

The fact that this phase-change type of deformation is a *function of time*, and the elastic type is not, has important consequences. Failure as a result of a rapidly applied large compressive load is by brittle fracture across surfaces parallel to or making small angles with the axis of load; as the rate of application is decreased failure will tend to occur as shear along surfaces which are at larger angles to the axis of load; if the application is slow enough and the thermodynamic potential relations are favorable the specimen will deform by "gliding along 45° planes," or by "flow."

If the load is not too great the shear may proceed in steps—"melting" at high energy points, shear of the remaining cohesive bonds, slipping, recementation by solidification, the cycle repeating itself as conditions again become favorable. The most favorable surface for this process is the 45°-plane along which the resultant shear stress is a maximum and equal to one-half the compressive load.

These statements need some qualification because the force and potential functions are not symmetric in space and therefore vary with orientation of the system. The curve of Fig. 1 is thus a function of a vector  $r$  and the lattice will therefore, if conditions are favorable, rupture or shear along surfaces across which the cohesive bond,  $F_m$ , is the least such as cleavage, parting, and twinning planes.

"Melting" can occur in specimens under tension, *viz.* along shear planes, but the phenomenon should not be so evident here because it will take place only at the free surfaces (see Eqs. (11b), (12b), (14b)).

#### DERIVATION OF EXPRESSIONS FOR "CREEP" OR "PLASTIC FLOW"

The creep relations will be derived first for a solid under compressive load and immersed in a liquid in which it is somewhat soluble.

Assume an initially "ideal solid" in which the thermodynamic potential is the same for all the faces and equal to the potential of the solid in solution (solute), *i.e.*, assume that the solid is in equilibrium with the saturated solution at temperature  $T$  and hydrostatic pressure  $p$ . If now the solid is loaded by a longitudinal compressive

force  $\pi$  the thermodynamic potentials at the stressed and free faces of the solid and of the solute will no longer be equal and the system no longer in equilibrium so long as the stress exists.

In order to derive our thermodynamic equations the system is first divided into hypothetical isolated parts, namely the regions at the stressed surface, at the free face, and of the solution bulk. We also assume any coexistence of phases necessary for our derivations. The physical interpretation follows readily from this procedure and moreover we avoid any confusion that might be introduced from a compromise<sup>11</sup> between the thermodynamic and the physical picture.

The following formulae were derived by ordinary thermodynamic methods applied to stressed systems<sup>12</sup> and have been somewhat simplified for purposes of clarity.

We have

$$(\partial \ln a_2 / \partial \pi)_{SF} = M / \rho RT \quad (9a)$$

and

$$(\partial \ln a_2 / \partial \pi)_{FF} = M\pi / \rho ERT, \quad (9b)$$

where Eq. (9a) refers to the stressed face (subscript SF) and (9b) to the free face (subscript FF).  $a_2$  denotes the activity of the solute,  $\pi$  the compressive stress,  $M$  the mole weight,  $\rho$  the density of the solid,  $R$  the gas constant ( $R=83.156$  bar cm), and  $T$  the absolute temperature.  $E$  is Young's modulus of elasticity in compression, *i.e.*,  $E=dX/de$  where  $X$  is the stress (negative for pressure) and  $e$  the extension per unit length in the direction of the stress. For small stresses  $E$  may be approximated by a constant, generally of the order of  $10^6$  bars.

On integrating (11a) we have, at the stressed face,

$$\pi - \pi_0 = (\rho RT / M) \ln (a_2 / a_{2_0}), \quad (10a)$$

where  $\rho$  is the mean value for the integration limits.

<sup>11</sup> P. W. Bridgman, *Phys. Rev.* 7, 215 (1916), derives an expression which may be correlated with (14a) and (14b). E. D. Williamson, *Phys. Rev.* 10, 275 (1917). H. C. Boydell, *Ec. Geol.* 21, 1 (1926). Boydell derives Poynting's expression which applies to a solid under hydrostatic pressure  $p_1$  and liquid at  $p_2$  where  $p_1 > p_2$ . Poynting's expression has the same form as (14a) of this paper.

<sup>12</sup> R. W. Goranson, *Thermodynamic Relations in Multi-component Systems* (Carnegie Inst. Washington. Publ. No. 403, 1930). For usage of activity see R. W. Goranson, *J. Chem. Phys.* 5, 107-112 (1937).