

between  $250^{\circ}$  and  $400^{\circ}$  have been measured; and the following equations expressing them in millimeters of mercury have been derived:

$$\text{For NaH: } \log_{10} p = -5700/T + 2.5 \log_{10} T + 3.956.$$

$$\text{For KH } \log_{10} p = -5850/T + 2.6 \log_{10} T + 3.895.$$

The vapor pressure equations for liquid sodium and potassium have been calculated from the following data: (1) the boiling points of these substances; (2) their heats of vaporization, derived from Trouton's rule (assuming the same constant as for mercury); and (3) the heat capacities of the liquids and the vapor. These equations are

$$\text{For Na: } \log p = -6200/T - 1.35 \log T + 12.4.$$

$$\text{For K: } \log p = -6000/T - 0.40 \log T - 0.0008T + 10.73.$$

The heat of reaction at ordinary temperatures has been calculated from the measurements, and found to be 13,860 calories per formula-weight of sodium hydride (NaH) and 14,240 calories per formula-weight of potassium hydride (KH).

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## A CORRELATION OF THE ELASTIC BEHAVIOR OF METALS WITH CERTAIN OF THEIR PHYSICAL CONSTANTS.

By JOHN JOHNSTON.

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As is well known, the effect of pressure acting on both the solid and liquid phase of a single substance is to raise or lower its melting point according as the process of melting is accompanied by an increase or a decrease of volume respectively, the latter being the exceptional case. But when pressure acts only on the solid phase, but not—or not to the same extent—on the liquid phase, the melting point is always lowered and by an amount which is many times as great as the corresponding change produced by the same pressure acting on both the liquid and the solid phase. For example, the melting point of ice is lowered by  $0.0075^{\circ}$  per atmosphere of equal pressure, but by about 12 times as much, or  $0.09^{\circ}$  per atmosphere, when the pressure acts only on the ice.<sup>1</sup> The latter type of pressure we shall for convenience in what follows designate by the term "unequal pressure."

A study of the work of Spring and others rendered evident a parallelism between the melting point of a substance and the ease with which it will, when subjected to (non-uniform) compression, flow or weld into a more or less solid block; namely, that the higher the melting point of the material, the less readily does it flow, or weld together, under compression.

<sup>1</sup> Cf. J. H. Poynting, *Phil. Mag.*, [5] 12, 32 (1881); Ostwald's "*Lehrbuch der Allgemeinen Chemie*," 2 Aufl., Vol. 2, II, pp. 374-9; or Roozeboom's "*Heterogene Gleichgewichte*," Vol. 1, pp. 213-7.

From this it is obvious that, if it be assumed that the process of flow is a manifestation of a real melting produced by the compression, the pressure must be unequal in character; that is, the pressure acting on the solid must be greater than that on the liquid phase. For, when the same pressure acts on both phases, the melting point of practically all substances is raised, and not lowered, as, on this explanation of the phenomenon, we assume it to be. It seemed of interest, therefore, to calculate the effect of unequal pressure in lowering the melting point of metals, to compute the amount of such pressure required to cause the metal to melt at or about the ordinary temperature, and to investigate if the pressure computed in this way can be correlated with any of the mechanical, or other, properties of the metals.

The equation made use of in calculating the effect of unequal pressure on the melting point is derived most readily in the way employed by G. N. Lewis in a parallel case—the calculation of the variation of osmotic pressure with temperature.<sup>1</sup>

Let  $A$  be the activity<sup>2</sup> of the substance in the solid phase, and  $A'$  the activity in the liquid phase. Now, if the pressure on the solid phase alone is increased by  $dP$ , then the temperature of equilibrium will be changed by an amount  $dT$ . Since both phases are initially in equilibrium, the activity of the solid ( $A$ ) and that of the liquid ( $A'$ ) must be equal; moreover, they must again be equal when equilibrium is re-established. Hence  $A = A'$ , and  $dA = dA'$ , or  $d \ln A = d \ln A'$ .

Now, the change in  $\ln A$  is due to temperature change alone; the change in  $\ln A'$  is due to change in temperature and change in pressure; that is,

$$d \ln A = \left( \frac{\partial \ln A}{\partial T} \right) dT$$

and

$$d \ln A' = \left( \frac{\partial \ln A'}{\partial T} \right) dT + \left( \frac{\partial \ln A'}{\partial P} \right) dP.$$

Equating the right hand members of these equations, we have

$$\left( \frac{\partial \ln A}{\partial T} \right) dT - \left( \frac{\partial \ln A'}{\partial T} \right) dT = \left( \frac{\partial \ln A'}{\partial P} \right) dP.$$

Substituting for the partial differentials their values from the fundamental thermodynamic equations,<sup>3</sup> and combining the left hand terms, gives

<sup>1</sup> THIS JOURNAL, 30, 680 (1908). I am much indebted to Prof. Lewis for bringing to my attention this method, which is so much more succinct than the mode of derivation which I had at first made use of.

<sup>2</sup> For a definition and discussion of the term "activity," see Lewis, "Outlines of a New System of Thermodynamic Chemistry," *Proc. Am. Acad.*, 43, 259 (1907); *Z. physik. Chem.*, 61, 129 (1907).

<sup>3</sup> Lewis, equations V and VIII, *Proc. Am. Acad.*, 43, 266, 267 (1907); *Z. physik. Chem.*, 61, 137, 138 (1908).

$$\frac{LdT}{RT^2} = \frac{VdP}{RT}$$

or

$$\frac{dT}{dP} = \frac{VT}{L} \quad (\text{I})$$

where  $V$  is the molal volume of the solid phase,  $T$  its melting point on the absolute scale (both phases under the same pressure), and  $L$  its molal heat of fusion. The quantities  $V$  and  $T$  are always positive, but  $L$  (as here used) is always negative; hence application of excess pressure on the solid phase always lowers the melting point.<sup>1</sup>

This differential equation is rigorously correct; but in order to integrate it, we must know how  $V$  and  $L$  change with the temperature and with the pressure. The variation of  $V$  is determined by the coefficients of expansion and of compressibility, which are known for comparatively few substances. With regard to the other factors, our knowledge of  $L$  at the ordinary melting point under atmospheric pressure is as yet extremely unsatisfactory in character and limited in scope, while our ignorance of its variation with either temperature or pressure is practically complete. However, in the case of the metals at least, this difficulty is not so serious, as is shown by the following considerations:

The variation of melting point with pressure, acting equally on both phases, for all the metals which have so far been investigated, has been found to be practically linear within the error of experiment.<sup>2</sup> It is a necessary consequence of this linearity that with increasing pressure the relation between  $L$  and  $(V-V')$  ( $V'$  is the molal volume of the liquid phase) must be linear, or, in the limiting case, remain practically constant. It is, therefore, very plausible that we are justified in assuming that the variation of  $L$  with  $V$  is linear. Integrating equation I on this basis, between the limits  $T_1$  (the ordinary melting point at 1 atm. pressure,

<sup>1</sup> This lowering is, of course, relative to the melting point when that pressure which now acts on the liquid alone (the solid being subject to pressure in excess of this) acts on both solid and liquid. In other terms: if the melting point is denoted by  $T$  with subscripts and superscripts to represent the pressure acting on the solid phase and liquid phase respectively, then  $T_{P+\Delta P}^P$  is always lower than  $T_P^P$ , the magnitude of this lowering being dependent on the excess of pressure  $\Delta P$  acting on the solid. Now  $T_P^P$  may be higher, or lower, than  $T_1^1$  (the ordinary melting point at atmospheric pressure), according as the volume change on melting is positive or negative; consequently, in some cases  $T_{P+\Delta P}^P$  may be higher than  $T_1^1$ , but this will be so only when  $\Delta P$  is small compared to  $P$ , a contingency which, we believe, does not affect the main considerations advanced in this paper.

<sup>2</sup> Tammann, *Z. anorg. Chem.*, **40**, 54 (1904) with K and Na; Johnston and Adams, *Am. J. Sci.*, **31**, 501 (1911); *Z. anorg. Chem.*, **72**, 11 (1911), with Sn, Bi, Cd, Pb at pressures up to 2000 atm.; Bridgman, *Proc. Am. Acad.*, **47**, 347 (1911), with Hg up to still higher pressures.

expressed on the absolute scale) and a given temperature  $\theta$ , we obtain the equation

$$P = \frac{L}{V} \ln \frac{T_1}{\theta}. \quad (\text{II})$$

Instead of the molal values we may substitute the heat of fusion ( $Q_1$ ) per gram of substance, and the density ( $D_1$ ) of the solid, at the ordinary melting point<sup>1</sup> ( $T_1$ ); making the necessary transformations, we obtain finally the equation

$$\varphi = 95.1 Q_1 D_1 \log \frac{T_1}{\theta}, \quad (\text{III})$$

which enables to calculate the melting pressure ( $\varphi$ , expressed in atmospheres) corresponding to the temperature  $\theta$ ; that is,  $\varphi$  is the pressure required to cause the substance to melt at the absolute temperature  $\theta$ .

This formula has been applied to the calculation of the excess pressure (acting on the solid only) required to cause the metal to melt at  $27^\circ$  (that is,  $\theta = 300^\circ$ ) in the case of all the metals<sup>2</sup> for which values of  $Q$  are given in Landolt-Börnstein-Meyerhoffer Tabellen (2 Aufl., p. 470). For some metals more than one value is given, but it is at present impracticable to determine which are most reliable; for this reason, the mean value was adopted in all such cases. For the same reason, the general mean value of the density, as given in the tables (pp. 224-9), was taken. The melting points are those now generally adopted.

The data and results are brought together in Table I, in which the metals are arranged in the order of increasing values of the melting pressure calculated in this way from equation III. It was conjectured that this order might bear some relation to that obtained when these metals are arranged with reference to the relative values of their elastic constants and mechanical properties.

<sup>1</sup> In the computations which follow, the value of the density at the ordinary temperature was used. This was done because of the uncertainty in the appropriate correction; moreover, our present knowledge of  $D$  at the ordinary temperature is so unsatisfactory that it would be altogether futile to apply any such correction, especially as the accuracy of the present values of  $Q$  is so doubtful.

<sup>2</sup> Excepting iron, on account of the uncertainty of what "iron" is, and the disparity of the recorded values. The value given for nickel in Landolt-Börnstein-Meyerhoffer Tabellen (p. 470) as a heat of fusion (taken from Pionchon, *Ann. chim. phys.*, [6] 11, 106 (1887)) was found, on reference to the original, to be a heat of *transformation* (occurring somewhere between  $230^\circ$  and  $400^\circ$ ); consequently nickel could not be included. (Similarly, Pionchon's values for iron given in *L.-B.-M.* (p. 470) are heats of *transformation*.) Mercury and gallium are omitted, since they are liquid at ordinary temperatures. The value of  $Q$  for aluminium is somewhat doubtful; it was calculated from the "total heat" (as given in *L.-B.-M.*) by means of the specific heat of aluminium (0.30) as given by Bontschew (*L.-B.-M.*, p. 383). No alloys could be included owing to lack of the necessary data; in any case the formula is applicable only to those alloys which melt completely at a definite temperature.

TABLE I.—LOWERING OF MELTING POINT OF METALS EFFECTED BY ONE ATM. UNEQUAL PRESSURE, TOGETHER WITH THE COMPUTED MELTING PRESSURES AT ORDINARY TEMPERATURES.

Metal.	Melting point.		Heat of fusion. $Q$	Density. $D$	$\Delta T_1^1$	$\varphi_{27}^2$
	$t$	$T_1$				
K	62	335	15.7	0.87	0.59	64
Na	97	370	31.7	0.98	0.29	266
Pb	327	600	5.4	11.37	0.24	1760
Sn	232	505	14.1	7.29	0.12	2200
Bi	270	543	12.5	9.80	0.11	3000
Cd	321	594	13.7	8.64	0.12	3300
Al	658	931	42.0	2.60	0.21	5100
Zn	419	692	28.0	7.1	0.084	6900
Ag	960	1233	23.0	10.50	0.12	14000
Cu	1083	1356	43.0	8.93	0.086	24000
Pd	1550	1823	36.3	11.4	0.11	31000
Pt	1755	2028	27.2	21.5	0.084	46000

The most obvious mechanical property with which to compare the series of  $\varphi$  values is the flow pressure.<sup>3</sup> This was determined for a series of metals, by Tammann, Verigin and Levkojeff;<sup>4</sup> later, and independently, by Kurnakov and Zhemchuzhny.<sup>5</sup> Arranged in the order of decreasing ease of flow, the metals follow in the order K, Na, Pb, Tl, Sn, Bi, Cd, Zn, Sb, a sequence which is identical with that deduced thermodynamically and presented in Table I. But not only is the sequence of  $\varphi$  values identical with that of the flow pressure; it is practically identical with the sequence obtained when the metals are arranged in the order of *any* of their elastic properties for which measurements have been made. This is shown by Table II, in which have been brought together all the

<sup>1</sup> This column, which represents the melting point depression produced by 1 atm. excess pressure acting on the solid, is added merely to give an idea of the magnitude of this quantity. The values given are calculated from the formula  $\Delta T_1 = T_1/41.30 QD$  which is easily derived from equation I.

<sup>2</sup> It should be observed that the values of  $\varphi$  given in the preliminary note (*J. Washington Acad. Sci.*, 1, 260 (1911)) were calculated by a formula which holds strictly only so long as  $\varphi$ , or the difference between  $T$  and  $\theta$ , is small. The more accurate mode of calculation from equation III of the present paper leads to somewhat higher numerical values of  $\varphi$ , but does not alter the order of the  $\varphi$  values; so that this change does not affect the argument.

<sup>3</sup> The amount of compression required to cause a material to flow is characteristic of the material under specified conditions; but at constant temperature it varies, as is obvious, with the size of the aperture through which the flow takes place; probably also it depends upon the shape of the aperture and upon other subsidiary factors. Hence, determinations of flow pressures are comparable only when they have all been made in the same apparatus and in the same way. This condition is fulfilled by the experimental observations cited, which lead to reliable relative values of the flow pressure for a series of metals.

<sup>4</sup> *Ann. Physik*, 10, 649 (1903).

<sup>5</sup> *Z. anorg. Chem.*, 64, 174 (1909).

data available on the elastic properties, namely, compressibility, hardness, tensile strength, elastic limit, elastic modulus and modulus of rigidity.

TABLE II.—RELATIVE VALUES<sup>1</sup> OF THE ELASTIC CONSTANTS OF METALS.

Metals in order as in Table I.	Compressibility. (a).	Hardness. (b).	Tensile strength.		Elastic limit.			Elastic (Young's) modulus. (g).	Rigidity modulus.	
			(c).	(d).	(e).	Lower. (f).	Upper. (f').		(h).	(i).
K	31.5	0.5	..	..	..	..	..	..	..	..
Na	15.4	0.4	..	..	..	..	..	..	..	..
Pb	2.2	1.5	2.0	21	0.3	25	102	17	5	0.80
Sn	1.7	1.8	2.1	36	4	34	55	34	16	1.50
Bi	2.8	2.5	..	..	..	..	..	32	12	..
Cd	1.9	2.0	..	48	..	28	109	71	17	2.31
Al	1.3	2.9	..	..	..	283	600	70	29	2.55
Zn	1.5	2.5	13	..	10	125	770	78	31	..
Ag	0.84	2.7	22	272	12	..	..	70	39	2.67
Cu	0.54	3.0	25	316	12	203	2780	108	42	4.37
Pd	0.38	4.8	..	..	27	..	..	103	46	..
Pt	0.21	4.3	29	..	26	..	..	161	52	6.46

From this table it is evident that, as the value of  $\phi$  increases, the compressibility decreases, and the values of the other elastic properties increase steadily. The exceptions to this statement are very few as regards any one property, and vary irregularly as we pass from one property to another; in other words, there are no systematic divergences between the sequence of the metals as derived from the thermodynamic relationship discussed in this paper, and that obtained when they are arranged progressively with reference to any one of their elastic properties. The slight divergences are no greater than one might expect from the uncertain character of the thermal data, on the one hand, and of the elastic constants on the other. Indeed, excellent agreement could have been obtained by selecting for each metal an appropriate value from the somewhat discordant data for the elastic constants in the Landolt-Börnstein-Meyerhoffer Tabellen; but it was deemed more commendable to take a general mean of all the values there given, as it was impracticable to determine just

<sup>1</sup> It is to be noted that the values given in the table are *relative* only, and are not always expressed in the same units (e. g., columns *c* and *d*, *e* and *f*, *h* and *i*).

(a) As given by Richards and collaborators, THIS JOURNAL, 31, 156 (1909).

(b) According to Rydberg, *L.-B.-M. Tabellen*, p. 57.

(c) *L.-B.-M. Tabellen*, p. 53.

(d) Wertheim (1848) quoted by Faust and Tammann, *Z. physik. Chem.*, 75, 118 (1911).

(e) *L.-B.-M. Tabellen*, p. 53.

(f) As determined by Faust and Tammann, *loc. cit.*

(g and h) General mean of the (sometimes very discordant) values given in *L.-B.-M. Tabellen*, pp. 43-45.

(i) Horton, *Trans. Roy. Soc. London*, (A) 204 (1905).

which values represent most accurately the true elastic constants of the various metals.

The purely elastic properties of metals have often been collated and compared, and it has been surmized repeatedly that these properties are some function of the melting point of the metal.<sup>1</sup> But, so far as the writer is aware, no one has advanced further than a statement of the general parallelism between elastic properties and melting point—a statement to which there are some notable exceptions (lead, aluminum (see Table II), also a large number of alloys), which seriously limited its scope and usefulness. When arranged with reference to the function of the melting point deduced in this paper, the above two metals cease to be exceptions.<sup>2</sup>

One other piece of presumptive evidence in favor of this point of view may also be mentioned, namely, a comparison of the values of  $\varphi$  with the flow pressures of tin as determined by E. Jänecke<sup>3</sup> at a series of temperatures. In default of knowledge of the variation of  $Q$  with temperatures and pressure, we may justifiably consider  $Q$  and  $D$  as constants. For any one metal therefore, equation III may be written, since  $T_1$  is also constant,

$$\varphi = K_1 - K_2 \log \theta \quad (\text{IV})$$

where  $K_1$  and  $K_2$  are constants, the values of which depend upon  $Q$ ,  $D$ , and  $T_1$ . The graph of equation IV, which gives the variation of  $\varphi$  with  $\theta$ , is very similar to the curve plotted from Jänecke's results; with increasing temperature both diminish at about the same decreasing rate.

From the above, then, it appears to be true that the mechanical properties of metals are correlated with the amount of pressure—assumed to act on the solid alone—requisite to cause the metal to melt at or near the ordinary temperature. This pressure in turn depends upon the melting point, the density, and the heat of melting of the metal. The first two of these quantities are known to be periodic functions of the atomic weight, and there is every reason to believe that the heat of melting, and therefore also  $\varphi$ , is. Therefore, reasoning from the observed parallelism, we should expect some, or all, of the elastic properties to be periodic functions. So far, thorough measurements have been made only on the compressibility, which, according to Richards, shows marked periodicity.

The remarkable concordance shown in the above table, which can

<sup>1</sup> No references are given to this, because the author found it impracticable to examine all of the voluminous literature in order to determine with whom each particular suggestion originated. Some of the points are discussed by Kurnakov and Zhemchuzhny (*Z. anorg. Chem.*, 60, 1 (1908); 64, 149 (1909)).

<sup>2</sup> The formula III could not be applied to alloys owing to lack of the necessary data. In any case the formula is applicable presumably only to such alloys as melt completely at a constant and definite temperature.

<sup>3</sup> *Metallurgie*, 8, 68–72 (1911).

hardly be due to coincidence, suggests that the "flow" of metals—or indeed, every *permanent* distortion of a crystallin solid—is due to an actual fusion (with subsequent resolidification) of the crystals. The validity of this view is supported by a large number of well known facts, *e. g.*, that a metal requires progressively less effort to cause it to weld—or to forge it—the higher its temperature. Moreover it is corroborated by a large number of observations, which demonstrate the existence of important differences between metal which has "flowed" or has been subjected to deformation of any kind and the same metal in the annealed condition.

All the available evidence<sup>1</sup> goes to show that there is: (*a*) a difference in the energy content of the strained and unstrained metal, which is manifested in a difference between the two forms, (1) in their electrolytic potential when immersed in a solution, (2) in their thermoelectric power, (3) in their heat of solution; (*b*) a difference in structure manifested in differences in (1) microscopic appearance, (2) mechanical properties—hardness, tensile strength, etc., (3) density,<sup>2</sup> (4) conductivity for heat or electricity, etc. For any one metal these differences vanish about a single temperature common to all,—thus for silver at about 260°—that is, at the temperature at which annealing proceeds with appreciable rapidity.

According to Beilby,<sup>3</sup> the process of deformation is always accompanied by a partial transformation of the metal to an "amorphous"<sup>4</sup> form, which acts as a cementing material for the untransformed grains. According to Faust and Tammann,<sup>5</sup> on the other hand, the change of properties on deformation is parallel to the production of smaller crystallites. Whichever be the correct interpretation—if indeed these views are mutually exclusive<sup>6</sup>—the fact remains that deformation of a metal is accompanied by changes in its properties. These changes are such that they would be rather difficult to account for reasonably, except on the very simple supposition that an actual melting has occurred.

Against this view it might be urged that the pressures required to cause the metals to melt about the ordinary temperature are so great that they are unlikely to occur in practice. But this objection loses

<sup>1</sup> Cf. G. T. Beilby, *Phil. Mag.*, [6] 8, 258-76 (1904), who discusses the evidence in detail.

<sup>2</sup> Kahlbaum, Roth and Siedler, *Z. anorg. Chem.*, 29, 197 (1902); Kahlbaum and Sturm, *Ibid.*, 46, 217 (1905); Spring, *J. chim. phys.*, 1, 593 (1903); *Rec. trav. chim.*, 23, 1 (1904). This subject is fully discussed by Johnston and Adams, *THIS JOURNAL*, 34, 563 (1912).

<sup>3</sup> *Loc. cit.*

<sup>4</sup> Beilby here uses the term "amorphous" to denote "a heterogeneous assemblage of molecules."

<sup>5</sup> *Z. physik. Chem.*, 75, 108-26 (1911).

<sup>6</sup> Cf. *postea*, p. 800.



weight when it is remembered that the brunt of any strain, to which a crystallin mass is subjected, is borne by a small number of crystals at any one time. When these crystals give way, others take up the strain, and so on. In this way, relatively very small total forces could produce very considerable pressures locally, pressures sufficient to cause melting at those points. This process would be like the method of tearing a pack of cards, which consists in holding them in such a way that the force comes on only one card at a time.

This point of view accounts plausibly for other aspects of the behavior of metals—for instance, the “hardening” of metals and the increase of strength following upon deformation; but before proceeding to discuss this, it seems advisable to outline a mechanical picture of the probable mode of action of unequal pressure upon a metal.

Poynting<sup>1</sup> and also Le Chatelier<sup>2</sup> have used this conception of unequal pressure to account for regelation—the consolidation of a mass of loose snow at  $0^{\circ}$  into a block of solid ice. The pressure, due to the superincumbent material, lowers the melting point at the surface of contact of adjacent grains by an amount  $\Delta t$ . The water formed flows out into the interstices of the snow grains, where it is at a pressure of 1 atm. but at a temperature of  $-\Delta t$ , and is in contact with ice at  $0^{\circ}$ ; consequently it freezes again. This process continues until all the interstices are filled up; that is, until a solid block of ice is formed.

Considerations analogous in every respect are applicable to systems of solid grains in contact with water or an aqueous solution. In such cases pressure acting only on the solid increases its solubility, and renders the solutions supersaturated as soon as they are out of contact with the *compressed* solid. Le Chatelier accounts in this way for the consolidation of natural beds of rock-salt, gypsum, calcium carbonate, etc.; and he showed by direct experiment that consolidation could be produced in this way.

The behavior of metals under the action of a differential compression we conceive to be identical with that pictured above for ice. Namely, that metal melts wherever the pressure reaches the appropriate value, flows into the interstices where the pressure is smaller and solidifies again, with the formation in general of very small crystals, by reason of the exceedingly rapid rate of recrystallization.

The effects of unequal pressure are analogous to those produced by a shearing stress; or perhaps one should say rather that the effects of a shearing stress are those produced by what we have termed unequal pressure. Now a longitudinal tensile stress can always be resolved into a uniform dilatation and a shearing stress, just as a longitudinal compres-

<sup>1</sup> *Phil. Mag.*, [5] 12, 32 (1881).

<sup>2</sup> *Z. physik. Chem.*, 9, 338 (1892).

sive stress can be regarded as composed of a uniform compression and a shearing stress. Hence the conception of unequal pressure, and its effect on the melting point of a crystallin substance, is equally applicable to all permanent deformations, whether produced by compression or by tension.

When pictured in the way outlined in the above paragraphs, it is obvious that one might expect a parallelism between the  $\varphi$  values and certain of the mechanical properties: in all cases, namely, in which the property in question—for instance, tensile strength or flow pressure—implies in any way a permanent deformation of the material, the latter being presumed always to be a manifestation or a real melting produced wherever the stress reaches the appropriate value. In regard to the purely elastic properties—those, *e. g.*, compressibility, which imply no *permanent* change in the material—the parallelism can hardly be ascribed to a melting; but it may very well be an expression of the fact that the elastic properties and the  $\varphi$  values as calculated in this paper are all functions of some one determining factor.<sup>1</sup> But even if this is so, it in no wise detracts from the plausibility of the view that deformation is conditioned by an actual melting; for there is no apparent necessary connection between the modes of action of stresses which produce deformation and of those which do not.

The possibility of accounting in this way for the flow of solids was considered by Tammann,<sup>2</sup> but summarily rejected by him on what appear to the writer to be insufficient grounds. In the first place he doubts the thermodynamic admissibility of the derivation of the formula for the lowering of equilibrium temperature by unequal pressure. In the second place, in his experimental work he was unable to detect any discontinuity in the rate of flow at the pressure indicated by the formula as the melting pressure at that particular temperature. To reason from this lack of discontinuity that the effect of unequal pressure upon the melting point is illusory might be justifiable if Tammann had been dealing with a single crystal; but dealing as he was with a conglomerate of crystals, flow began whenever the pressure on any one of them exceeded the melting pressure under the particular conditions. Indeed the behavior of ice in this respect is precisely similar to that of the metals—a fact specifically noted by Tammann himself—the only difference being that the absolute values of the pressure are lower than for the common metals.

Tammann concludes:<sup>3</sup> “From the work on the velocity of flow of crystallin substances it follows that the flow is not conditioned by a previous

<sup>1</sup> This question is treated later, p. 801.

<sup>2</sup> *Ann. Physik*, [4] 7, 198 (1902); *Krystallisieren und Schmelzen* (Leipzig, 1903), pp. 173–81.

<sup>3</sup> *Loc. cit.*

melting, but that the *plasticity, the reciprocal of the viscosity, is a property characteristic of the substance.*" In order to account for the fact that the velocity of flow, and hence the "plasticity," of ice increases very considerably with the pressure, it must be assumed that its viscosity diminishes greatly with pressure. This assumption may hold, for water at low temperatures and low pressures is an exception to the general rule that the viscosity of liquids is increased by pressure;<sup>1</sup> to the writer nevertheless it seems less forced to account for the flow by the aid of the argument advanced in this paper: namely, that flow is the result of a partial melting. On this basis we can readily see why increased pressure, which causes more ice to melt and hence increases the amount of water present, should increase the plasticity. Moreover, so far as the writer has been able to ascertain, this explanation conflicts with none of the recorded observations on the flow either of ice or of any other substance. Indeed it receives direct confirmation from some recently published work of Hess on the plasticity of ice;<sup>2</sup> he found, as Tammann previously had also observed, that at a given temperature a considerable movement of the plunger takes place under a pressure much lower than that deduced thermodynamically (on the assumption that the pressure acts *equally* on both the ice and the water produced by the melting), and presents indisputable evidence that the ice in these circumstances had actually melted.

The mode of action outlined in this paper, besides accounting plausibly for the magnitude of some of the mechanical properties of metals, can also be adduced to explain observations on the structure of metal which has "flowed," or has been subjected to deformation of any kind. The process of "flow," or of deformation, of a metal is always accompanied, as we have seen, by a number of changes, among others by a "hardening" of the metal; this term is used to denote an increased resistance to stress, and is in one sense unfortunately chosen, for Faust and Tammann<sup>3</sup> have shown that in some cases the "hardness," as measured by the sclerometer, is not affected by the process of "hardening." Faust and Tammann, by microscopic observation of the specimens, were able to determine with a precision of about 1% the pressure or tension required to produce the first permanent deformation of a number of metals; and found that this lower elastic limit is the same for pressure as for tension. Further slow increase of pressure above the lower elastic limit causes this limit to recede to higher pressures; until finally an upper elastic limit, the flow pressure, is reached. This again shows that increase of pressure produces an increased rigidity of the metal; which is in accordance with the idea, first enunciated by Beilby, that the change in properties of

<sup>1</sup> R. Cohen, *Ann. Physik*, **45**, 666 (1892); Hauser, *Ibid.*, **5**, 597 (1901).

<sup>2</sup> *Ibid.*, **36**, 449-93 (1911).

<sup>3</sup> *Z. physik. Chem.*, **75**, 118 (1911).

metals on hammering, rolling, etc., is a direct consequence of the deformation which occurs during the process.

Now these facts accord well with the argument of the present paper; for, exactly as in the case of the consolidation of loose snow to a block of ice, as soon as the stress reaches an appropriate value (the lower elastic limit), melting and flow into the interstitial spaces take place, with immediately subsequent recrystallization; this process continues until this flow is no longer possible (the upper elastic limit), whereupon increased stress produces rupture of the material. Now, the actual process of flow diminishes the volume of the spaces into which flow is possible, and to this extent diminishes the inequality of pressure acting on liquid and solid; hence it requires progressively higher pressures absolutely (though at the same temperature the same *excess* of pressure on the solid) to produce flow; in other words, the rigidity of the material is increased.

A phenomenon analogous in every respect to that observed by Faust and Tammann has been recorded by Bridgman<sup>1</sup> in some very recent work on the collapse of thick walled cylinders under high hydrostatic pressure. Bridgman found, namely, that with every successive application of pressure, yield is not resumed until the previous pressure maximum has been reached or exceeded; this behavior is just what we should expect if flow is conditioned by a true melting.

It is important to observe, in passing, that uniform (hydrostatic) pressure is without *permanent* effect on the properties of metals. Thus Faust and Tammann found that the elastic limit of metal which had been subjected to high hydrostatic pressure remains unchanged; while, as regards the physical properties (density, etc.) it is generally recognized that the only effect of hydrostatic pressure is a temporary change in these properties, which vanishes again whenever the pressure is removed. In all discussions of the effect of pressure, therefore, it is essential that we distinguish carefully between uniform and non-uniform compression, since their effects are so dissimilar.

It is a well known fact that the resistance to flow of eutectics (which are always fine grained) is always greater than that of their components;<sup>2</sup>

<sup>1</sup> *Physic. Rev.*, 34, 1 (1912).

<sup>2</sup> This was demonstrated conclusively by Kurnakov and Zhemzhuzhny (*Z. anorg. Chem.*, 60, 1 (1908); 64, 149 (1909)), who present results—in part from the literature, in part original—for a large number of alloys (and also for some pairs of organic substances) which demonstrate this fact. It has been further confirmed by Tammann, who recently (*Nachr. Ges. Wiss. Göttingen*, 1911, 181) described experiments with a few alloys, carried out in quite a different way, from which he draws the conclusions that this increased strength is a direct consequence of the fact that the alloys are finer grained than their components (but offers no explanation as to why a fine grained conglomerate should be stronger than one composed of coarser particles); further that the increased strength of metals which have been chilled is a direct consequence of the decreased size of the grains produced by rapid cooling of the melt.

further, that the varieties of steel possessing the greatest tensile strength (*e. g.*, vanadium steels) are very fine grained. From the standpoint adopted in this paper one might reason that such metals are strong *because* they are fine grained; hence, if we wish to make a steel of high tensile strength, we should endeavor to obtain a very fine grained structure, producing this by whatever means (addition of foreign material, heat treatment or mechanical treatment) may be found suitable for this purpose.

It was noted above that the deformation of metals is accompanied by the appearance of an "amorphous" phase, according to Beilby; by the production of smaller crystallites, according to Faust and Tammann. Neither author speaks definitely of the mode in which the change takes place, nor do they, as far as one can judge, consider it as a manifestation of real melting, with immediately subsequent resolidification. When looked at in this way the divergence between their points of view disappears. For, as is well known, the size attained by a crystal depends, *ceteris paribus*, on its rate of formation; so that Beilby, with presumably a relatively rapid rate of recrystallization, obtained in his flowed metal crystals so small that the metal was apparently "amorphous"; Faust and Tammann, on the other hand, using a totally different method in which the rate of recrystallization was presumably not so great, obtained relatively larger crystal particles.

A point worth mentioning in this connection is this, that the appearance of the cut and polished surface of a metal is not necessarily an altogether fair criterion of the structure of the massive metal. For, as Beilby has demonstrated conclusively, the process of polishing (and obviously, of cutting also) is the result of flow; while in accordance with the viewpoint presented in this paper, flow is the result of a partial melting. Therefore, it is a safe assertion that between the apparent structure of the polished surface and the actual structure of the massive metal, there must always be some differences, which may be so large that examination of the surface only would lead to totally misleading conclusions with regard to the structure of the massive metal.

Kurnakov and Zhemzhuzhny<sup>1</sup> made parallel measurements of the electrical conductivity and flow pressure of series of binary alloys, and found that for given binary systems minimum conductivity and maximum flow pressure occur at the same composition. This exemplifies the general rule that the conductivity of an alloy is less than that of its component metals. Moreover the conductivity of a metal generally decreases when the metal undergoes deformation (*e. g.*, drawing to wire, hammering, or rolling). Now if we interpret these facts with the aid of the idea that the specific conductivity of a given material diminishes

<sup>1</sup> *Loc. cit.*

progressively, other things being equal, with the size of the component particles—an idea which is substantially correct for powdered metals—we find them to be in complete harmony with the conclusion reached on other grounds: namely, that the size of grain of alloys or of metal which has been deformed is less than that of the pure annealed metals.

### Summary and Conclusion.

In the foregoing pages we have discussed the idea that the "flow," or permanent distortion, of metals is conditioned by a real melting, not of the whole mass of metal at any one instant, but of successive groups of particles (namely, those on which the brunt of the strain momentarily falls); and have shown how this idea serves to correlate some properties of metals which at first sight would appear to bear no relation to each other. It leads, namely, to the fact that there is a parallelism between all the elastic properties of metals for which quantitative measurements have been made and the pressure—assumed to act on the solid phase, but not, or not to the same extent, on the liquid phase—which is required to lower the melting point to ordinary temperature. This pressure is a function of the melting point, latent heat of melting, and density at the melting point, of the metal; hence, if these quantities are known for any substance, we can predict the relative order of magnitude of any of its properties which imply deformation of the material.

The same mode of reasoning is equally valid for any crystallin substance, and could be applied to all salts (including silicates and other geologically important substances) if the necessary data were available. At the present time, values of the latent heat of melting are few and far between, so that no general discussion of this part of the subject is practicable now.

The equation discussed in this paper cannot be applied to glasses; for since they are merely supercooled liquids, the value of  $Q$  is zero and hence  $dT/dP$  is infinit. But this is not so contradictory as at first sight it may seem; for glasses behave as liquids of exceedingly high viscosity, provided always that, conformably with this high degree of viscosity, sufficient time be allowed for the motion to take place.

In conclusion, let us give a brief indication of a connection between the relations discussed in this paper and the conception of "molecular vibration frequency," a conception which has been very fruitful in the hands of Nernst,<sup>1</sup> Lindemann,<sup>1</sup> Grüneisen,<sup>2</sup> and others. It has been established, namely, that a large number of apparently diverse physical properties of a substance—melting point, specific heats, coefficients of thermal expansion and compressibility, electrical resistance—may be

<sup>1</sup> This work has been published in a series of recent papers which have appeared in *Sitz. Akad. Wiss. Berlin, Ann. Physik, Z. Elektrochem., and Physik. Z.*

<sup>2</sup> *Ber. physik. Ges.*, 1911, 426, 591.

considered to be functions of a characteristic quantity, the molecular "vibration frequency."<sup>1</sup>

Expressions containing this quantity have been derived by means of which the actually observed variation with temperature of certain of the above properties can be reproduced with remarkable accuracy. Now the flow pressure  $\phi$  at the temperature  $t$  is determined by a complicated expression, the value of which depends upon  $t$ ,  $T_1$  (the ordinary melting point),  $L$  (the heat of melting at  $T_1$ ),  $V$  (the specific volume at  $T_1$ ) and upon the variation of  $L$  and  $V$  with pressure and temperature; that is, for any particular substance,  $\phi$  depends upon the above constant quantities and upon the specific heats and coefficients of thermal expansion and of compressibility; each of these quantities is some function of the "vibration frequency," consequently the flow pressure  $\phi$  is also a function of this same characteristic parameter.

In view of the state of our knowledge (at the best, very approximate only at the present time) of the experimental data and of certain of the relations involved, it seems premature to endeavor to deduce a definite mathematical relation between  $\phi$  and the frequency, or even to determine the exact form of the function. The existence of such a relationship accounts simply for the parallelism between the calculated  $\phi$  values (of Table I) and the mechanical properties of metals brought together in Table II; for all of these quantities are functions of the vibration frequency, a fact which indicates that all the mechanical properties of metals will be found to be periodic functions of their atomic weights, since the vibration frequency itself is doubtless such a periodic function.

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## SULFIDE OF TELLURIUM.

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When hydrogen sulfide gas is passed into a slightly acid solution of tellurous acid or the solution of a tellurous salt, a dark colored precipitate is formed and continues to separate as long as any tellurium remains in the solution. At the moment of formation this precipitate is dark reddish brown in color, but after a short time it becomes still darker, until it is quite black. When dried and heated the substance softens, and on cooling forms a gray, somewhat lustrous mass. On being heated still higher it gives off sulfur.

<sup>1</sup> For a discussion of the exact significance of this quantity, the reader may be referred, in addition to the papers cited above, to recent papers by Einstein in *Ann. Physik*.