

about $-2 \text{ cm}^3/\text{mol}$ and if diamond was to be impossible in the mantle, the bond energy of graphite would need to be 80 kcal greater than diamond. Even if diamond had never been seen, data on the energies and lengths of carbon bonds as seen in organic molecules would certainly lead us to expect diamond at quite moderate pressures. In fact quantum mechanical calculations would be adequate in this case.

The problem of predicting the possibility of a phase change over the mantle P - T range thus resolves itself into two questions (if we assume that T and S are rather unimportant to a first approximation). First, can the volume change be guessed? Second, can the bond energies or lattice energies be guessed with any degree of significance? It is normally the latter question that involves difficulty; but less so if we do not require an accurate transition pressure. For a long time to come experimental methods will be required, but at least some guidance for experiment seems possible. The limited success of Fersman's approach to bond energies (see MASON, 1966, p. 85) from which it follows that

$$\sum \Delta H_f \text{ oxides} \approx \sum \Delta H_f \text{ compound}$$

emphasizes the difficulty of finding energy differences between structural states as these are often small differences between very large values (e.g. compare the lattice energies of quartz and cristobalite).

2. Changes in coordination

Phase changes induced by high pressures most frequently involve changes in coordination numbers. There are important exceptions (e.g. the olivine-spinel transition discussed by KAMB, 1968). Most of the discussion that follows is involved with examples where changes in coordination occur.

A typical simple example is illustrated by KCl. This is known to change from the NaCl structure (6-coordination) to the CsCl structure (8-coordination) at moderate pressures. The ratio of the radii of K^+ and Cl^- (0.734) is almost exactly on the theoretical cross-over from 6- to 8-coordination. Without any change in bond lengths ΔV would be about $-8 \text{ cm}^3/\text{mol}$. For the transition to occur in the mantle pressure range, the ΔH of transition must not exceed 280 kcal/mol, and as this figure is greater than the lattice energy of the 6-coordinated form (163 kcal) the transition must be considered feasible.

If we consider the simple Born lattice energy equation:

$$U = \frac{NAe^2 z_1 z_2}{R} \left(1 - \frac{1}{n} \right),$$

and assume that both R and n are similar, then the lattice energies of the two forms are given by

$$\frac{U_1}{U_2} = \frac{A_1}{A_2},$$

where U is the lattice energy and A the Madelung constant for the structure concerned. In this case, on account of the small value of the U 's, a reasonable prediction can be made of the energy barrier (see FYFE *et al.*, 1958).

Another such simple case is shown by the rather high pressure transition of ZnO from the four coordinated sphalerite structure to the halite structure. Again, assuming no change in bond lengths, ΔV is about $-2.5 \text{ cm}^3/\text{mol}$. In this case a rather good lattice energy for the NaCl structure can be obtained from analogous transition metal oxides allowing for crystal-field terms (FYFE, 1963). The transition is feasible and the transition pressure can be estimated with significance.

An interesting case is provided by magnesium oxide. This oxide is certainly a possible mantle phase, particularly where silicates are replaced by oxides including stishovite. It has been suggested that MgO may change from the halite to the CsCl structure. Simple spherical ions such as Mg^{2+} and O^{2-} are rather incompressible. In this case, unless large repulsive oxygen overlap is to be introduced, the Mg-O bond length in periclase must lengthen in an 8 coordinate structure. If the volume of the latter is calculated assuming that O-O penetration does not occur, it will be larger than in the periclase structure. If the volume is made smaller, ΔV will still be small and a large barrier introduced. Thus, from present data, MgO in the CsCl structure does not appear easily accessible at least not till such pressures are achieved that the ionic model ceases to be relevant.

Magnesium does occur in 8-coordination in some silicate structures, for example pyrope. But in this case, oxygen atoms linked to magnesium are also linked to either aluminium or silicon with quite covalent bonds. These linkages all reduce the ionic charge on oxygen and can remove the spherical symmetry of the charge cloud. Such influences are unlikely with the simple oxide.

That the stishovite transition in SiO_2 is feasible is also easily shown but in this case, on account of the large lattice energies involved, calculation of the barrier with significant accuracy is difficult. First, SiO_2 in the rutile structure, even with the same cell volume as TiO_2 , would have a smaller volume than quartz, by about $4 \text{ cm}^3/\text{mol}$. The lattice energies of rutile and quartz differ by about 240 kcal (experimental values) so that given the true volume of stishovite this barrier can be overcome and the real barrier must be less. A reasonable guess of both cell volume and barrier can be derived by consideration of bond distances and energies involved in the formation of TiF_6^{2-} and SiF_6^{2-} in aqueous solution (FYFE, 1963). We may note, that once pressures are high enough that SiO_2 in the rutile structure is favoured, we may then expect a large array of silicates with 6-coordinated silicon to also be in the realms of possibility; the heats of formation of most compounds from the oxides in the appropriate structural state being rather small (cf. $\text{FeO} + \text{SiO}_2 \rightarrow \text{FeSiO}_3$ and $\text{FeO} + \text{TiO}_2 \rightarrow \text{FeTiO}_3$). Thus phases such as KAlSi_3O_8 (orthoclase) in a dense structure should be possible in the stishovite stability field as suggested by KUME *et al.* (1966).

The high-spin-low-spin transition in FeO and hence in all iron oxygen compounds has been discussed by FYFE (1960) and more recently by STRENS (1969). This transition, which seems feasible in the mantle, has considerable bearing on iron-magnesium geochemistry in the deep mantle and on the optical properties of this region. While it must lead to denser iron compounds (the diamagnetic ferrous ion being small) it may also lead to iron compounds with rather different compressibilities than those with which we are familiar. The transition in octahedrally coordinated iron oxygen compounds has not been observed. The calculations of the transition region in the mantle both by Fyfe and Strens seem inadequate as neither have taken into account all the factors involved, but at least Strens calculations show it to be feasible (more detailed work is in progress by Fyfe and McLellan).

3. Phases containing volatiles

While phase changes in rather simple compounds can often be rationalized and predicted, as soon as we come to consider multi-atom compounds, problems increase. In the lower crust and upper mantle, most water

is contained in rather complex structures such as micas and amphiboles while in some regions, serpentine minerals may be significant. With our present knowledge, carbon dioxide is mainly found in rather simple carbonates. RUBEY (1951) in his classic essay on sea water discussed the evolution of the hydrosphere, and showed convincingly that water and other volatiles have been slowly added to the surface from the mantle. It is of some importance to understand how volatiles may be trapped in the deep mantle for this has bearing on many geochemical problems including evolution of the oceans, atmosphere and life.

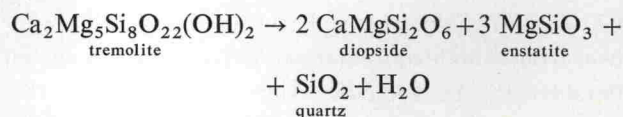
It is a striking fact, that most of the complex hydrate minerals with which we are familiar cannot persist far into the mantle. First we may consider the serpentine minerals. BOWEN and TUTTLE (1949) showed that at low water pressure (1–2 kb) serpentine breaks down to less hydrous phases at temperatures near 500°C . Let us consider the simplified reaction



The ΔV_0 of this reaction is about $5 \text{ cm}^3/\text{mol}$. As breakdown occurs in the region $5\text{--}600^\circ\text{C}$, we would anticipate maximum thermal stability where ΔV tends to zero. From data in SHARP's (1962) tables we would expect this inflection to occur near 30 kb. KITAHARA *et al.* (1966) have observed such inflection in the vapour pressure curve. The general form of the phase diagram is shown in fig. 1.

The form of vapour pressure curve of fig. 1 is not normally observed in low pressure studies, but once the mantle pressure range is considered, most curves will follow such a pattern. Two types of mineral are of particular interest in deep water retention; the micas (in particular phlogopite) and amphiboles (in particular hornblendes). Not much data is available for hornblendes as yet, but tremolite provides a model.

For the reaction



$$\Delta G_0 = 18 \text{ kcal} \quad \Delta V_0 = -5.5 \text{ cm}^3.$$

From the available data (CLARK, 1966) it would be expected that tremolite would have a maximum thermal stability at about 1000°C , and after about 10 kb the