

gradients and fluctuations. The calculated tensile strengths, F_m , are all much higher than the observed values which are indicated roughly by S_0 in the plot. In the following discussion F_m is used as the ideal elastic tensile strength and $r_m - r_0$ as the ideal maximum safe elastic extension. The actual values may be only about a tenth or less of these maxima.

It should be noted that these considerations are made for the case where the "two-phase" transfer mechanism does not operate. Care must therefore be exercised in drawing comparisons between theoretical and empirical results and this will be shown more clearly later.

TEMPERATURE

If the temperature of the system is increased, at constant pressure thermal energy is absorbed with increase in the internal pressure. The system expands doing work against the external surroundings until a new positional equilibrium is attained for the new F . In this way we obtain a family of curves for different T . Ignoring for the time being the change in slope of these curves and considering only the large scale differences, we note that the effective zero ordinate of the $F-r$ plot moves up and r_0 increases to some larger $(r_0)_T$. Similarly the mean minimum potential $(\phi_0)_T$ moves to a larger $(r_0)_T$ and higher up the right limb of the potential energy well which is therefore becoming shallower and shallower in the direction of increasing r . Eventually the right wall of this well would vanish and no further readjustments yield a stable configuration; the system actually breaks down long before this point is reached. If in this breakdown a reorganization in potential and kinetic functions of the components can take place for a new minimum $(\phi_0)_T$ the system melts, and if such a redistribution cannot be effected the system sublimates. The size and nature of the elemental units in this breakdown will depend on the variations in the interatomic bonds, the structure splitting up across bonds of least cohesive strength.

In this connection it might be of interest to note that if the thermal energy be assumed as proportional to v^{-3} , or to r^{-2} , the internal pressure contribution from this source will be propor-

tional to r^{-3} . Under increasing hydrostatic pressure the other internal pressure terms of higher power, here assumed as r^{-9} , eventually dominate over the r^{-3} term and at an increasing rate. The thermal expansion should therefore decrease under hydrostatic pressure and approach zero at very high pressures. This conclusion, in conjunction with the third law, means that, for this model, the entropy must be zero at infinitely high pressure for all temperatures.⁸ At moderate pressures the smaller powers of $1/r$ will play more effective roles and the initial rate of decrease of dilatation should, as for compressibility, be less for simple ionic lattices since here the attractive r^{-2} term is initially more effective than the r^{-3} term.

HYDROSTATIC PRESSURE

The same type of reasoning applies to systems under hydrostatic pressure at constant temperature but in this case the increase in potential is equal to the work done on the system. The system decreases in volume until an equilibrium between internal and external pressure has been achieved. The most stable pressure or phase configuration is the one best able to withstand the external pressure and therefore the one of higher density. A change of phase under pressure may take place either by reorganization of form (potential or work energy) or in part by change of form and in part by change of momenta (conversion to thermal energy). The pressure at which the latter type of phase change occurs will be a function of temperature; the former should be independent of temperature.

Silicate glasses should in general behave somewhat abnormally because these glasses are in a metastable energy state, i.e., the configuration stable for the high temperature kinetic and potential energy relationships has been frozen into the system. The internal forces should therefore be tensions but the configuration is presumably prevented from collapsing by the randomness of orientation inherited as a result of the previous thermal kinetic energy, that is to say, the glass is not only metastable from considerations of heterogeneous or phase equi-

⁸This was also suggested by G. N. Lewis, *Zeits. f. physik. Chem.*, Cohen Fest. Band 130, 532-538 (1927), from other considerations.