REACTIONS IN SOLIDS

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INTRODUCTION

Within the last ten years many investigators, in quite diverse fields, have been studying reactions which take place in heterogeneous systems involving two or more solid phases. The problem is quite complex but the mass of data which has been accumulated now presents some degree of conformity. A complete historical development of the subject is unnecessary in this review and only the salient features of the various kinds of reactions are here discussed.

I—RECRYSTALLIZATION AND CRYSTALLOGRAPHIC CHANGE

When a crystalline metal has been subjected to cold-working, some of the atoms become displaced from the regular lattice of the crystals with the formation of a number of deformed regions. The process of restoration of the uniform lattice is called recrystallization. The theoretical treatment of the subject has been attempted in a recent paper by J. A. M. van Liempt.[1]

Crystallographic change is essentially a transformation from a metastable crystal lattice to one of greater stability.[2] From a consideration of the equilibrium $CaCO_3 = CaO + CO_2$, Langmuir[3] came to the conclusion that reactions of this type, which result in the production of two solid phases and a gas, can occur only at the interface between the two solid phases. Hume and Colvin extend this conception to the change from one crystal form to another. According to these authors three factors govern the course of the reaction: (1) rate of nucleation; (2) particle size; and (3) linear rate of preparation of the interface between the two solids.

The nuclei of the new lattice form at the surface of the solid, especially where it is deformed, and the formation of nuclei is preceded by a period of induction which depends upon the previous history of the substance. Mechanical deformation, according to van Liempt[1], should not be necessary, since the surface of the particle constitutes of itself a deformed area.

II—REACTIONS IN WHICH A SOLID DECOMPOSES TO GIVE A GAS AND A SOLID

A considerable amount of work has been done upon the dissociation of hydrates, carbonates, sulfates, etc. The investigations have, until recently, been limited to applications of the phase rule to these systems and the discrepancies[4] which appeared in the results of different investigations have led some to the conclusion that equilibrium in such systems either does not exist or is very difficult to attain[5].

For this type of reaction Langmuir (loc. cit.) suggested that the reaction took place at an interface between the two solid phases and in 1929 Hume and Colvin[6] showed that, in the decomposition of potassium hydrogen oxalate hemihydrate, the decomposition starts along crystal edges and spreads throughout the crystal at definite velocity when the temperature

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[1] Z. anorg. Chem. *195*, 366 (1931).
[2] J. Hume and J. Colvin, Phil. Mag. (7), *8*, 589 (1929).
[3] Irving Langmuir, J. A. C. S. *38*, 2263 (1916).
[4] Huttig and Lewinter, Zeit. Augen. Chem. *41*, 1034 (1928).
[5] Huttig and Frankenstein, Z. anorg. Chem. *185*, 403, 413 (1930).
[6] Proc. Roy. Soc. *125*, 635 (1929).

is constant. The same authors with Coppock[7] showed that potassium chlorate decomposition follows essentially the same mechanism. In a later paper Hume and Colvin[8], in an ingenious piece of research, have shown that, in the decomposition of $CuSO_4.5H_2O$ at low vapor pressures the velocity of propagation of the interface remained remarkably constant at constant temperature.

III—REACTIONS OCCURRING BETWEEN TWO SOLIDS

These reactions may include reactions such as:

$$BaCO_3 + Na_2SO_4 = BaSO_4 + Na_2CO_3$$

$$CaSO_4 + SiO_2 = CaSiO_3 + SO_3$$

$$BaO + PbCl_2 = BaCl_2 + PbO$$

They are generally carried out with powdered mixtures of the two reactants. This field has been reviewed in several papers in Germany notably by Tammann[9] and Hedvall[10]. The former shows that true equilibrium cannot exist in such systems. The reactions are in general characterized by a period of rapid initial reaction which occurs at a more or less definite temperature and a slower reaction which may or may not reach completion. The first rapid reaction takes place at the points of contact between the particles while the decrease of reaction rate is assumed to be due to the necessity, for at least one of the reactants, of diffusing through the layer of reaction product. Jander[11] and his co-workers have developed this field considerably.

The temperature at which a reaction begins is the point at which the atoms or molecules of one of the reactants become capable of position change due to increased vibrational energy. In some cases, a change of crystalline form takes place at this temperature;[12, 13] in some cases, a marked increase in electrical conductivity takes place. Ion deformation and the presence of impurities often influence the rate of reaction.

These apparently varied factors complicate the study of reactions between solids but it seems reasonable to hope that they may not be so different in their origin. Reaction between two solids takes place at the temperature at which the atoms have a certain mobility. In a mixture prepared by grinding the ingredients together it is highly probable that much deformation of the crystals should take place. The molecules, atoms or ions in these deformed regions will become capable of position change at a much lower temperature than those in the perfect lattice. Consequently the first rapid reaction may be assumed to be due to the presence of these deformed portions of the particles. Upon the removal of the deformation either by reaction with the other substance or by recrystallization, the reaction becomes slower. This may be due to the slow rate of diffusion through the reaction product or to the fact that only a few of the atoms or molecules, on the surface of the now perfect crystal, have sufficient energy to be capable of reaction. Let us assume that the latter factor is the major one. When one of the substances is undergoing a crystallographic change at the reaction temperature, the supply of these atoms or molecules which have the capability of position change is continuously replenished and the reaction will proceed to completion sometimes

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[7] Trans. Faraday Soc. *27*, 283 (1931).

[8] Proc. Roy. Soc. *A 132*, 548 (1931).

[9] Tammann, Zeit. Angew. Chem. *39*, 869 (1926).
Tammann, Trachr. Geo. Wiss. Gottingen Math-physik Klasse 277 (1930).

[10] Hedvall, Zeit, Elektrochem. *36*, 853 (1930).

[11] Jander and co-workers, Zeit. anorg. Chem. *163*, 1-30 (1927); *166*, 31 (1927); *168*, 113 (1928); *174*, 11 (1928); *190*, 65 (1930); *190*, 397 (1930); *196*, 321 (1931); *200*, 245 (1931); *202*, 135 (1931).
Zeit. Angew. Chem. *41*, 73 (1928).

[12] Z. anorg. Chem. *197*, 399 (1931).

[13] Booth and Ward J. Phys. Chem. *36*, 961 (1932).

with considerable velocity. At temperatures below the transition point the number of atoms or molecules having the necessary energy is much lower but not necessarily negligible. The confirmation of Tammann's conception of diffusion being the main factor rests upon the fact that, when the fraction of a substance which has reacted is plotted against the logarithm of the time, a straight line results.

The writer has observed that when the results of Hume and Colvin (loc. cit.) upon the decomposition of $CuSO_4.5H_2O$, are plotted in this manner a straight line is also obtained. It is therefore possible that the diffusion theory is not to be accepted and that crystallographic transformation or the energy of the atoms or molecules on the crystal surface may be the controlling factors.