ON THE EFFECT OF GENERAL MECHANICAL STRESS ON THE TEMPERATURE OF TRANSITION OF TWO PHASES, WITH A DISCUSSION OF PLASTICITY.

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THIS note is to present a thermodynamic formula of considerable generality, and to discuss some of its special cases. The need for such a formula arose in connection with experiments on the effect of high pressures on melting points and polymorphic transitions.[1] In these experiments the specimens were placed in open containing vessels of steel, which may be expected to offer some restriction to the free propagation of changes of hydrostatic pressure throughout the mass of the specimen. The question at issue was: what is the effect on a transition (or melting) point of unknown extra stresses not hydrostatic in nature? It was a surprise to me, after a careful search, to find that this problem has received very meager attention, although it is one capable of solution by ordinary thermodynamic methods. For instance, Voigt's encyclopædic work on "Krystall Physik" does not mention the problem, although it contains numerous examples of the use of the thermodynamic potential for solid bodies under strain. Formulas have, however, been given by James Thomson[2] and Gibbs,[3] among others, for the restricted case of a fluid in contact with an isotropic solid under elastic stress.

The conditions to which the general formula applies are as follows. Two phases of a pure substance, either gaseous, liquid, or crystalline solid, are initially in equilibrium under a hydrostatic pressure p and at absolute temperature θ_0. The two phases are in contact across a membrane of such a nature as to be permeable to the reacting phases, so that the transition from one phase to the other may run across the membrane, but such that it may support a difference of stress between the two sides, so that the normal component of stress on the two phases on opposite sides of the membrane need not be the same. A mechanical stress system, ${}_1X_x$, ${}_1Y_y$, ${}_1Z_z$, ${}_1Y_z$, ${}_1Z_y$, ${}_1X_y$, in addition to the hydrostatic pressure is applied to the phase (1), and a different stress system ${}_2X_x$, ${}_2Y_y$, etc., to the second phase. The *total* normal stresses (including the original

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[1] P. W. Bridgman, Proc. Amer. Acad., 47, 345 and 439, 1912; 51, 53, 1915. Phys. Rev., N. S., 3, 126 and 163, 1914; 6, 1 and 94, 1915.

[2] James Thomson, Phil. Mag. (4), 24, 395.

[3] J. Willard Gibbs, Scientific Papers, vol. 1, p. 184.

hydrostatic pressure) across the surfaces of separation are now ${}_1N_\nu$, and ${}_2N_\nu$. In accordance with the usual practice of elasticity, the stress is considered positive if a tension. It is required to find the change of temperature τ necessary to bring the phases into equilibrium again across the surface of separation. The formula follows.

$$\tau = \frac{\begin{array}{l} W_1 + \frac{1}{3}\left(\frac{\partial v_1}{\partial p}\right)_\tau ({}_1X_x + {}_1Y_y + {}_1Z_z)(p + {}_1N_\nu) - v_1({}_1N_\nu + p) \\ \qquad - W_2 - \frac{1}{3}\left(\frac{dv_2}{\partial p}\right)_\tau ({}_2X_x + {}_2X_y + {}_2Z_z)(p + {}_2N_\nu) + v_2({}_2N_\nu + p) \end{array}}{\begin{array}{l} \frac{\lambda'}{\theta_0} + \left(\frac{\partial v_2}{\partial \tau}\right)_p \left\{\frac{1}{3}({}_2X_x + {}_2Y_y + {}_2Z_z) - p - {}_2N_\nu\right\} \\ \qquad - \left(\frac{\partial v_1}{\partial \tau}\right)_p \left\{\frac{1}{3}({}_1X_x + {}_1Y_y + {}_1Z_z) - p - {}_1N_\nu\right\} \end{array}}.$$

This formula is rigorously exact within the limits over which the coefficients remain constant, but the following approximation is good to small quantities of the first order:

$$\tau = \frac{\theta_0}{\lambda}\Big[W_1 + \frac{1}{3}\left(\frac{\partial v_1}{\partial p}\right)_\tau ({}_1X_x + {}_1Y_y + {}_1Z_z)(p + {}_1N_\nu) - v_1({}_1N_\nu + p)$$
$$- W_2 - \frac{1}{3}\left(\frac{\partial v_2}{\partial p}\right)_\tau ({}_2X_x + {}_2Y_y + {}_2Z_z)(p + {}_2N_\nu) + v_2({}_2N_\nu + p)\Big].$$

The following additional terms used in the formula need explanation. λ is the heat absorbed (in the appropriate mechanical units per gm. of substance) when (2) changes to (1) at p, θ_0, and λ' is the corresponding heat of transition under equilibrium conditions under the altered stress at $\theta_0 + \tau$. W_1 is the work done by the stress system ${}_1X_x$, ${}_1Y_y$, etc., when applied isothermally to ONE GRAM of the phase (1), and similarly for W_2. W is to be calculated by the ordinary rules; in the case of a solid it may be found accurately enough by supposing the extra stress system applied to the phase at $p = 0$. It is to be noticed that because of the conditions of mechanical stability, W is essentially positive. $(\partial v/\partial p)_\tau$ is the " compressibility " of 1 *gm.* of the substance, and $(\partial v/\partial \tau)_p$ the " dilatation " of 1 gm.

It is easy to find the change in the latent heat under the changed conditions of equilibrium.

$$\Delta\lambda = \lambda' - \lambda = \frac{\tau}{\theta_0}\lambda + \tau({}_1\gamma_X - {}_2\gamma_X) + \theta_0\left(\frac{\partial v_1}{\partial \tau}\right)_p \left[\frac{{}_1X_x + {}_1Y_y + {}_1Z_z}{3}\right]$$
$$- \theta_0\left(\frac{\partial v_2}{\partial \tau}\right)_p \left[\frac{{}_2X_x + {}_2Y_y + {}_2Z_z}{3}\right].$$

${}_1\gamma_X$ and ${}_2\gamma_X$ are the specific heats under constant stress.

The formulas were derived by ordinary thermodynamic methods; it is hardly worth while to reproduce the wearisome details. The method is to carry the substance around a complete cycle, writing down the two conditions that the total change of energy and of entropy of the cycle shall be zero. The changes of energy and of entropy of the two phases separately were obtained from Voigt's general thermodynamic potential for solids under stress. It is important to notice that we cannot in this general case write down the conditions of equilibrium by demanding that the thermodynamic potentials of the two solid phases be equal, as we can when dealing with fluid phases by using the potential $Z = E + pv - \theta s$. The thermodynamic potential as usually given for elastic solids is good only within the range of the small strains contemplated by the theory of elasticity, and is not good for the comparatively large changes of volume involved in a transition. It probably would not be difficult to extend the thermodynamic potential for solid bodies so as to attain this greater generality, but it was not necessary for the purpose in hand.

The formulas in the form given above apply only to homogeneous isotropic solids, or more generally to crystalline solids characterized by only one constant of thermal dilatation. The extension is immediate, however, to the most general crystalline solid with its 28 constants, comprising 21 elastic constants, 6 thermal expansion constants, and one specific heat. The 21 elastic constants are buried in the expression for W. The only formal change necessary is to replace, wherever it occurs,

$$\tfrac{1}{3}(\partial v/\partial \tau)_p[X_x + Y_y + Z_z] \text{ by } a_1X_x + a_2Y_y + a_3Z_z + a_4Y_z + a_5Z_x + a_6X_y,$$

where the "a's" are the six constants of thermal expansion. This produces no change in the approximate value for τ, but does enter the formula for $\Delta\lambda$.

It is evident that by a double application of the formula the still more general case may be treated of two phases initially in equilibrium under any stress system not hydrostatic. It is not worth while to further complicate matters by giving a single formula which shall apply to this general case.

Special Cases.

1. If the stress applied to the two phases is the same increment of hydrostatic pressure dp, the expression immediately reduces to Clapeyron's equation, as it should, by putting ${}_1N_\nu = {}_2N_\nu = -(p + dp)$; ${}_1X_x + {}_1Y_y + {}_1Z_z = {}_2X_x + {}_2Y_y + {}_2Z_z = -3dp$.

2. If the pressure on (1) is left unaltered and the stress on (2) is raised

to the hydrostatic pressure $p + dp$, we find immediately

$$\tau = -\frac{\theta_0}{\lambda} v_2 dp.$$

This is the well-known expression for the depression of the transition point by a pressure exerted on one phase only. It has been discussed by Planck, Poynting, Ostwald, Tammann, Lewis, and has recently been made the basis of a theory of plasticity by Johnston. We will return to this matter.

3. The formula for τ contains a theorem by its very form; the tangential stress on the surface of separation does not enter. The transition temperature of two phases under a given stress is therefore the same across all planes over which the normal stress is the same, and is not affected by the tangential stress at the surface of separation. A special case of this is that if shearing stresses are applied to two opposite faces of a cubical solid in equilibrium with a liquid or another solid the transition point is depressed by the same amount on all six faces of the cube, irrespective of whether these are the faces to which the shearing stress is applied or not.

4. Consider now the problem of the introductory paragraph for the case of a melting solid. A liquid (1) and a solid (2) in the form of a uniform cylinder are in equilibrium at p, θ_0. A mechanical tension is applied to the solid. We have to consider two faces of the solid, that freely exposed to the liquid, and that where the tension is applied. At the free surface we put

$$ {}_1N_\nu = {}_2N_\nu = -p,$$

and find

$$\tau = -\frac{\theta_0 W_2}{\lambda},$$

a result independent of the initial pressure. The freezing point is therefore lowered, and the solid melts at the unstressed surface. It is to be noticed that W varies as the square of the applied stress, but it is not necessary for this reason to restrict the *stresses* to which the formula is applicable to small quantities of the first order. It is only necessary that the strains produced by the stresses remain small. Thus for steel, a stress as high as the elastic limit produces a strain of only 0.001.

At the stressed surface, if we suppose the membrane such that the solid would melt to a liquid at normal pressure p, we find,

$$\tau = \frac{\theta_0}{\lambda} v_2 X_x$$

or the melting point is raised, and no transition takes place at this surface, unless there is liquid present to freeze to the solid.

5. Imagine a cylinder of solid at its melting point and in equilibrium with it at one end only the liquid. Additional hydrostatic pressure dp is applied to the liquid, producing in the solid a one sided stress ${}_2X_x = -dp$. The normal stresses in solid and liquid across the surface of separation are in this problem equal. We find that at the surface of separation the melting point is raised by

$$\tau = \frac{\theta_0}{\lambda}(v_1 - v_2)dp,$$

and at the free surface it is depressed by the same amount as in the preceding problem. At the stressed surface the change of melting point is exactly the same as if the entire solid were subjected to the increment of hydrostatic pressure dp.

This has application to problems like that of a weighted wire melting its way through a block of ice, or the melting produced under the runners of a sleigh by its own weight. The usual treatments are faulty in that they assume hydrostatic pressure in the solid, whereas the stresses in these cases are not hydrostatic pressures, but are one-sided stresses to which the usual Clapeyron's equation does not apply. The above discussion shows, however, that immediately at the point where the pressure is applied, the usual expression of Clapeyron does hold.

A combination of the results of these last two paragraphs has immediate application to the experimental question mentioned in the introduction which started this inquiry. Suppose we have a liquid and solid in equilibrium, and we change the pressure supposedly equally on both phases by an increment dp of hydrostatic pressure, but that, because of imperfections in the apparatus, we actually apply an additional stress not hydrostatic to limited portions of the surface of the system. It is easy to see that melting or freezing takes place at the free surfaces with such changes of volume as to tend to produce throughout the mass just that change of hydrostatic pressure which we thought we had applied.

6. If instead of a liquid and a solid, we consider two solid phases, we see that the transition point may be either raised or lowered. If the normal stress across the surface of separation is unaltered by the applied stress system, then the transition point is always lowered when a stress system is applied exclusively to (2), and raised when applied to (1). The differentiation between (1) and (2) is provided by the sign of λ. There is, however, this difference between a liquid and a solid, and two solids. If the two solids are in equilibrium under hydrostatic pressure

and we try to increase pressure uniformly on both phases, but because of restraints in the apparatus actually apply it to only one of the phases, the reaction will in some cases *not* so run as to redistribute the pressure uniformly throughout the mass. That is, one phase may act as a protecting covering for another, so that the reaction need not run on passing the transition line, but will run at some remoter pressure, when the strength of the covering is exceeded. Such cases are not common, but do occur sometimes; ice V and VI afford an example.

7. Let us now consider the behavior of *crystalline* phases, either two polymorphic solids in contact, or a solid and liquid. We restrict ourselves to the cases usually met in practise where the phases are in elastic equilibrium at the surface of separation without the interposition of a permeable membrane; that is, we assume ${}_1N_\nu = {}_2N_\nu$. For those cases in which ${}_1N_\nu = -p$, the depression of the transition point is of the second order in the applied stress, and for those for which ${}_1N_\nu \neq -p$, the depression is of the first order. In both cases, the effect of the orientation and the specific crystalline constants on the depression is of a higher order. That is, the fact that the substance is crystalline enters the result only in so far as the surface stresses are determined by the orientation of the crystal. Given a crystal under a specified state of internal stress, and with specified stresses across the surface of separation from another phase, and the shift of the transition point is entirely determined by these elements alone (to quantities of the order concerned), and does not involve at all the orientation of the surface with respect to any of the elements of symmetry of the crystal. This result is evidently of importance as affecting the uniqueness of transition or melting points determined experimentally.

APPLICATION TO PLASTICITY.

The fact that the melting point of a solid at a free surface is always depressed by any stress system whatever is suggestive and of considerable importance.[1] This fact offers the possibility of a theory of plasticity, in some respects similar to a previous theory, but free from some of its objections. This previous theory, suggested by Poynting,[2] and lately developed in much greater detail by Johnston,[3] depends on the fact that the melting point is always lowered by the application of hydrostatic pressure to the solid phase only, and lowered by an amount greatly exceeding the rise that would be produced by the same pressure applied hydrostatically to both phases. This formula was given above under

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[1] This fact was stated by Gibbs.

[2] J. H. Poynting, Phil. Mag. (5), 12, 32, 1887.

[3] J. Johnston, Jour. Amer. Chem. Soc., 34, 788, 1912.

special case (2). For the purposes of this theory we consider that when a solid is stressed the pressure is taken up unequally by the miscroscopic crystalline grains, and that on some of these grains the pressure may be very intense. If it is so intense as to depress the melting point to the temperature of the surroundings, melting takes place at these grains, and we have flow of the metal as a whole, with the phenomena of plasticity.

The theory in this form seems to me to be open to several objections. It is most difficult to conceive how in any actual solid there is anything corresponding to the fictitious membrane which maintains the solid under hydrostatic pressure, while permitting the liquid to flow freely away. Certainly if in the solid there are any grains about which the surrounding material is not closely packed, the conditions of elastic equilibrium demand that at the surface at which the melting is to occur the normal stress be less than the average. In other words, no matter how intense the average pressure throughout any individual grain, at the free surface of this grain where the melting is to take place there can be no normal stress, and hence the conditions of the theorem do not apply. Another objection is that experimentally the plastic flow of a well-annealed metal begins at the same numerical value of the stress, whether in compression or tension. The fundamental formula gives a change of melting point directly proportional to the stress; under a tension the melting point is raised, and there should be no plastic flow at all. In other words, the theory accounts qualitatively for plasticity in compression but not in tension.

The theory modified as above is evidently not open to these objections. A solid subjected to any stress system whatever, either tension, compression, or shear, experiences a *depression* of the melting point at the *unstressed* surface (or at a surface stressed by less than the average amount) and melting will take place at that surface if the stress is high enough. This statement is free from all hypothesis as to the nature of the contact between the surfaces of the grains. The picture we form of a plastic flow is essentially the same as in the previous theory; that is, under some conditions flow is produced by an actual local melting, followed by regelation with equalization of pressure on all the grains. This local melting takes place when any grain is subjected to more than its share of the stress and so is subjected to a stress not hydrostatic.

It is now of interest to inquire of how wide application this contributory agent in plasticity is. Several reasons lead me to the opinion that it has not the universal importance that Johnston maintains in his theory, but that in most solids at points far below the melting point the more important part of the mechanism of plastic flow is of quite distinct origin.

One of these reasons is the effect of temperature on rate of flow. Tammann and his pupils[1] have found that the rate of flow under constant stress very nearly doubles for every 10° rise of temperature. This holds over considerable temperature ranges—to far below the melting point. If plasticity is really due to local melting, one would not expect so rapid a change, but would rather expect the rate to perhaps more nearly double when the distance to the melting point is approximately halved. Another reason is to be found in the values of the maximum stresses that solids will support without plastic yield. It is well known that the flow point may be raised by the previous application of stress. This is in all probability due to a readjustment of the crystalline grains so that the load is distributed more equally. On the above theory this readjustment is brought about by actual melting and regelation. But it is also well known that there is an upper limit beyond which the plastic limit cannot be raised. This upper limit is presumably reached when the readjustment between the grains has proceeded so far that each grain is uniformly stressed by its proper share. According to the theory under discussion, this upper limit should be reached at the theoretical stress, assumed uniformly distributed, requisite to depress the melting point to the prevalent temperature. As a matter of fact, the upper plastic limit is never so high. The following table shows the upper limit found experimentally by Tammann and Faust,[2] and the computed values taken from Johnston's paper. The table includes all the metals common to the two papers. The actual values are from 8 to 40 times too low, divergences so large as to belong to another order of magnitude. If Johnston's theory is correct, this would mean that after prolonged flow the internal readjustment of stress between the grains is still so imperfect that some grains always bear from 8 to 40 times their share of stress. If the maximum stress is computed by the newer formula suggested above, values are found which are of the order of 10 times greater again than Johnston's. The

Metal.	Flow Point.	
	Observed, Kgm./cm.^{2}	Calculated, Kgm./cm.^{2}
Pb	102	1,760
Sn	55	2,200
Cd	109	3,300
Al	600	5,100
Zn	770	6,900
Cu	2,780	24,000

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[1] N. Werigin, J. Lewkojeff, and G. Tammann, Ann. Phys., 10, 647, 1902–03.

[2] O. Faust and G. Tammann, Zs. phys. Chem., 75, 108, 1910.

conclusion seems forced upon us that under ordinary conditions the mechanism of plasticity must be different from a partial melting. Pertiment suggestions as to what the mechanism may be are common in the literature.[1]

In some cases, however, plasticity by melting must be a real effect. Of course it must be of importance in the immediate neighborhood of the melting point. This means that no crystal continues rigid up close to the melting point, but softens in the immediate neighborhood. Experiments have been made on the plasticity of crystals near the melting point, and conclusions drawn as to the molecular mechanism. It is probable that a large part of this plasticity is due to minute traces of impurity just as is the increase of specific heat below the melting point. But quite apart from the effect of impurities, these considerations show that every crystal will be plastic near the melting point, independent of any special molecular mechanism, the plasticity being called into play by the very forces which must be applied to detect its existence. This kind of plasticity may also possibly enter at the very beginning of flow of a badly annealed piece of metal, in which the load is very unequally distributed among the grains.

Plasticity is to be expected not only near a melting point, but also near any polymorphic transition point, since any inequality of stress on the different grains produces a change of the transition point and consequently a reaction from one solid phase to another, accompanied by a change of volume and a readjustment that will show itself as flow. This plasticity will exist both above and below the transition point. In general, the range of plasticity about a transition point will be larger than about a melting point, because the heat of transition is usually less than the heat of melting. Because of the wide existence of polymorphism, this agent must be of geological importance.

To sum up these remarks on plasticity; under certain conditions plasticity is produced by an actual melting with regelation of those crystalline grains which bear the brunt of the stress. This local melting is governed by the equations for an unequally stressed solid, and not by the equations for a solid under hydrostatic pressure in equilibrium with a liquid not under pressure. This contribuory agent in plasticity does not seem, however, to be largely effective in the majority of the cases of practice. For some substances an analogous effect, due to displacement of polymorphic transition points, is of more importance.

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[1] J. A. Ewing and W. Rosenhain, Phil. Trans. 193 (A), 353, 1900. J. C. W. Humfrey, Phil. Trans. 200 (A), 225, 1903, for example.