[8]

$$\varphi_2 = ABe^{-r/\rho}, \tag{2'}$$

(B, ρ constants) which gives for the whole crystal

$$\Phi_2 = 12ABe^{-r/\rho}\{1+\tfrac{1}{2}e^{-(\sqrt{2}-1)r/\rho} + 2e^{-(\sqrt{3}-1)r/\rho}+\cdots\}. \tag{3'}$$

This includes the atoms at the corners of the cube and in the centers of all the faces on all four cubes surrounding the atom considered here.

For ρ two values were used: $\rho = 0.345$A, which Born and Mayer found to fit best the behavior of alkali-halides, and $\rho = 0.2091$A which Bleick found theoretically for the interaction of two Ne atoms. Unfortunately, it is not possible to determine A and B directly from the normal value of r, $r_0 = 3.83$A and the normal heat of sublimation because the zero point energy plays a considerable part in the heat content and displaces the lattice distance by about 0.05A beyond the value given by the minimum of the potential energy alone.

A method of trial and error leads to[9] (N, Avogadro number)

$$NA = 6.706\times10^{-35}\text{ erg cm}^6,\quad B = 1.270\times10^{49}\quad \text{for } \rho = 0.345.$$

$$NA = 4.729\times10^{-35}\text{ erg cm}^6,\quad B = 0.9484\times10^{52}\quad \text{for } \rho = 0.2091.$$

These give as the heat of sublimation,[10] the value 1655 cal. The experimental values are rather uncertain.

There are three elastic constants, given by[11]

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[2] P. Othmer, Zeits. f. Allgem. und anorg. Chemie **91**, 209 (1915). A. Goetz, R. C. Hergenrother and A. B. Focke, Phys. Rev. **34**, 546 (1929); A. Goetz, Phys. Rev. **35**, 193 (1930); A. Soroos, Phys. Rev. **41**, 516 (1932).

[3] F. A. Lindemann, Phys. Zeits. **11**, 609 (1910).

[4] W. Braunbeck, Zeits. f. Physik **38**, 549 (1926).

[5] N. Raschevsky, Zeits. f. Physik **40**, 214 (1927).

[6] F. Simon and Cl. v. Simson, Zeits. f. Physik **25**, 160 (1924).

[7] E. Jones (Lennard-Jones) and A. E. Ingham, Proc. Roy. Soc. **A107**, 636 (1925).

[8] M. Born and J. E. Mayer, Zeits. f. Physik **75**, 1 (1932); W. Bleick, Dissertation, The Johns Hopkins University (1933). W. E. Bleick and T. E. Mayer, J. Chem. Phys. **2**, 252 (1934).

[9] The value of $NAB = 8.517\times10^{14}$, which we find for $\rho = 0.345$, is to be compared with $N\times10^{-12}e^{-2.660/\rho} = 13.53\times10^{14}$ which would follow from J. E. Mayer and M. Huggins, J. Chem. Phys. **1**, 633 (1933), if one puts the radius of $2\text{Av} = \text{K}^+ + \text{Cl}^-$. Furthermore, the value of NA is to be compared with the theoretical values of 3.3 and 3.7×10^{-35} calculated by F. London, Zeits. f. physik. Chemie **B11**, 222 (1930).

[10] A. Eucken, Verh. D. Phys. Ges. **18**, 4 (1916); A. Eucken and F. Hauck, Zeits. f. physik. Chemie **134**, 161 (1928); F. Born, Ann. d. Physik **69**, 473 (1922).

[11] M. Born, *Dynamik der Krystallgitter*, p. 536, 548, 554, Leipzig, 1923; M. Born and M. Goeppert Mayer, *Handb. d. Phys.* **24**, 2nd half, 2nd Ed., p. 630, Berlin, 1933. c_{11}

$$c_{11}=\frac{1}{\sqrt{2}r^3}\left\{\sum\frac{r}{3}\frac{d\varphi}{dr}+\sum\frac{1}{r}\frac{d}{dr}\left(\frac{1}{r}\frac{d\varphi}{dr}\right)x^4\right\}$$

$$=\frac{d}{dV}\frac{N\Phi}{2}+\frac{1}{2V}N\sum\frac{1}{r}\frac{d}{dr}\left(\frac{1}{r}\frac{d\varphi}{dr}\right)x^4, \quad (4)$$

$$c_{12}=\frac{1}{2V}N\sum\frac{1}{r}\frac{d}{dr}\left(\frac{1}{r}\frac{d\varphi}{dr}\right)x^2y^2, \quad (4')$$

$$c_{44}=\frac{d}{dV}\frac{N\Phi}{2}+c_{12}, \quad (4'')$$

where V is the mol volume.

At the minimum of the potential energy $d\Phi/dV=0$ so that there are only two elastic constants, because $c_{12}=c_{44}$. This does not hold, however, for other distances, where the general form must be used.

By using (2) and (2′) one finds[12]

$$c_{11}=\frac{NA}{V}\left\{B\frac{r^2+r\rho}{\rho}e^{-r/\rho}\left[1+\frac{2r+\sqrt{2}\rho}{r+\rho}e^{-(\sqrt{2}-1)r/\rho}\right.\right.$$
$$\left.+2\frac{3r+\sqrt{3}\rho}{r+\rho}e^{-(\sqrt{3}-1)r/\rho}+\cdots\right]$$
$$\left.-\frac{24\times 2.544}{r^6}\right\}+\frac{d}{dV}\frac{N\Phi}{2}, \quad (5)$$

$$c_{12}=\frac{NA}{V}\left\{\frac{B}{2}\frac{r^2+r\rho}{\rho^2}e^{-r/\rho}\left[1+2\frac{3r+\sqrt{3}\rho}{r+\rho}\right.\right.$$
$$\left.\left.\times e^{-(\sqrt{3}-1)r/\rho}+\cdots\right]-\frac{24\times 1.137}{r^6}\right\}. \quad (6)$$

The Frequency

According to Debye the maximum frequency of a cubic crystal is

$$\nu=w(3N/4\pi V)^{\frac{1}{3}} \quad (7)$$

where w is the sound velocity. In dependence of the direction this is given by a determinant of the third order. The method used by Born and Kármán[13] which consists in a development into powers of $3c_{12}-c_{11}/c_{11}-c_{12}$, cannot be applied here because this quantity is by no means small.

But on the other hand there is no particular reason why one should average just in the way proposed by Debye, using in (7) the quantity found from

$$1/w^3=\overline{(1/w_1{}^3)}+\overline{(1/w_2{}^3)}+\overline{(1/w_3{}^2)},$$

where w_1, w_2, w_3 mean the three roots of the characteristic equation and the bars an averaging over the direction. It is much simpler to form one of the symmetric functions of the roots and average. We have used

$$D^3\overline{w^6}=D^3\overline{w_1{}^2w_2{}^2w_3{}^2}=c_{11}c_{44}{}^2$$
$$+c_{44}[(c_{11}-c_{44})^2-4c_{12}{}^2][\overline{\cos^2(xr)\cos^2(yr)}$$
$$+\overline{\cos^2(yr)\cos^2(zr)}+\overline{\cos^2(zr)\cos^2 xr}]$$
$$+[(c_{11}-c_{44})^3-12(c_{11}-c_{44})c_{12}{}^2+16c_{12}{}^3]$$
$$\times\overline{\cos^2 xr\cos^2 yr\cos^2 zr} \quad (8)$$

in which D is the density. In terms of numerical values and the atomic weight M this becomes

$$\nu^6=V(9N^2/16\pi^2M^3)\{c_{11}c_{44}{}^2$$
$$+\tfrac{1}{5}c_{44}[(c_{11}-c_{44})^2-4c_{12}{}^2]+(1/105)$$
$$\times[(c_{11}-c_{44})^3-12(c_{11}-c_{44})c_{12}{}^2+16c_{12}{}^3]\}. \quad (9)$$

The Equation of State

The total energy at 0° abs. and any volume is given by the lattice energy plus the zero point energy $\frac{3}{2}Nh\bar{\nu}$ ($\frac{1}{2}h\nu$ for each degree of freedom).

$$U=\frac{N\Phi}{2}+\frac{3}{2}Nh\bar{\nu}. \quad (10)$$

The limiting ν calculated in (9) is for the Debye spectrum 4/3 of the average $\bar{\nu}$ meant above. At

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measures the tension in one direction due to an expansion in the same direction with the cross dimensions kept constant, c_{12} measures the tension in the cross direction which tries to contract the specimen and determines largely the Poisson constant, c_{44} measures the shearing stress. The summation is to be extended over all the lattice points with the coordinates x, y, z.

[12] A calculation of the numerical factors of r^{-6} was effected by directly summing up over the nearest 168 atoms, i.e. up to and including a distance $3r$. Then an integration was performed over a continuum reaching from a sphere of radius $3r$ to infinity and from this half the contribution of the atoms at distance $3r$, which had already been taken into account in the summation, was subtracted. The values calculated in that way were 2.541 and 1.135. But in a cubic crystal one must have

$$(x^4+2x^2y^2)/r^4=(x^4+x^2y^2+x^2z^2)/r^4=x^2r^2/r^4=x^2/r^2=\tfrac{1}{3}.$$

As $2.541+2\times 1.135=\frac{1}{3}$ of 14.433 instead of 14.454 (3), the constants were raised to the values above.

[13] Born, ref. 11, p. 647, Born and Goeppert-Mayer, p. 672; M. Born and Th. von Kármán, Phys. Zeits. **14**, 15 (1913); L. Hopf and G. Lechner, Verh. d. D. phys. Ges. **16**, 643 (1914).

TABLE I. *Frequency, elastic constants and energy.* r in A, energy in kilojoule, $\rho=0.345$A, $\Theta=h\nu/k$ in degree kelvin.

r	3.73	3.78	3.83	3.88	3.93	3.98	4.03	4.08
Θ	94.31	81.90	72.80	66.58	60.31	54.47	48.98	43.68
$c_{11}\times10^{-10}$	3.901	2.742	2.015	1.573	1.207	0.9064	0.6606	0.4583
$c_{12}\times10^{-10}$	2.273	1.613	1.183	0.9198	0.7028	0.5249	0.3800	0.2609
$c_{44}\times10^{-10}$	2.115	1.592	1.262	1.048	0.8657	0.7122	0.5830	0.4737
$\frac{N\Phi}{2}$	−7.627	−7.647	−7.600	−7.501	−7.356	−7.129	−6.974	−6.756
$\frac{3}{2}Nh\frac{3}{4}\nu$	0.882	0.766	0.681	0.623	0.564	0.510	0.458	0.409
$-U$	6.745	6.881	6.919	6.878	6.792	6.619	6.516	6.347

TABLE II. *Pressure.* (Fig. 1.) V in cc, pressure in 10^8 dynes/cm², $\rho=0.345$A.

r	3.73	3.78	3.83	3.88	3.93	3.98	4.03	4.08
V	22.26	23.17	24.10	25.06	26.04	27.05	28.08	29.14
$\frac{\partial \ln \nu}{\partial V}$	0.167	0.143	0.109	0.097	0.102	0.102	0.104	0.113
p_1	15.82	2.08	−7.93	−12.82	−16.29	−18.73	−20.30	−21.28
p_2	15	10.9	7.42	6.04	5.74	5.18	4.78	4.62
0° p	$\underline{31}$	$\underline{13.0}$	$\underline{-0.51}$	$\underline{-6.78}$	$\underline{-10.55}$	$\underline{-13.55}$	$\underline{-15.52}$	$\underline{-16.66}$
70° p_3	17	15.6	12.61	11.65	12.67	13.10	13.88	15.50
p	$\underline{48}$	$\underline{28.6}$	$\underline{12.10}$	$\underline{4.87}$	$\underline{2.12}$	$\underline{-0.45}$	$\underline{\underline{-1.64}}$	$\underline{-1.16}$
76° p_3	19	17.6	14.16	13.04	14.13	14.57	15.41	17.17
p	$\underline{50}$	$\underline{30.7}$	$\underline{13.65}$	$\underline{6.26}$	$\underline{3.58}$	$\underline{1.02}$	$\underline{\underline{-0.10}}$	$\underline{0.51}$
100° p_3	29	25.8	20.46	18.67	20.07	20.55	21.56	23.84
p	$\underline{60}$	$\underline{38.8}$	$\underline{19.95}$	$\underline{11.89}$	$\underline{9.52}$	$\underline{7.00}$	$\underline{\underline{6.04}}$	$\underline{7.18}$

higher temperatures, the free energy pro mole at constant volume is

$$f=U+F, \qquad (11)$$

where

$$F=\int_0^T CdT-\int_0^T \frac{C}{T}dT=-T\int_0^T \frac{dT}{T^2}E. \qquad (11')$$

Here C is the specific heat and $E=\int_0^T CdT$. The pressure is given by

$$p=-\partial f/\partial V \qquad (12)$$

and is accordingly made up of three parts:

$$p=p_1+p_2+p_3. \qquad (12')$$

p_1 is the elastic tension

$$p_1=-(\partial/\partial V)(N\Phi/2). \qquad (12'')$$

p_2 is the zero point pressure

$$p_2=-\frac{\partial}{\partial V}\frac{3}{2}Nh\bar{\nu}=-\frac{\partial}{\partial V}\frac{3}{4}\cdot\frac{3}{2}Nh\nu. \qquad (12''')$$

Both these values depend only on V, not on T. At higher temperature, one has to add the thermal pressure[14]

$$p_3=-(\partial F/\partial V)=E(\partial \ln \nu/\partial V). \qquad (12'''')$$

Here it has been assumed that F/T is a function of ν/T only. F and E can be found tabulated.[15]

It is necessary for possible existence of a state that

$$(\partial p/\partial V)<0. \qquad (13)$$

If a p, V curve for constant T shows a minimum, the crystal breaks down (cannot exist) beyond that minimum.

THE DISCUSSION OF THE RESULTS

All total pressures are underlined, the minimum pressure for each temperature is doubly underlined. The results are shown in the Tables I–IV.

If, according to this interpretation, the melting point is given by

$$p=0, \quad \partial p/\partial V=0, \quad \partial^2 p/\partial V^2>0, \qquad (14)$$

it follows that the compressibility of the crystal at the melting point must be infinite. The same should be true for the coefficient of expansion.

In considering the tables, one sees that for the equilibrium distance $r=3.83$A $\Theta=73$ for $\rho=0.345$ and $\Theta=96$ for $\rho=0.2091$ while the experimental value is $\Theta=85$. For $\rho=0.2091$, Θ is

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[14] $F/T=-\int_0^T(E/T^2)dT=-\int_0^T(E/T^2)\nu d(T/\nu)$. If we put $T/\nu=x$ and assume that C is a function of x only $E=\int CdT=\nu\int Cdx$. $F/T=-\int x^2dx\int Cdx$ is a function of x only, say $\psi(x)$, $(\partial\psi/\partial x)=-(E\nu/T^2)$. Then

$$(\partial F/\partial V)=T(\partial\psi/\partial x)(\partial x/\partial V)$$
$$=-(T^2/\nu^2)(\partial\psi/\partial x)(\partial\nu/\partial V)=(E/\nu)(\partial\nu/\partial V).$$

[15] F. Simon, Handb. d. Physik **10**, 368 (1926), Berlin.

TABLE III. *Frequency, elastic constants, energy.* r in A, energy in kilojoule, $\rho=0.2091$ A.

r	3.73	3.78	3.83	3.88	3.93	3.98	4.03
Θ	128.5	111.2	96.46	82.81	70.56	59.06	48.44
$c_{11}\times 10^{-10}$	7.165	5.169	3.660	2.523	1.673	1.0383	0.5724
$c_{12}\times 10^{-10}$	3.908	2.796	1.957	1.328	0.8594	0.5118	0.2578
$c_{44}\times 10^{-10}$	3.761	2.821	2.099	1.547	1.1263	0.8057	0.5634
$\frac{N\Phi}{2}$	−7.891	−7.923	−7.841	−7.666	−7.425	−7.143	−6.830
$\frac{3}{2}Nh\frac{3}{4}\nu$	1.202	1.040	0.902	0.775	0.660	0.552	0.453
$-U$	6.689	6.883	6.939	6.891	6.765	6.591	6.377

TABLE IV. *Pressure* (in 10^8 dynes/cm²), volume in cc, $\rho=0.2091$ A. (Fig. 2.)

r	3.73	3.78	3.83	3.88	3.93	3.98	4.03
V	22.26	23.17	24.10	25.06	26.04	27.05	28.08
$\frac{\partial \ln \nu}{\partial V}$	0.168	0.156	0.156	0.160	0.169	0.185	0.198
p_1	14.72	−2.45	−14.17	−21.91	−26.69	−29.39	−30.56
p_2	20	16.3	14.09	12.39	11.17	10.20	8.98
0° p	35	13.8	−0.08	−9.52	−15.52	−19.19	−21.58
50° p_3	7	7.8	8.84	10.20	11.98	14.39	16.87
p	42	21.6	8.76	0.68	−3.54	−4.80	−4.71
61° p_3	11	11.3	12.56	14.13	16.26	19.19	22.10
p	46	25.1	12.48	4.61	0.74	0	0.52
65° p_3	12	12.7	13.94	15.59	17.84	20.96	24.02
p	47	26.5	13.86	6.07	2.32	1.77	2.44
100° p_3	25	25.1	26.64	28.85	32.05	36.64	41.00
p	60	38.9	26.56	19.33	16.53	17.45	19.42

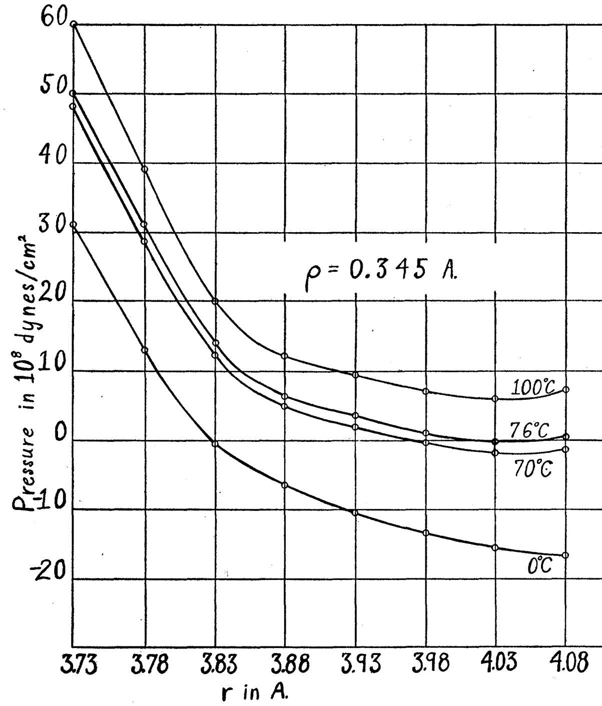

FIG. 1.

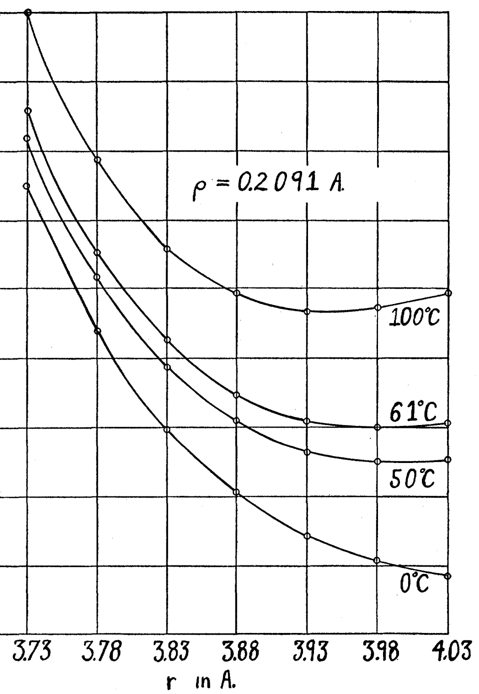

FIG. 2.

FIG. 1. pr isotherms for argon. $\rho=0.345$A, the value Born and Mayer found for the alkali-halides.
FIG. 2. pr isotherms for argon. $\rho=0.2091$A, the value found by Bleick and Mayer for He atoms.

83 for $r=3.88$, which corresponds to 50°. On theoretical grounds, one should expect to have ρ rather alike for argon and neon and therefore prefer $\rho=0.2091$.

The melting points are both too low, 76° and 61° compared with 84° observed. It is true that we have, following Born, used only a first approximation insofar as we considered the vibrations as purely harmonic around the given lattice distance with the frequency appropriate for that distance. A higher approximation would need rather lengthy calculations, but one should expect that the effect would be to lower the melting point still further.

The thermal pressure is determined essentially by $\partial \ln \nu/\partial V$. A higher melting point would result if $\partial \ln \nu/\partial V$ would be lower; then a higher temperature would be necessary for the same thermal pressure. A smaller $\partial \ln \nu/\partial V$ means a slower falling off of the repulsive forces.

In comparing the melting points and Θ's (or ν's) for the two ρ-values, one might be astonished to find the higher T with the lower $\nu(\rho=0.345)$ in contradiction to the Lindemann formula. But we are comparing here for constant heat of sublimation, while the variation of ν in the Lindemann formula measures essentially the variation of this heat. From an inspection of the table, $\partial \ln \nu/\partial V$ is seen to vary little with V, in agreement with Grüneisen.[16]

HELIUM

The properties of condensed helium have recently been the subject of much experimentation.[17, 18] It is found that crystallized helium can exist only under pressure (25 atm. at 0°). Simon[18] has already interpreted this as due to a zero point pressure $p_2 > |p_1|$.

He has given as provisional data:

Heat of sublimation: 11 cal. = 46.1 joule.

The density of solid He at 4° and under a pressure that provides equilibrium ($\sim$100 atm.?) is found to be 0.23 ($V=17.4$ cc), the compressibility at 3.7° and 115 atm. is about 1.5×10^{-9} abs. units and the characteristic temperature $\Theta=32.5$.

Now the potential energy of two helium atoms has been calculated from the model by Slater and Kirkwood[19] to

$$\varphi=\{7.7e^{-2.43-(r/a_0)}-0.68(a_0/r)^6\}10^{-10}\text{ erg} \tag{15}$$

where a_0 is the Bohr radius.[20] With this, the same calculation as for argon was performed under the assumption that solid helium, like argon, has a face centered cubic lattice. The result is given in the Tables V and VI.

One sees that there is a pressure minimum at 0° at about 3.12A. The pressure there is positive, so that the crystalline helium cannot exist without pressure. However, the volume is much smaller than the experimental one (13 cc against 17.4; at $V=17.4$ and $r=3.45$ one is already far beyond the maximum of p_1, all the elastic constants are negative). The minimum pressure is too high, about 1250 atm. instead of 25 atm., finally Θ is too large (about 55° instead of 32°). On the other hand, the heat of sublimation seems about right.

There are two possible explanations for these deviations: The repulsion is considerably larger than given by (15), or the assumed lattice is wrong. Now the only other lattice that might be plausible is the body centered cubic one. While the face-centered lattice has a mol-volume $Nr^3/\sqrt{2}$, the body centered has one of $N(4/3\sqrt{3})r^3$, which, for the same r is larger by the factor 1.088. On the other hand, the summation of φ over the lattice leads to a decrease of the numerical factor for the repulsive energy from 12/2 to 8/2 while for the attraction this summation results only in a decrease of the factor from $\frac{1}{2}\times14.454$ to[7] $\frac{1}{2}\times12.253$. That means that for the same φ the minimum of the potential energy and the place where $-p_1$ has a maximum are shifted to smaller r. Therefore, even with this lattice, this maximum of $-p_1$ would occur around $V=13.5$ cc.

Accordingly, an attempt has been made to repeat the calculation with a changed potential energy for the face centered lattice. The repulsion was increased by a factor 3. This moves the minimum pressure out to the distance where it

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[16] E. Grüneisen, Ann. d. Physik **39**, 257 (1912).

[17] W. Keesom and co-workers, Leid. Comm. No. 184b, 190b, 216b, 219e, 221e. Suppl. 67b, 71e, 76b. Physica **1**, 128, 161 (1934).

[18] F. Simon, Nature **133**, March 24 and April 7, 1934.

[19] J. C. Slater and J. G. Kirkwood, Phys. Rev. **37**, 682 (1931).

[20] It might be remarked that this amounts to a $\rho=0.219$, very close to the Mayer-Bleick value for neon.

TABLE V. *Energy, elastic constants and frequency for He. Energy in joule, r in A.*

r	2.8	3.0	3.05	3.10	3.15	3.20	3.25
Θ	169.5	80.8	68.75	57.29	46.41	34.35	
$c_{11}\times 10^{-8}$	164.6	26.47	16.99	9.856	4.648	0.901	−1.666
$c_{12}\times 10^{-8}$	94.86	14.77	9.228	5.151	2.204	0.089	−1.344
$c_{44}\times 10^{-8}$	80.36	18.29	13.35	9.577	6.715	4.540	2.940
$\frac{N\Phi}{2}$	−1586	−756.4	−645.5	−536.1	−434.3	−321.4	
$\frac{3}{2}Nh\frac{3}{4}\nu$	598.0	593.5	570.8	544.7	516.5	487.4	
$-U$	+988	+162.9	+74.7	−8.6	−82.2	−166.0	$-U$

TABLE VI. *Pressure.* Pressure in 10^8 dyne/cm², V in cc.

r	3.0	3.05	3.10	3.15	3.20
V	11.58	12.14	12.78	13.41	14.06
$\frac{\partial \ln \nu}{\partial V}$	0.379	0.322	0.310	0.333	0.677
p_1	−3.52	−4.12	−4.43	−4.51	−4.45
p_2	22.5	18.4	16.9	17.2	$\sim$33
0° p	19.0	14.3	12.5	12.7	$\sim$28.5
4° p_3			0.021	0.041	0.21

should be (actually a little further), namely to 3.50A ($V=18.4$ cc). That reduces Θ to 50, the minimum pressure is reduced to about 530 atm. but it gives a positive energy content, that is to say a negative heat of sublimation. The zero point energy is then about 450 joules, the lattice energy about 250, having been cut to about $\frac{1}{2}$ of its former value by the increase of the distance and the repulsive term. The compressibility also comes out far too small. Without further calculations it cannot be said what has to be done to improve the agreement. We reserve this calculation and shall only indicate that a slower falling off of the repulsion might be necessary.

SUBSTANCES WITH HIGH MELTING POINTS

Approximations for substances with melting points sufficiently high that the classical specific heat is reached should simplify the calculations considerably because in that case the zero point energy can be neglected and E in equation (12'''') can be replaced by $3RT$. However, we do not know the potential energy in the metals well enough to perform the calculation and in the case of ionic crystals there is still a certain difficulty in calculating the frequencies correctly.[21] Attempts at an approximate calculation were made. The lattice energy U was developed into a power series up to the 3rd power

$$U=U_0+(U''/2)(V-V_0)^2+(U'''/6)(V-V_0)^3.$$

For $\partial \ln \nu/\partial V$ two alternate approximations were made, either $\partial \ln \nu/\partial V$ was assumed constant or ν^2 was put proportional to $\partial^2 U/\partial r^2$. For the first case the calculations were very simple. If the experimentally found coefficient of expansion is given by

$$\alpha=\alpha_0(1+\beta T).$$

then the melting point should be given by

$$T=1/2\beta.$$

For the second assumption the calculations are rather complicated but in both cases the calculated melting points are far too low.

The general results of this paper, however, should hold for all substances. The existence of an upper limit of temperature for the stability of a crystal is based on the appearance of a minimum in the p, V isotherm, shifting to more positive pressures with increased temperature. Now such a minimum should appear in the p, V curve of every crystal, because with increasing volume the elastic tension must finally go to 0. On the other hand, the thermal pressure should increase to infinity. It is namely given by (12''''). ν goes to 0 at a certain volume, probably with the first power of the deviation from that volume. Accordingly $\partial \ln \nu/\partial V$ must go to positive infinity when this volume is approached and the combination of the negative elastic tension, decreasing with volume, and the positive thermal pressure, increasing to infinity with increasing volume, must give a minimum. Because of the factor E in the thermal pressure this minimum will always shift to more positive pressures with increasing temperature. But, of course, for a numerical calculation the exact energy formula must be known.

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[21] See, for example, Born and Goeppert-Mayer, Handb. d. Physik **24**, 2nd half, 733, 2nd edition.