experimental error, showing that the polar effects for such substituents are additive. This may not be true for disubstituted compounds in which one

of the groups is electron donating while the other is electron attracting.

PITTSBURG, CALIFORNIA

On the Role of the Gaseous Phase in Solid State Reactions[1]

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The early work on reactions between powdered solids has been questioned recently by a group of Russian investigators. These workers claim that many of the reactions previously reported to proceed by solid state diffusion processes occur in reality by a vaporization mechanism. They conclude that solid state reactions between powders do not generally occur except at very high temperatures since the contact area between the particles presents too small a cross section for rapid diffusion. The ambiguities associated with the experimental methods used to differentiate between solid state and gas phase mechanisms are discussed briefly. Criteria are developed whereby it is possible to determine conclusively when a vaporization mechanism *cannot* be the principal mode of mass transport. These are applied to a number of reactions between powdered solids which occur rapidly at low temperatures. It is found that a vaporization mechanism is untenable for at least two of these reactions and that the above generalization as regards powder reactions is questionable.

In reactions between powdered solids such as the reaction

$$MgSO_4(s) + CaO(s) \longrightarrow CaSO_4(s) + MgO(s)$$

it is generally difficult to determine whether the reaction proceeds by solid state diffusion processes or whether mass transport through the gaseous phase ($SO_3(g)$) is involved. This question was the subject of heated controversy between European investigators some thirty years ago (for example, refs. 2, 3). The conflicting viewpoints regarding mechanism apply to numerous reactions, all of which are listed by Hedvall,[4] who has tabulated most "solid state" reactions studied prior to the 1940's. The reactions in question involve reactants where either vaporization (dissociation) is *possible* or where liquid phases *can* form. Another characteristic is that the reactions all proceed rapidly at relatively low temperatures (approximately 500°, some lower). The question that was basic to the entire controversy is whether solid state reactions can occur at all at such low temperatures.

The viewpoint that the reactions in question are, for the most part, purely solid state reactions apparently predominated, as evidenced by statements in the more recent literature and texts on the subject.[4-6]

In the last several years, Ginstling and co-workers have re-examined several of these reactions and claim to have shown that they proceed by transport of molecules through the gaseous phase.[7-9] These investigators have reverted to the viewpoint that solid state reactions between powdered solids are unlikely processes except at very high tempera-

tures. Their reasons for this belief are, however, quite different from the reasons previously presented. They fully accept reactivity in the solid state as a fact, but offer the contention that the contact area between powder particles offers so small a cross section for diffusion that appreciable mass transport will only occur when diffusion coefficients are very large, i.e., at high temperatures. They, therefore, conclude that the reactions studied by Hedvall, Tammann, Jander and co-workers are really not solid state reactions at all and these workers misinterpreted their results.

The reason that this question has not been resolved is that no means have been available up to the present whereby solid state and other mass transport processes may be unambiguously differentiated in powder compacts. Consider the experiments of Ginstling and co-workers where the reactants are separated so that there is no direct contact at all. The fact that the reaction is observed to proceed under these conditions led the authors to conclude that some of the so-called "solid state" reactions are not solid state reactions at all but that they proceed by dissociation of the salt followed by a gas-oxide interaction. Although this experiment demonstrates dramatically that gas phase mass transport is taking place under the experimental conditions, it *does not* disprove Hedvall's contention that mass transport by solid state diffusion is occurring under a different set of conditions, namely, when the reactants are in intimate contact in a powder compact. Since solid state reactions, particularly powder reactions, are quite sensitive to experimental conditions, any experiment designed to elucidate the mechanism which requires *changing* the conditions, immediately assumes an uncertainty.

In the present communication, criteria are developed whereby it is possible to gain knowledge regarding the mechanism of a reaction without disturbing the system. These considerations are limited to the determination of what is *not* occurring; specifically, it will be shown that in certain instances the possibility of a mechanism involving a vaporization step can be ruled out completely.

(1) Presented in part at the 134th Meeting of the American Chemical Society, Chicago, Illinois, September, 1958.

(2) D. Balarew, Z. anorg. Chem., 160, 92 (1927).

(3) G. Tammann, ibid., 160, 101 (1927).

(4) J. A. Hedvall, "Einfuhrung in die Festkorperchemie," Friedr. Vieweg, Braunschweig, 1952, p. 169 ff., p. 257 ff.

(5) W. E. Garner, "Chemistry of the Solid State," Butterworths, London, 1955, p. 307.

(6) G. Cohen, Chem. Revs., 42, 527 (1948).

(7) A. M. Ginstling, J. App. Chem. USSR, 24, 629 (1951) (transl.).

(8) A. M. Ginstling and T. R. Fradkina, ibid., 25, 1199, 1325 (1952) (transl.).

(9) M. E. Pozin, A. M. Ginstling and V. V. Pechkovsky, ibid., 27, 261. 404 (1954) (transl.).

When there are only two possible mechanisms (vaporization or solid state), it may be possible to specify the actual mechanism uniquely. The consideration of such a case leads to the conclusion that the generalization of Ginstling, et al., regarding the occurrence of solid state powder reactions at low temperatures is questionable.

Theory

The principle upon which the present discussion is based is as follows. Under a given set of conditions, a reaction which proceeds by a mechanism involving a vaporization step has a well-defined maximum rate. If the observed reaction rate is significantly greater than this maximum, the above mechanism is not the principal mode of mass transport.

A reaction which proceeds by a vaporization mechanism involves at least the steps[10]

$$MgSO_4(s) \longrightarrow MgO(s) + SO_3(g) \qquad (I)$$

$$SO_3(g) + CaO(s) \longrightarrow CaSO_4(s) \qquad (II)$$
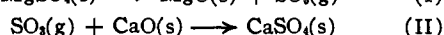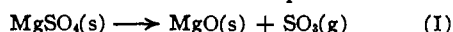
The rate of the over-all reaction cannot exceed the rate of the dissociation step (step I). The mechanism which leads to a maximum rate of dissociation is one where the gas simply "evaporates" off the surface into a vacuum. The rate is limited only by the available surface area. In any real dissociation, the rate may further be limited by one or more of the following: the rate of nucleation and growth of the product layer ($MgO(s)$), transport of gas through the product layer and rate of diffusion of product gas from the surface. The rate calculated on the basis of an "evaporation" model is the maximum rate, both for a dissociation reaction and for a metathesis reaction involving a dissociation step. This maximum rate can be calculated from equation (1), which relates maximum rate of vaporization to vapor pressure[11]

$$\mu = \frac{\alpha P}{(2\pi M_g RT)^{1/2}} \qquad (1)$$

where μ is the rate of gas evolution in moles/sec. cm.[2]; P is the dissociation pressure; M_g, the molecular weight of the gas and α the coefficient of evaporation. The surface area per equivalent of solid reactant is

$$A = \frac{6M_s}{\rho x d} \qquad (2)$$

where M_s is the molecular weight of the dissociating solid, ρ its density, x the number of moles of gas evolved per mole of reactant and d the particle diameter. M_s/x defines the equivalent weight of dissociating solid in this context. The product of equations 1 and 2 is the initial rate of reaction (since d is the initial particle diameter) in fraction converted per second ($\mu A = r$)

$$r = \frac{\alpha 6 M_s P}{\rho x d (2\pi M_g RT)^{1/2}} \qquad (3)$$

Evaluating constants and taking α as unity gives

$$r = \frac{265 M_s P}{\rho x d (M_g T)^{1/2}} \qquad (4)$$

(10) A specific example is cited for convenience only. The arguments apply to any reaction where a dissociation step occurs.

(11) E. H. Kennard, "Kinetic Theory of Gases," McGraw-Hill Book Co., New York, N. Y., 1938, p. 69.

where P is atmospheres, ρ in g./cm.[3], d in cm., T in °K., M_s and M_g in grams per mole.

The assumptions made in deriving equation 4 do not invalidate the calculation of a maximum rate. The maximum value of the coefficient of evaporation is assumed. The rate of the reverse reaction is neglected. The increase in dissociation pressure due to the surface-free energy of the small particles is neglected. This seems justifiable since the increase is only of the order of 1% for particles 10^{-5} cm. in diameter, assuming a surface tension of 1000 dynes/cm.

It is possible to stop here and make use of equation 4 directly. If the observed initial reaction rate is greater than that calculated from equation 4, then the reaction must be proceeding primarily by a mechanism other than one involving a vaporization step. It is preferable, however, to make use of this equation in another form for two reasons. One is that reaction rates are rather difficult to measure for most of the reactions under consideration since there is no net weight change. By using equation 4 in another form, it is possible to circumvent the necessity of obtaining conventional rate data. The other reason will become apparent from the considerations below.

It has been shown recently that the temperature at which the initial rate of a reaction attains a value of approximately 1% conversion per minute can be determined readily from a differential thermal analysis.[12] This value of reaction rate is substituted for r in equation 4 and P calculated as a function of T. A second equation relating P and T is the thermodynamic relationship

$$\ln P = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \qquad (5)$$

where ΔH^0 is the enthalpy and ΔS^0 the entropy of dissociation per mole of gas. From equations 4 and 5, a temperature can be calculated. This temperature has the significance that it is the lowest possible temperature at which a reaction proceeding by a vaporization mechanism can have an initial rate of 1% conversion per minute. For convenience, let this temperature be designated as the "dissociation temperature," T_d. If a reaction is observed to have an initial rate of 1% conversion per minute at a temperature lower than the "dissociation temperature," then the reaction must be proceeding at least primarily by a mechanism other than one involving a vaporization step.

Experimental

Differential thermal analysis patterns of 50-50 weight % mixtures of U_3O_8 with various metal powders (stoichiometrically, a large excess of metal) were obtained on a Robert L. Stone Company differential thermal analysis unit. The metals in question are Fe, Nb, Cr and Ni. The measurements were performed in static argon with a rate of temperature rise of approximately 16°/min. In order to prevent attack on the platinum–platinum–10% rhodium thermocouples, they were coated with a film of Al_2O_3. X-Ray analysis of the U_3O_8–metal mixtures after heating shows that U_3O_8 is completely reduced to UO_2 in each case, except in the reaction with Ni where a small quantity of U_3O_8 was present in the residue.

The Fe and Cr metal powders were prepared electrolytically; Nb, by interaction of the oxide and carbide, and Ni by hydrogen reduction of the oxide. The average particle

(12) H. J. Borchardt, submitted for publication.

sizes in microns as measured on a Fisher sub-sieve sizer are: U_3O_8, 7.8; Fe, 5.6; Nb, 9.5; Cr, 4.4; Ni, 3.6.

Results and Discussion

For the U_3O_8–metal mixtures, the reactions may be proceeding by a vaporization mechanism

$$U_3O_8(s) \longrightarrow 3UO_2(s) + O_2(g) \qquad (6)$$

$$O_2(g) + metal(s) \longrightarrow metal\ oxide(s) \qquad (7)$$
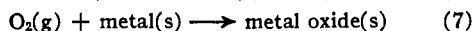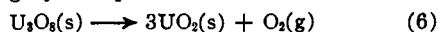
that is, dissociation of U_3O_8 in the presence of an oxygen getter. Alternately, the mechanism may involve only a solid state diffusion process. The "dissociation temperature" for U_3O_8 is calculated to be 613°, using thermodynamic data given by Coughlin.[13] The temperatures at which the rate of U_3O_8 reduction attains a value of 1% conversion per minute, as obtained from DTA, are tabulated below

(1)	U_3O_8 + Fe	500°
(2)	U_3O_8 + Nb	491°
(3)	U_3O_8 + Cr	800°
(4)	U_3O_8 + Ni	896°

Since the first two reactions attain an initial rate of 1% conversion per minute below 613°, they must be proceeding at least primarily by a mechanism other than one involving dissociation of U_3O_8 and oxygen gas phase transport. What this basically means is that the dissociation pressure of U_3O_8 is much too low at these temperatures (491°, 500°) to account for the observed reaction rates. If the only alternative mechanism involves solid state diffusion processes, it would follow that reactions 1 and 2 are truly solid state reactions.

A possible source of error in this analysis arises from the manner in which particle size is used. It may be argued that an average particle size is measured, and it is possible that the observed reactivity is due to the smaller particles. This, however, would not change any of the conclusions. If it were assumed that the reacting particles were an order of magnitude smaller than average, the calculated dissociation temperature would be 570°, still considerably above the observed reaction temperatures. Even an assumption of 1000 Å. particles would not bring the calculated dissociation temperature below the reaction temperatures for reactions 1 and 2. The reason for this is evident by considering equation 5, rearranged as

$$T_d = \frac{\Delta H^0}{\Delta S^0 - 4.58 \log P} \qquad (8)$$

Log P as calculated from equation 4 is approximately -9 and ΔS^0 is 39.2. Therefore, $T_d \cong \Delta H^0/80$, and an order of magnitude error in particle size, or for that matter, any of the quantities appearing in equation 4 (when calculating P) changes T_d only by approximately 6%, a two order of magnitude error by 12%, etc. This is the other reason mentioned above, for using equation 4 in a modified form. By taking advantage of the fact that the dissociation pressure is very sensitive to temperature or, conversely, temperature very insensitive to dissociation pressure, a formalism is ob-

(13) J. P. Coughlin, "Contribution to the Data on Theoretical Metallurgy," XII, Bureau of Mines, Bull. 542, 1954.

tained which allows conclusions to be drawn even where there are very large uncertainties in the input data. By this means, data in the literature can sometimes be analyzed where the experimental conditions are not completely described. Thus, for example, it is possible to say that the metathesis reactions between $MgSO_4$ and other metal oxides reported by Hedvall[4] are not proceeding by the gas phase transfer of $SO_3(g)$ molecules.

The approximation that $T_d \cong \Delta H^0/80$ appears to hold for systems other than the U_3O_8 dissociation. ΔS^0's were calculated for numerous reactions of the type Solid I → Solid II + gas from data in Circular 500.[14] This includes reactions where O_2, Cl_2, CO_2, H_2O and SO_3 is the gaseous product. ΔS^0 for most of the reactions falls with 10% of 40 e.u. Similarly, the log P term is fairly constant from system to system. The rate r is fixed by definition of T_d. The value of log $P = -9$ is based on a particle size of 7.8 μ which may, at most, be two orders of magnitude too large. Equivalent weights and densities do not vary over many orders of magnitude from system to system. In this respect U_3O_8 is an extreme, hence, $T_d \cong \Delta H^0/75$ is probably a better approximation in the general case.

Another possible source of error arises from the manner in which the thermodynamic quantities have been applied. A calculated dissociation pressure is utilized, based on the dissociation of U_3O_8 as written in equation 6. It is well known[15] that the reaction does not occur as written but that oxides intermediate between U_3O_8 and UO_2 form and that the equilibrium oxygen pressure above these intermediates is considerably less than that above U_3O_8. This fact is only further assurance, however, that the calculated dissociation temperature is truly a minimum. When considering this and other one-sided assumptions made throughout this analysis, it probably is safe to conclude that the reactions proceed *entirely* rather than "primarily" by a mechanism other than one involving a vaporization step.

It may be concluded definitely that the reduction of U_3O_8 by Fe and Nb is *not* proceeding under our conditions by a mechanism involving the dissociation of U_3O_8 to lower oxides and $O_2(g)$. If the only alternative class of mechanisms is one involving solid state diffusion processes and this appears to be the case, then it follows that the *generalizations* of Ginstling, *et al.*, are questionable.[16] The same comments hold as regards the Hedvall reactions involving $MgSO_4$.

(14) F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties," Nat. Bur. Standards, Cir. 500, 1952.

(15) J. J. Katz and E. Rabinowitch, "The Chemistry of Uranium," Pt. 1, McGraw-Hill Book Co., New York, N. Y., 1951.

(16) Many of the specific objections raised by these investigators to the earlier work, however, appear valid. A number of metathesis reactions studied in this Laboratory, particularly reactions involving BaO and SrO, appear to proceed by other than solid state diffusion processes. This work will be reported in a future publication.