REACTIONS IN THE SOLID STATE

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CONTENTS

I. INTRODUCTION

The properties of solids may be divided into two groups: (*1*) structure-insensitive or coöperative properties, and (*2*) structure-sensitive properties (136). Structure-insensitive properties are well defined under given external conditions and are independent of the history of the specimen and of its dimensions. Structure-sensitive properties, on the other hand, are directly affected by factors like the mode of preparation of the specimen, the pretreatment, and the particle size and shape. To the structure-insensitive group of properties belong, among others, the chemical formula, the lattice dimensions, the true density, the specific heat, the thermal expansion, and for ideal lattices the electric conductivity and the absorption spectra. Examples of structure-sensitive properties are the mechanical strength and the actual value of the cohesion, and the electric conductivity and the absorption spectra (particularly the long-wave-length band) of real crystals.

The chemical reactivity, like several other properties, is structure-insensitive in only a few instances; usually it is structure-sensitive, as is exemplified most strikingly by the circumstance that the catalytic activity of a solid, or the ability to luminesce, may vary tremendously with different modes of preparation or

treatment. In the subsequent discussion of reactions in the solid state considerable space is devoted to the few known structure-insensitive reactions since they, although of subordinate significance practically, provide a basis for a general understanding of structure-sensitive reactions.

Reactions in the solid state are defined as chemical processes in which one or more solid reaction products are formed with diffusion of elementary particles within their interior. The layer of reaction products increases by chemical reaction with the reactants adjacent to its boundaries. The reactants may be in any state of aggregation, but in this paper we are mainly concerned with reactions between solid reactants in which diffusion in the solid state is obviously required. Chemical changes of solids which do not involve penetration of particles through solid phases are, by definition, outside the scope of the present discussion. Furthermore, we omit reactions between metals, such as formation or decomposition of intermetallic phases and diffusion and transformation processes, since they are treated adequately in the metallographic literature. We restrict ourselves to reactions of inorganic solids which throughout will be considered as isotropic crystals. This simplification appears justified, since reactions between solids overwhelmingly occur with mixtures or between aggregates of fine powders. In principle, the considerations apply also to amorphous substances.

II. HISTORICAL NOTES

Despite their abundance, reactions in the solid state have remained unrecognized for a long time. After some familiarity had been gained on solid-phase diffusion in metals—the first observation of this kind seems to be due to Faraday (27) in 1820—Spring claimed in 1885 (137) to have observed reactions between inorganic solids; but his interpretation of the observations was partly erratic. In 1910 Cobb (15) described reactions between quartz and alumina with calcium carbonate or calcium sulfate, typical reactions in the solid state which, however, were not recognized clearly by him. Since 1912 it has been pointed out by Hedvall (43, 44, 45, 46) that reactions in the solid state occur frequently and represent indeed an important branch of chemistry. In the past thirty years intensive investigations have been carried out in this field, as evidenced by the monographs of Hedvall (52) and Jost (99).

III. THERMODYNAMIC RELATIONS

Except for cases of miscibility of reactants and product phases, equilibrium is usually not possible in reactions in the solid state and reactions proceed exothermically until at least one of the reactants is completely consumed. In practice, of course, complete reaction is difficult to achieve; it is essential that mixtures of fine powders be pulverized repeatedly to remove the barrier of product layers between the reactants. The equilibrium conditions have been discussed in detail by Tammann (142). For the attainment of a state of equilibrium either liquid or gaseous phases must partake in the reaction, or the heat of reaction must be small, and the difference of entropies of reactants and products

must not be zero. In the last case, equilibrium occurs at a single temperature,[1] where the stability of the system is reversed. Below the equilibrium temperature the products are formed, and above the equilibrium temperature they are decomposed into the reactants, the reaction always proceeding exothermically.

The number of phases which may be formed in mutually soluble solids is determined by the constitution diagram. However, since concentration gradients are prerequisites for the occurrence of diffusion, only phases having two or more degrees of freedom can be formed at ordinary pressures, while phases with one degree of freedom appear as interfaces between the layers of products (125). Thus, in a binary system only one-phase layers are possible as reaction products. The thermodynamic requirements are, however, by no means a safe criterion for determining which phases actually will be formed in a reacting system. Since the particle motion in solids is strongly resisted and requires large energies
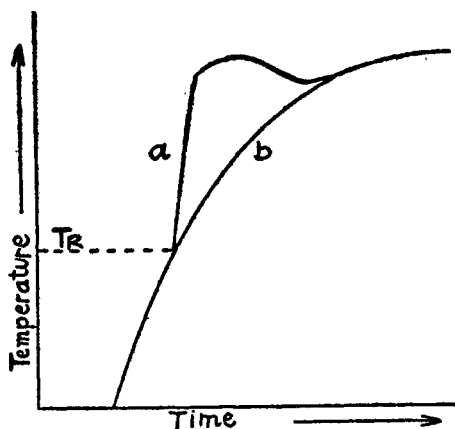

Fig. 1. Observation of solid-state reactions by means of heating curves (Hedvall (47))

of activation, unstable phases might form and coexist with other phases for practically unlimited times, if the temperature is sufficiently low. Even when the reaction products are the thermodynamically required phases, they may appear in thermodynamically unstable states characterized by an excess energy content. These states are designated as active phases, and their rôle in the reactivity of solids cannot be overemphasized. These are discussed more fully in a later section.

Systems composed exclusively of solids are exothermic, and in order to investigate these reactions isothermically, the rate has to be kept at an appropriate low value, for instance, simply by pressing the reactants against each other in the form of pellets instead of using powder mixtures. On the other hand, the fact that powder mixtures can be readily heated up, owing to the low specific heats and low heat conductivities of crystals, may be utilized in the study of the reactions by means of heating curves (47), as illustrated in figure 1. Upon heating

[1] At high pressures equilibrium might exist at all temperatures if the molar volume of the products is larger than the sum of the molar volumes of the reactants. Such cases are of little practical significance.

the powder mixture, reaction begins to proceed with great intensity at a certain temperature (T_R). Thereafter, the temperature of the mixture (curve a) is considerably higher than the temperature obtained with the same mixture after reaction has ceased to occur (curve b). The "reaction temperature," although not sharply defined, is useful for characterizing a reaction system. From the area enclosed between curve a and curve b and from the analytically determined yield of the reaction, the heat of the reaction can be approximately calculated (142). In cases in which the heat of reaction is large, the reaction may sometimes proceed almost explosively as the "reaction temperature" is reached. Owing to the rise in temperature after reaction has begun to occur, liquid phases may be formed. It is, therefore, necessary to ascertain whether a reaction proceeds throughout as solid-phase reaction or in the later stages with liquid phases as vehicle.

IV. TYPES OF REACTIONS

Independent of the number of reactants, the reactions in the solid state can be considered as being composed of reactions between two components only, because chemical combination is possible only at the phase boundary between adjacent phases. An illustration of such subdivision is the formation of the ternary compounds $2CaO \cdot Al_2O_3 \cdot SiO_2$ and $CaO \cdot Al_2O_3 \cdot 2SiO_2$ from quartz, alumina, and calcium oxide, where it was found (95) that two of the three components combine as a first step, and then the third component reacts with this combination as a second step. Therefore, in classifying reactions in the solid state only reactions between two components need be considered.

Frequently, instead of the reactants directly, one uses compounds which decompose at the temperatures of the reaction into the desired reactants and into gaseous products: for instance, reactions between oxides may be attained by heating mixtures of carbonates, nitrates, sulfates, etc. Any accompanying gas development does not basically alter the nature of the solid-phase reaction. Such compounds are preferably used when the reactants proper are of low stability (for example, barium carbonate instead of barium oxide), or when the enhanced reactivity of freshly formed solids is of advantage, as is described in a subsequent section.

A. Additive reactions

The simplest and most frequently occurring type is the additive reaction $A + B \rightarrow AB$, where A and B may be elements or compounds. If the product (AB), through which the reaction has to proceed by diffusion, is not miscible with A and B, it is formed as a separate new phase between A and B. If AB is entirely or partly miscible with A or B, it is generated as one or two new phases within the original phases. It is also possible that A and B form consecutively products of different composition so that several phases may be present between the reactants.

Reactions between elements: An example of reactions between elements is that of the tarnishing of metals, in which a salt (oxide, halide, sulfide, etc.) is

formed by reaction with a non-metal. A coherent diffusion layer may be formed in all instances in which the equivalent volume of the salt is greater than that of the metal (118). A few tarnishing reactions are structure-insensitive and are outstanding illustrations of the fundamental mechanism of reactions of solids. Mostly, however, such reactions are complex processes, as indicated by the examples listed in table 1, for which no adequate theory has as yet been developed.

Reactions between elements and compounds: These reactions constitute a comparatively small group of combinations like the following (10):

$$Mn + Mn_3O_4 \rightarrow 4MnO; \quad Fe + 2FePO_4 \rightarrow Fe_3(PO_4)_2$$
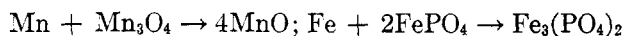
Reactions between compounds: Compounds which combine additively are mostly binary; there are however exceptions, for example, the formation of magnesium orthosilicate from the metasilicate and magnesium oxide (39, 96) may be mentioned.

TABLE 1

Examples of tarnishing reactions

REACTING COMPONENTS	REACTION PRODUCTS IDENTIFIED IN TARNISH LAYER	REFERENCES
Al + air (or O_2).............	Amorphous, ϵ-, β-, γ-Al_2O_3	(12, 140)
Cu + air (or O_2).............	Cu_2O, CuO	(74)
Fe + air (or O_2).............	Fe-O*, FeO, Fe_3O_4, Fe–Fe_2O_3,* α-, γ-Fe_2O_3	(6, 29, 117, 154)
Cu–Zn* + O_2................	Cu_2O, ZnO	(20)
Cr–Ni* + air................	Cr_2NiO_4	(79)

* – designates solid solution.

There have been prepared solid solutions of systems exhibiting either complete miscibility, like CoO–ZnO (44), CoO–MgO (44, 73), CoO–MnO (45), CoO–NiO (45, 73), NiO–MnO (48), NiO–MgO (48, 73), CaO–CdO (114), BaO–SrO (14, 24), Fe_2O_3–Cr_2O_3 (116, 166), or exhibiting partial miscibility, like Al_2O_3–Cr_2O_3, Al_2O_3–Fe_2O_3 (116), Fe_2O_3–Mn_2O_3 (166), CdO–MnO, MgO–MnO (115).

Compounds are formed either by combination of salts to yield double salts, such as Ag_2HgI_4 from silver iodide and mercuric iodide (103), Ag_4PbI_6 from silver iodide and lead iodide (152), or by combination of an acidic reactant with a reactant of basic nature to yield a salt. Reactions of the acid oxides SiO_2, TiO_2, ZrO_2, WO_3, MoO_3, V_2O_5, Sb_2O_3, As_2O_3 with the basic oxides BaO, BeO, CaO, CdO, CuO, FeO, MgO, NiO, PbO, SrO, ZnO have been early reported (142). The formation of stannates (45), uranates (145), columbates, and tantalates (92) was likewise described at an early stage. In more recent years particularly, chemical reactions of oxides have been explored systematically, i.e., reactions involving the formation of compounds like silicates, aluminates, spinels, titanates, ferrites, chromites, etc. For a survey of this field, reference is made to the monograph by Hedvall (52). The compounds formed may exhibit appreciable miscibility with one or both of the reactants (13, 17, 71, 105).

A special group of unusually intensive reactions comprises reactions involving a peroxide as a reactant which decomposes in the course of the reaction at temperatures at which the peroxide itself ordinarily is stable. As a result of the decomposition of the peroxide, other substances or the reaction products may be oxidized. In reactions between BaO_2 and Cr_2O_3, U_3O_8, MnO, or Fe_2O_3, the chromate, uranate, manganate, and ferrate are rapidly formed (49, 61, 67). In other cases, a substance may become oxidized without combination with the peroxide, for instance, Cu_2O by BaO_2 at 260°C. (61), or the reaction with the peroxide may be accelerated by the decomposition, even when no oxidation is possible, for instance, BaO_2 + SiO_2 or TiO_2 (67), CeO_2 + SiO_2, WO_3, or V_2O_5 (142). Reaction between BaO_2 and SiO_2 sets in at 300°C. These reactions occur in the solid state, since BaO_2 dissociates at 795°C. and liquid phases, owing to the presence of traces of $Ba(OH)_2$ in BaO_2, do not exist below 390°C.

No general rules have been found for additively reacting systems except that the reaction temperatures often approximately coincide with the temperatures at which self-diffusion becomes appreciable within one of the reactants (142). A relation of the temperatures of measurable self-diffusion to the absolute melting temperatures was first proposed by Tammann and Mansuri (144). The ratio between the two temperatures is approximately 0.3 for metals, 0.5 for inorganic substances, and 0.9 for organic compounds.

B. Exchange reactions

The second mode of reaction between two solids is by exchange of constituents according to one of the following schemes:

$$A + BC \rightarrow AC + B \tag{a}$$

$$AB + CD \rightarrow AD + BC \tag{b}$$

$$ABX + CB \rightarrow CBX + AB \tag{c}$$
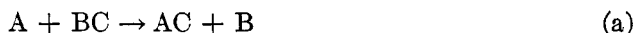
In these reactions, which involve diffusion through two product layers, it is possible to have a considerable variety of phase arrangements, determined by the miscibilities of product and reactant phases and by the reaction mechanism (nature of mobile particles and their relative velocities). The way in which the products may be arranged between the reactants is either beside each other or tandem. An illustration of the possibilities is the following simple case: in the reaction AB + $CD \rightarrow BC$ + AD, the product AD may be miscible with AB, while all other phases are not miscible. If the reaction is carried out by a migration of B and D only, B diffusing from AB through the product layer towards CD and D diffusing from CD towards AB, the succession of layers $(B, D)A \mid BC \mid CD$ may occur. If, on the other hand, A and C are the mobile particles in the reaction, the layers might be $AB \mid BC \mid AD \mid CD$, without formation of a solid solution of AB and AD. In equivalent mixtures the reactants should, of course, ultimately be completely consumed. The conditions of phase formation are still more complicated when ternary or higher compounds react, and when products of different nature are formed during the course of a reaction.

Examples of reactions according to scheme (a) are found in the exchange of the metal of a salt for a more electropositive one such as: $Cu + HgCl_2 \rightarrow CuCl + HgCl$; $Fe + CuO \rightarrow FeO + Cu$; $Fe + PbSO_4 \rightarrow FeSO_4 + Pb$; $Mg + ZnS \rightarrow MgS + Zn$ (142); $Mg + CdO \rightarrow MgO + Cd$; $2Al + 3NiO \rightarrow Al_2O_3 + 3Ni$; $Zn + CuO \rightarrow ZnO + Cu$; $Sn + CuO \rightarrow SnO + Cu$ (37); $Cu + AgCl \rightarrow CuCl + Ag$; $Co + Cu_2O \rightarrow CoO + 2Cu$ (162). In such systems reactions have been observed to be rapid when the heat of reaction is large.

Reactions conforming to scheme (b) are exemplified by the following: $CuI + Ag_2S \rightleftharpoons (Cu, Ag)_2S + (Cu, Ag)I$; $Cu_2Se + Ag_2S \rightleftharpoons (Cu, Ag)_2S + (Cu, Ag)_2Se$ (152); $BaO + 2CuI \rightarrow BaI_2 + Cu_2O$; $BaO + PbCl_2 \rightarrow BaCl_2 + PbO$; $BaO + NiBr_2 \rightarrow BaBr_2 + NiO$; $BaO + 2TlBr \rightarrow BaBr_2 + Tl_2O$; $CaO + NiCl_2 \rightarrow CaCl_2 + NiO$; $CaO + PbCl_2 \rightarrow CaCl_2 + PbO$ (57); $PbS + CdSO_4 \rightarrow PbSO_4 + CdS$; $HgCl_2 + 2KI \rightarrow HgI_2 + 2KCl$; $PbCl_2 + 2KI \rightarrow PbI_2 + 2KCl$ (102). For each system in this group individual reaction temperatures were found. These temperatures are, in corresponding cases, lower for barium oxide than for calcium oxide, indicating that the basic strength of the reactant influences the reaction temperature. On the other hand, the observed temperatures in the reactions between barium oxide and cupric halides (51) coincided with the temperatures at which self-diffusion becomes appreciable in the halide (153).

Exchange reactions between alkali halides have been investigated extensively (107). In all instances in which the lack of miscibility precluded establishment of equilibrium, large cations combined with large anions, and small cations with small anions—for instance, sodium bromide and potassium chloride react to form sodium chloride and potassium bromide—whereas no reverse reaction takes place. This is a direct result of the requirement that reactions in systems without miscibility have to proceed exothermically. Thus with alkali halides the direction of reaction can be derived from the difference in lattice energy of the compounds involved.

Reactions according to scheme (b) may also occur in combination with other reactions. For instance, an easily oxidizable sulfide may react with a basic oxide with formation of free metal in the following way:

$$4MeO + 4Me'S \rightarrow 4Me'O + 4MeS$$

$$4Me'O + MeS \rightarrow 4Me' + MeSO_4$$
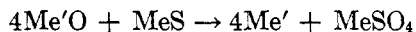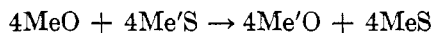
These reactions take place between barium oxide and sulfides of copper or lead (8).

In the presence of oxygen the products of exchange reactions may become oxidized. Thus, reactions of sulfides, phosphides, carbides, and silicides with basic oxides yield directly sulfates, phosphates, carbonates, and silicates of the basic oxide in question (63). Frequently these reactions proceed at relatively low temperatures and may be used to prepare compounds of low thermal stability. It should be noted that nitrates are not obtainable from nitrides in this way. The reaction temperatures of these systems vary individually, but under comparable conditions are lower, the more basic the oxide.

Reactions according to scheme (c) comprise a large group of reactions in which an oxygen-containing acid group is exchanged between one basic oxide and another: $MeO + Me'XO_n \rightarrow Me'O + MeXO_n$. Reactions of this type, explored by Hedvall (60), are listed in table 2. The reaction temperatures in this group again show the correlation with the basic nature of the oxide involved; moreover, in contrast to the other types described, these reactions have in common the fact that the reaction temperatures for a given basic oxide are approximately constant and independent of the nature of the other reactant (carbonate, sulfate, phosphate, or silicate). The same is also approximately true in corresponding reactions between CaO, SrO, BaO and spinels like $ZnAl_2O_4$, $CoAl_2O_4$, $CoCr_2O_4$, $FeCr_2O_4$, $CuAl_2O_4$ (50). Some reactions, which at first glance appear to proceed as additive reactions, are actually exchange reactions of the same type; for example, the formation of cobaltite from Co_3O_4 and ZnO (62), or of ferrites from Fe_3O_4 and MgO, CoO, NiO, MnO (7) takes place in the following way:

$$ZnO + CoOCo_2O_3 \rightarrow ZnOCo_2O_3 + CoO, \text{ etc.}$$
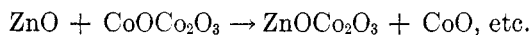
A satisfactory explanation for the exceptionally constant reaction temperatures in this last group for a given oxide cannot yet be given (52, 56), but this regularity appears to hold rigorously and is only suspended—for reasons discussed in a later section—when the acidic reactant undergoes crystallographic transition below the temperature at which it normally would react with the basic oxide.

V. FORMAL REACTION KINETICS

The over-all reaction rates are determined by the following factors:

1. The spatial and temporal sequence in which all possible phases appear.
2. Phase boundary processes, which may include
   (a) transfer of matter from one phase to the other,
   (b) chemical reactions,
   (c) formation of nuclei and growth of the reaction products.
3. Diffusion in the layer of reaction products.

In order to ascertain the rate-determining conditions it is useful to trace the chemical potential of the diffusing particles in the different phases. A simple example is given in figure 2, which shows an additive reaction between two solid components (A, B) yielding only one definite product (AB) immiscible in A or B. When only the component A is able to move, two different cases are possible:

(a) The phase boundary processes are so rapid that equilibrium is continuously established at the boundaries during the entire course of the reaction. Under these conditions the diffusion in the product layer alone is rate-determining.

(b) The phase boundary processes are not infinitely rapid compared with the diffusion velocity. Since both the transition of A particles from phase A to phase AB at phase boundary I and the formation of fresh AB at phase boundary II require time, equilibrium is not established at the phase boundaries. The diffusing substance is accumulated at phase boundary II. Under conditions otherwise equal, the gradient of the chemical potential is smaller than in case

TABLE 2

Reaction temperatures of exchange reactions between alkaline earth oxides and salts of oxygen-containing acids

SALT COMPONENT	REACTION TEMPERATURE WITH BaO °C.	REACTION PRODUCTS	REACTION TEMPERATURE WITH SrO °C.	REACTION PRODUCTS	REACTION TEMPERATURE WITH CaO °C.	REACTION PRODUCTS
Carbonates:						
$SrCO_3$	395	$BaCO_3 + SrO$				
$CaCO_3$	345	$BaCO_3 + CaO$	465	$SrCO_3 + CaO$		
$MgCO_3$	345	$BaCO_3 + MgO$	455	$SrCO_3 + MgO$	525	$CaCO_3 + MgO$
Sulfates:						
$SrSO_4$	370	$BaSO_4 + SrO$				
$CaSO_4$	370	$BaSO_4 + CaO$	450	$SrSO_4 + CaO$		
$MgSO_4$	370	$BaSO_4 + MgO$	440	$SrSO_4 + MgO$	540	$CaSO_4 + MgO$
$ZnSO_4$	340	$BaSO_4 + ZnO$	425	$SrSO_4 + ZnO$	520	$CaSO_4 + ZnO$
$CuSO_4$	345	$BaSO_4 + CuO$	420	$SrSO_4 + CuO$	515	$CaSO_4 + CuO$
Phosphates:						
$Sr_3(PO_4)_2$	350	$Ba_3(PO_4)_2 + SrO$				
$Ca_3(PO_4)_2$	340	$Ba_3(PO_4)_2 + CaO$	450	$Sr_3(PO_4)_2 + CaO$		
$Pb_3(PO_4)_2$	335	$Ba_3(PO_4)_2 + PbO$	455	$Sr_3(PO_4)_2 + PbO$	525	$Ca_3(PO_4)_2 + PbO$
$Co_3(PO_4)_2$	355	$Ba_3(PO_4)_2 + CoO$	465	$Sr_3(PO_4)_2 + CoO$	520	$Ca_3(PO_4)_2 + CoO$
$CrPO_4$	340	$Ba_3(PO_4)_2 + Cr_2O_3$	465	$Sr_3(PO_4)_2 + Cr_2O_3$	515	$Ca_3(PO_4)_2 + Cr_2O_3$
$Ag_4P_2O_7$	330	$Ba_3(PO_4)_2 + Ag_2O*$	450	$Sr_3(PO_4)_2 + Ag_2O*$	510	$Ca_3(PO_4)_2 + Ag_2O*$
Silicates:						
$CaSiO_3$ (wollastonite)	355	Barium silicate $+ CaO$	455	Strontium silicate $+ CaO$		
$MgSiO_3$ (enstatite)	355	Barium silicate $+ MgO$	455	Strontium silicate $+ MgO$	560	Calcium silicate $+ MgO$
$MnSiO_3$ (rhodonite)	355	Barium silicate $+ MnO$	465	Strontium silicate $+ MnO$	565	Calcium silicate $+ MnO$
Al_2SiO_5 (sillimanite)	355	Barium silicate $+ Al_2O_3$	430	Strontium silicate $+ Al_2O_3$	530	Calcium silicate $+ Al_2O_3$

* Dissociates subsequently into $Ag + O_2$.

(a), and the reaction is slowed down. With increasing width of the layer of AB, the influence of diffusion on the rate increases, so that finally case (b) might change into case (a).

Case (a) is simpler than case (b) because there all phase boundary processes can be neglected. On the other hand, in the primary stages of the reaction,
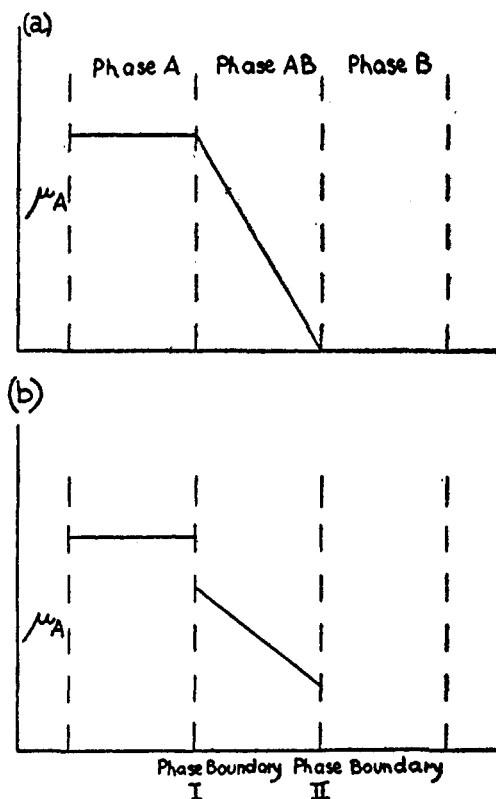
FIG. 2. Gradient of chemical potential of diffusing reactant

where the diffusion layers are extremely thin, or where there is very rapid diffusion, the phase boundary processes may become predominant and may be studied undisturbed by diffusion effects.

The conditions outlined can be expressed in a general way. Introducing a "reaction resistance" (W_R) for the phase boundary processes defined as the reciprocal of the velocity of all phase boundary processes, and introducing a corresponding "diffusion resistance" (W_D) for the diffusion processes in the product layer (28), the reaction rate may be written:

$$\frac{dn}{dt} = C \frac{\Delta\mu}{W_R + W_D} \tag{1}$$

where $\Delta\mu$ represents the free-energy change involved in the reaction. If we have case (a) of figure 1, $W_D \gg W_R$. The rate is diffusion controlled and equation 1 is transformed into:

$$\frac{dn}{dt} = C\,\frac{\Delta\mu}{W_D} = C\,\frac{\Delta\mu}{\dfrac{1}{D}\displaystyle\int_{\text{Phase boundary II}}^{\text{Phase boundary I}} d\xi/A} \tag{1a}$$

where D = diffusion coefficient as defined by Fick's law (4, 99),

ξ = thickness of diffusion layer, and

A = cross-sectional area of diffusion layer.

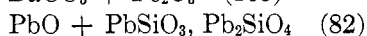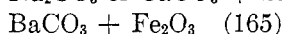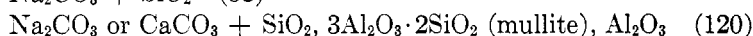If the diffusion layer has a constant cross section, and if furthermore D also has a constant value, the reaction rate becomes:

$$\frac{dn}{dt} = \frac{A}{\xi}\,CD\Delta\mu = \frac{A}{\xi}\,k \tag{1b}$$

Expressing finally the reaction rate in terms of the growth of the product layer, the rate is:

$$\frac{d\xi}{dt} = \frac{k'}{\xi}; \qquad \xi^2 = k't \tag{1c}$$

This equation has been frequently verified, notably in a number of tarnishing reactions (21) and in additive reactions between solids, for example, in the following systems:

$BaCO_3 + SiO_2$ (85)

$BaCO_3 + MoO_3$ (85)

$Na_2CO_3 + SiO_2$ (38)

Na_2CO_3 or $CaCO_3 + SiO_2$, $3Al_2O_3 \cdot 2SiO_2$ (mullite), Al_2O_3 (120)

$BaCO_3 + Fe_2O_3$ (165)

$PbO + PbSiO_3$, Pb_2SiO_4 (82)
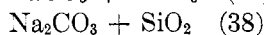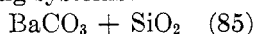
When—as is frequently the case—the reacting systems consist of mixtures of fine powders containing one of the reactants in large excess, the measurements may be evaluated by a relation proposed by Jander (85)

$$(1 - \sqrt[3]{1-\alpha})^2 = \frac{C}{R^2}\,t = C''t \tag{2}$$

where α = fraction of completion of reaction, and R = grain radius of the minor component assumed to be monodisperse and completely surrounded by the excess reactant. This equation appears to be applicable to many experimental results, although based on the assumption of a linear concentration gradient and a constant diffusion cross section which is not true for spherical particles. Serin and Ellickson (132) demonstrated that equation 2 for spherical particles is not nearly as good an approximation to the exact solution based on Fick's law as is equation 1c for the linear case. These authors recalculated Jander's (85) experimental data, using the exact equation:

$$1 - \alpha = \frac{6}{\pi^2} \sum_{n \text{ odd}} \frac{1}{n^2} \exp \left(-n^2 \pi^2 Dt/R^2 \right) \quad \text{[2]}$$

(2a)
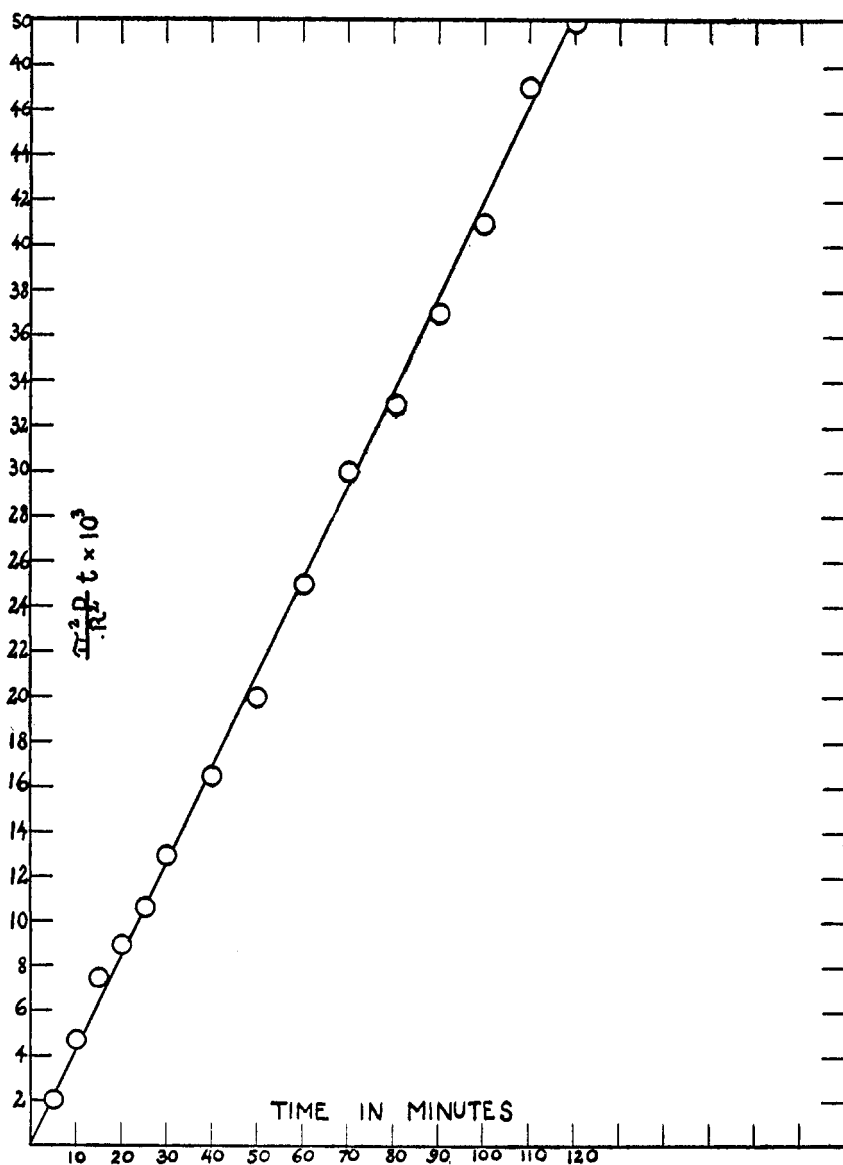
Fig. 3. Reaction rate of system $BaCO_3 + SiO_2$ (Serin and Ellickson (132))

In figure 3 are given the results for the reaction between barium carbonate and silicon dioxide at 830°C.; and figure 4 shows that the dependence of the rate on

[2] This equation was previously given by Dünwald and Wagner (19) but not applied to reactions between solids.

the grain radius of barium carbonate, the minor constituent in these measurements, was in agreement with the theoretical requirements.
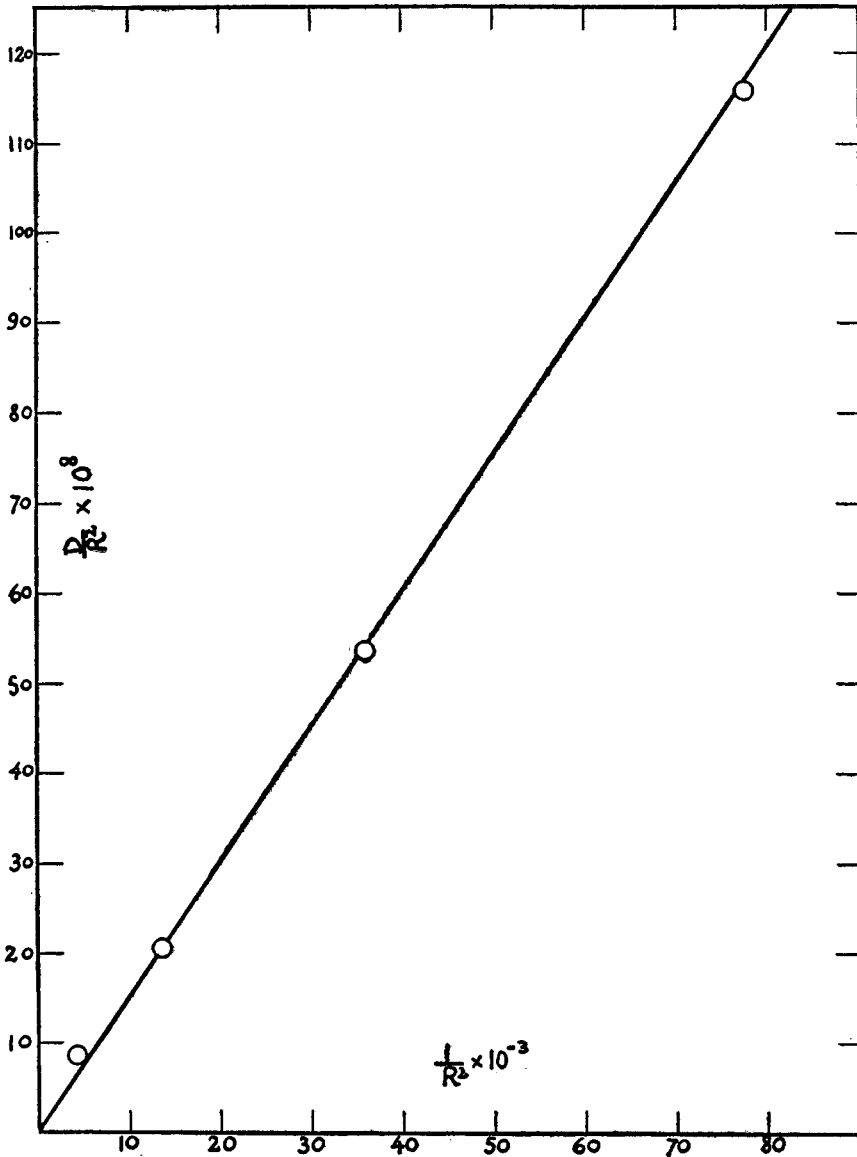
FIG. 4. Dependence of reaction rate in system $BaCO_3 + SiO_2$ on grain diameter of $BaCO_3$ (Serin and Ellickson (132)).

When the phase boundary processes cannot be neglected (case (b), figure 2) $\Delta\mu$ may be divided into two parts, $\Delta\mu'$ and $\Delta\mu''$, representing the changes of chemical potential due to the phase boundary processes and to the diffusion, respectively. Since, with increasing thickness of the diffusion layer, the in-

fluence of the phase boundary processes diminishes until it eventually vanishes, in a first approximation $\Delta\mu'$ may be assumed to be proportional to $1/\xi$ in the form (99):

$$\Delta\mu' = \Delta\mu \frac{b}{\xi + b}$$

(i.e., for $\xi = 0$: $\Delta\mu' = \Delta\mu$, and for $\xi \to \infty$: $\Delta\mu' = 0$). Thus the gradient of the chemical potential across the diffusion layer becomes:

$$\Delta\mu'' = \Delta\mu - \Delta\mu' = \Delta\mu \frac{\xi}{\xi + b}$$

which, introduced in rate expression 1b, yields:

$$\frac{dn}{dt} = CD\Delta\mu \frac{A}{\xi + b}$$

or transformed for integration:

$$\frac{d\xi}{dt} = \frac{k'}{\xi + b}; \qquad \xi b + \xi^2 = kt \tag{1d}$$

In the first stages of the reaction where the diffusion layer is thin, equation 1d reduces to linear growth: $\xi \sim k''t$. Subsequently, the rate should obey the complete expression 1d; thereafter, when the diffusion layer has become sufficiently thick, the square law of equation 1c should apply. Indeed, equation 1d has been confirmed in the oxidation of iron by carbon dioxide (112) and by water vapor (29).

For small values of ξ, equation 1d can be transformed (99) into:

$$b^2(e^{\xi/b} - 1) \sim k''t \tag{1e}$$

which likewise has been confirmed in some tarnishing reactions (143), although in a stage where the square law would be expected actually to hold. Similar empirical equations of the form:

$$\frac{1}{t} = \frac{1}{\alpha_1 e^{b_1\xi}} + \frac{1}{\alpha_2 e^{b_2\xi}} \tag{1f}$$

have been reported to represent the oxidation of copper, iron, zinc, and aluminum under certain conditions (108).

In the other extreme, where $W_R \gg W_D$, the rate is controlled solely by the phase boundary reactions. Owing to the complex nature of phase boundary processes, general rate expressions cannot be formulated but have to be established individually in each particular case. Under special conditions some reactions have been observed to proceed with constant speed (reduced form of equation 1d), such as:

$MgO + Ag_2SO_4 \to MgSO_4 + Ag_2O$ (respectively, $2Ag + \frac{1}{2}O_2$)   (83)

$3MgO + 2Ag_3PO_4 \to Mg_3(PO_4)_2 + 3Ag_2O$ (respectively, $6Ag + 1.5O_2$)   (83)

$MgO + Mg_2P_2O_7 \to Mg_3(PO_4)_2$ (84)
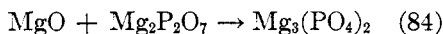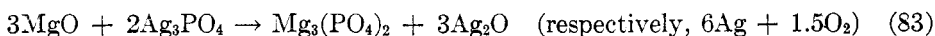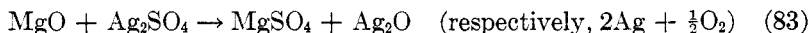
Sometimes, solid materials can be investigated only in powder form. Since reactions between solids are exothermic in the absence of reacting gases or liquids, and since the heat conductivities of non-metallic solids are usually low, the powder mixtures become heated during reaction, and kinetic derivations holding for isothermic systems cannot be used. A method to evaluate approximately kinetic measurements of non-isothermic systems is due to Jander (86). The temperature coefficient of the reaction rate may be expressed empirically as an exponential function: $k = C \exp(-Q/RT)$. When the reaction is initiated at a given temperature (T_e), the temperature of the reaction mixture rises almost instantaneously to the maximum temperature (T_i), from which it gradually decreases to the external temperature (T_e) as the reaction progresses. In the beginning we have thus $k_i = C \exp(-Q/RT_i)$, and at any time thereafter $k = C \exp(-Q/RT)$, where $T > T_e$. This yields:

$$k = k_i \exp\left(-\frac{Q}{R}\frac{T_i - T}{T_i \times T}\right) \tag{3}$$

Assuming that $T_i - T$ is proportional to the thickness of the product layer formed, and since $T_i \times T$ is approximately constant, we obtain $k = k_i \exp(-c\xi)$, which, introduced into equation 1c, yields:

$$\xi^2 = 2k_i t \exp(-c\xi) \tag{1g}$$

This equation was found (86) to describe adequately the observed rates of the reactions:

$$BaCO_3 + WO_3 = BaWO_4 + CO_2 + 10 \text{ kg.-cal.}$$

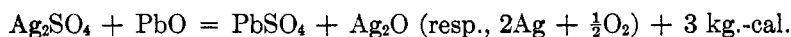$$Ag_2SO_4 + PbO = PbSO_4 + Ag_2O \ (\text{resp., } 2Ag + \tfrac{1}{2}O_2) + 3 \text{ kg.-cal.}$$

The rate constants determined by these or other equations are more or less structure-sensitive and cannot be employed directly to establish a reaction mechanism. Occasionally this might be due to a concentration dependence of the diffusion coefficients. Two reasons, however, appear to be mainly responsible for this state of affairs. The first is the complexity and irreproducibility of the phase boundary processes. The state of solid surfaces and the degree of contact between them are ill-defined and scarcely reproducible, especially in reactions in the solid state where the boundaries of the reaction layer expand continuously. While the kinetic treatment of nucleation and growth in the change from one phase to a new one offers considerable difficulties (155), the practically more important case of heterogeneous systems involving solids can hardly be treated theoretically at the present. Thus, despite their great significance in reactions of solids, phase boundary processes can seldom be brought under controlled conditions. It is, therefore, advisable to choose—if feasible—for kinetic investigations conditions such that equilibrium is continuously maintained at the phase boundaries; that is, that the phase boundary processes do not influence the reaction rate (case (a), figure 2). This, for instance, will be the case when the reactants are separated by a product layer of sufficient thickness.

The second reason is that for establishing a general law for a reaction it is also required that the solids involved in the diffusion be internally in equilibrium. The rate is primarily governed by the gradient of the chemical potential of the reacting particles, which potential is only defined when the particles in each single phase are arranged in such fashion that a state of minimum free energy is maintained within each phase throughout the course of the reaction. Only then is the reaction structure-insensitive. When the partaking phases are not in equilibrium internally, the rates become structure-sensitive and can be influenced to a large extent by incidental or deliberately created external conditions. The majority of solid-phase reactions are structure-sensitive, since solids usually contain enough non-equilibrium lattice disturbances to have a considerable effect on their chemical behavior. The energy required for motion of lattice defects or of particles influenced or created by lattice disturbances is lower than the migration energy of equilibrium particles.

Subsequently reaction mechanisms are discussed, first of solids internally in equilibrium, thereafter of the practically much more important reactions of non-equilibrium solids. The discussion of equilibrium crystals is limited to ionic crystals or to crystals whose building stones are at least ionic in nature. Only for such substances has an approximate but apparently adequate theory been developed. The mechanisms obtained offer also a qualitative basis for the understanding of reactions of non-equilibrium solids. In this case the reactions may be performed by motion of charged or of uncharged particles (53).

VI. THEORETICAL ASPECTS OF PARTICLE MOTION IN SOLIDS: STRUCTURE-INSENSITIVE REACTIONS

A. Empirical facts on diffusion and conductivity in crystals

A vast literature of experiments on diffusion and electric conduction in solid salts has been accumulated. The general results may be summarized as follows (4, 99, 110):

Diffusion in solid salts or in systems of solid salts occurs frequently, especially in temperature regions ranging from a few hundred degrees below the melting points up to the melting points of the salts. The diffusion obeys Fick's laws and may accordingly be investigated in experimental arrangements which permit the use of conveniently integrated forms of Fick's laws (4, 99).

Electrolytic conduction likewise occurs frequently in solid salts in the same temperature regions in which diffusion can be observed (147). This conduction yields important information about self-diffusion in crystals. Unlike conductance in solution, we may have in solids unipolar or bipolar conductivity. In the former instance the current is wholly transported by ions of one sign. By determining the transport numbers of the ions in a salt the mobile constituent or constituents are found, and the same kind of particles are the vehicle for the self-diffusion. Moreover, self-diffusion coefficients may be obtained approximately from the conductivity (23, 151, 156), for instance, by means of the Einstein relation: $D = k \times T \times B$, where D = diffusion coefficient, k = Boltz-

mann's constant, T = absolute temperature, and B = mobility of the ion in question.   Otherwise, self-diffusion coefficients are not readily determined.   In a few cases they have been measured directly with radioactive isotopes.   In the case of lead iodide the self-diffusion coefficient of the lead ions has been measured directly and found to be in satisfactory agreement with the value calculated from the conductivity (69, 128).   It is also possible to obtain a fair agreement for the diffusion coefficient of silver ions in silver chloride from measurements of the rate of exchange of radioactive silver ions (106) and from conductivity data (104).

The temperature coefficients of diffusion and of conductivity are always positive and can be represented by one or several expressions of the form:

$$D = A \exp(-Q/kT); \text{ respectively, } D = A_1 \exp(-Q_1/kT)$$
$$+ A_2 \exp(-Q_2/kT) + \cdots$$
$$\kappa = A'' \exp(-Q/kT); \text{ respectively, } \kappa = A_1'' \exp(-Q_1/kT)$$
$$+ A_2'' \exp(-Q_2/kT) + \cdots$$

where κ = the conductivity.   It is noted that D and κ differ in the pre-exponential factors, whereas the Q-values representing energy terms are the same in both cases.   An expression with two exponential terms is required for cases of bipolar conductivity, each term belonging to the motion of one kind of ion.   A two-term expression appears furthermore in most instances of unipolar conductivity, owing to a rather sharp change of the temperature coefficient of the motion of the mobile ion.   In this case the conductivity at higher temperatures invariably has larger A- and Q-values than has the conductivity at lower temperatures. Figure 5 illustrates this behavior for different specimens of silver bromide according to a recent investigation by Shapiro and Kolthoff (134).   Silver bromide is a unipolar conductor (133, 147), the silver ion being the mobile constituent. Figure 5 also exhibits the characteristic fact that the high-temperature conductivity is fairly reproducible, whereas the low-temperature branch of the conductivity is structure-sensitive and varies from specimen to specimen or with different treatments of a given specimen.   In the case of bipolar conductivity the corresponding behavior would yield a four-term expression.   Analogous conditions prevail, of course, in diffusion.

Many solids exhibit pronounced electronic conductivity, and even the most perfect ionic conductors may under certain circumstances acquire a feeble electronic conductivity.   Electronic conduction plays an important part in certain reactions in the solid state.   In general it is structure-sensitive, the value of the conductivity being strongly affected by the presence of impurities or by deviations from the stoichiometric composition.   Conduction in compounds is either really metallic or of a specific nature usually designated as semiconductivity, and occasionally either may occur in the same substance depending on the state of the specimen (Cu_2Se (123); Cu_2Te (122)).   A comprehensive tabulation of electronic conductors and a tentative classification on the basis of elec-

tronic structure have recently been given by Meyer (109). Semiconductivity proper is characterized as follows (99, 130):

As in metals, the Hall effect is found in electronic conductors, the sign of the Hall coefficient, however, being positive or negative depending on the chemical
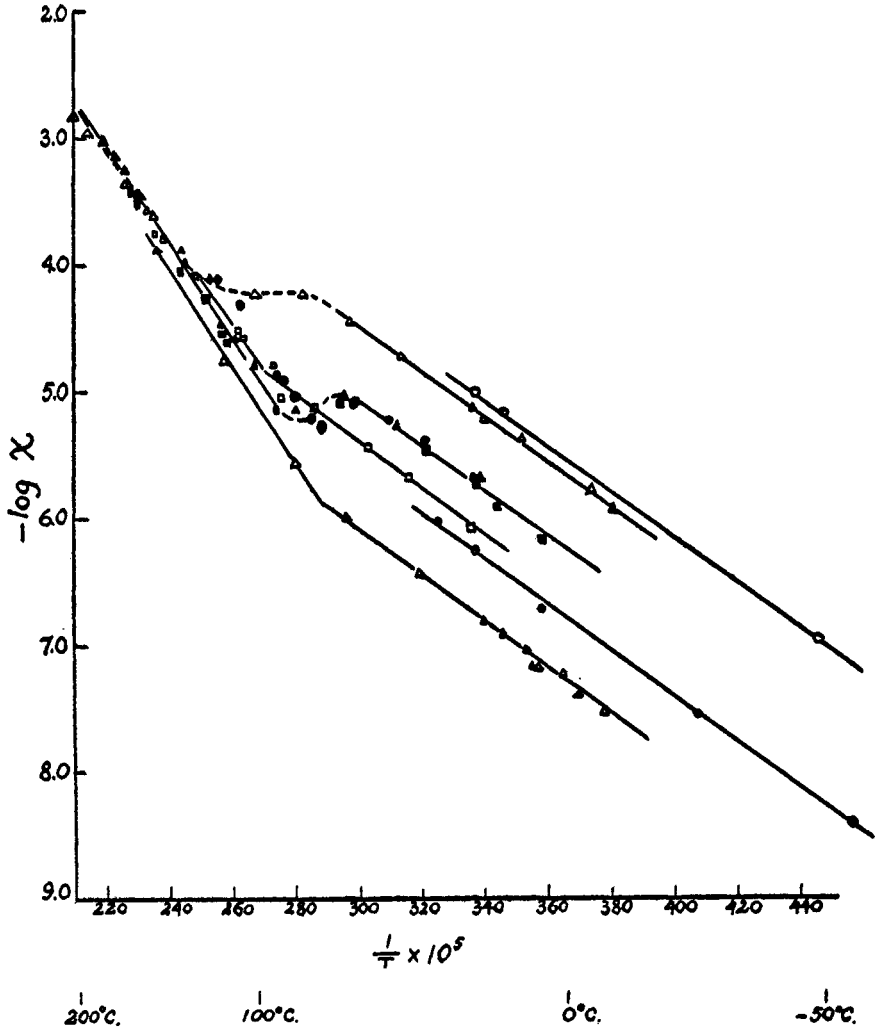

FIG. 5. Electrical conductivity of silver bromide (Shapiro and Kolthoff (134))

nature of the substance. In some preparations of cuprous oxide a change of the sign of the Hall coefficient from negative to positive with increasing temperature has been observed (127).

Also as in the case of metals, thermoelectric forces are developed in combinations of electronic conductors (159).

The temperature coefficient of semiconductivity is positive and follows an exponential expression of the form:

$$\kappa_\epsilon = A_\epsilon \exp\left(-Q_\epsilon/kT\right)$$

analogous to the temperature dependence of ionic conductivity. The values of A_ϵ and Q_ϵ vary greatly with the history of the specimen.

B. The state of solids being internally in equilibrium

A quantitative discussion must be limited to the reproducible (high-temperature) part of diffusion and conduction which apparently is structure-insensitive, in contrast to the poorly reproducible low-temperature motion. An adequate theoretical interpretation of the phenomena described is due primarily to Schottky and Wagner (126, 157, 164) after preliminary work by Frenkel (31), later extended by Jost (98, 100), Mott and Gurney (110), and others (9, 119). Schottky and Wagner showed that an ideal crystal at finite temperatures is in equilibrium only when a definite fraction of lattice particles have left their normal sites and are occupying certain positions of disorder. The possible states of disorder are pictured schematically in figure 6, showing a binary crystal of the composition MeX. The crystal in ideal order is illustrated in figure 6a. Figure 6b represents the possibility that ions of one sign have moved into interstitial positions (in the case of a cubic face-centered lattice most likely into the centers of the cubes), leaving an equal number of lattice sites vacant. Ions in interstitial positions are indicated by $\bigcirc$ and vacant lattice sites (holes) by $\square$. In figure 6c both anions and cations occupy interstitial positions in equivalent numbers, in which case no vacant lattice sites need be formed. Figure 6d shows the occurrence of positive and negative lattice holes in equivalent numbers without any ions having had to move into interstitial positions. Figure 6e finally shows the possibility that anions and cations occupy wrong lattice sites in equivalent numbers.

In principle, all types of disorder may occur simultaneously. In ionic lattices the cases of figures 6c and 6e (interstitial disorder of ions of both signs without formation of lattice holes, and the interchange of lattice positions) are improbable for energetic reasons, but of practical importance are the cases of figure 6b (interstitial disorder of one kind of ions with equal number of lattice holes) designated as Frenkel disorder, and figure 6d (formation of lattice holes of both kinds of ions) designated as Schottky disorder. In Schottky disorder the ions which have left their lattice sites occupy additional layers of regular lattice points deposited at the surfaces of the crystals. Interchange of lattice positions may, however, occur in molecular or in metallic lattices.

Frenkel disorder is likely to occur when anion and cation of the crystal differ substantially in size, and when polarization of the lattice is strong. This is the case with silver chloride and bromide, where all evidence points to a Frenkel disorder of the silver ions (100, 104). Schottky disorder is favored when anion and cation are of similar size, and when polarization of the lattice is weak, as, for instance, with most alkali halides (100, 126). Usually the degree of disorder

```
Me   X   Me   X   Me   X   Me        Me   X   Me   X   □   X   Me
                                                  (Me)
X   Me   X   Me   X   Me   X         X   □   X   (Me)Me   X   Me   X

Me   X   Me   X   Me   X   Me        Me   X   Me   X   Me (Me) X   Me

X   Me   X   Me   X   Me   X         X   Me   X   □   X   Me   X
                                           (Me)              (Me)
Me   X   Me   X   Me   X   Me        Me   X   □   X   Me   X   Me

              a                                   b
```

```
Me   X (Me)Me   X   Me (X) X   Me        Me   □   Me   X   Me   X   Me

X   Me (Me)X (X)Me   X (Me)Me   X        X   Me   X   Me   □   Me   X

Me (Me)X   Me   X   Me   X (X)Me        □   X   □   X   Me   X   Me

X (Me)Me   X   Me (X)X   Me   X        X   Me   X   Me   [      ]   X

Me   X (X)Me   X (Me)Me   X   Me        Me   X   □   X   Me   □   Me

              c                                   d
```

```
Me   X   Me   Me   X   Me   X

X   Me   X   Me   X   X   Me

Me   Me   X   Me   X   Me   X

X   X   Me   X   Me   X   Me

Me   X   X   Me   X   Me   X

              e
```
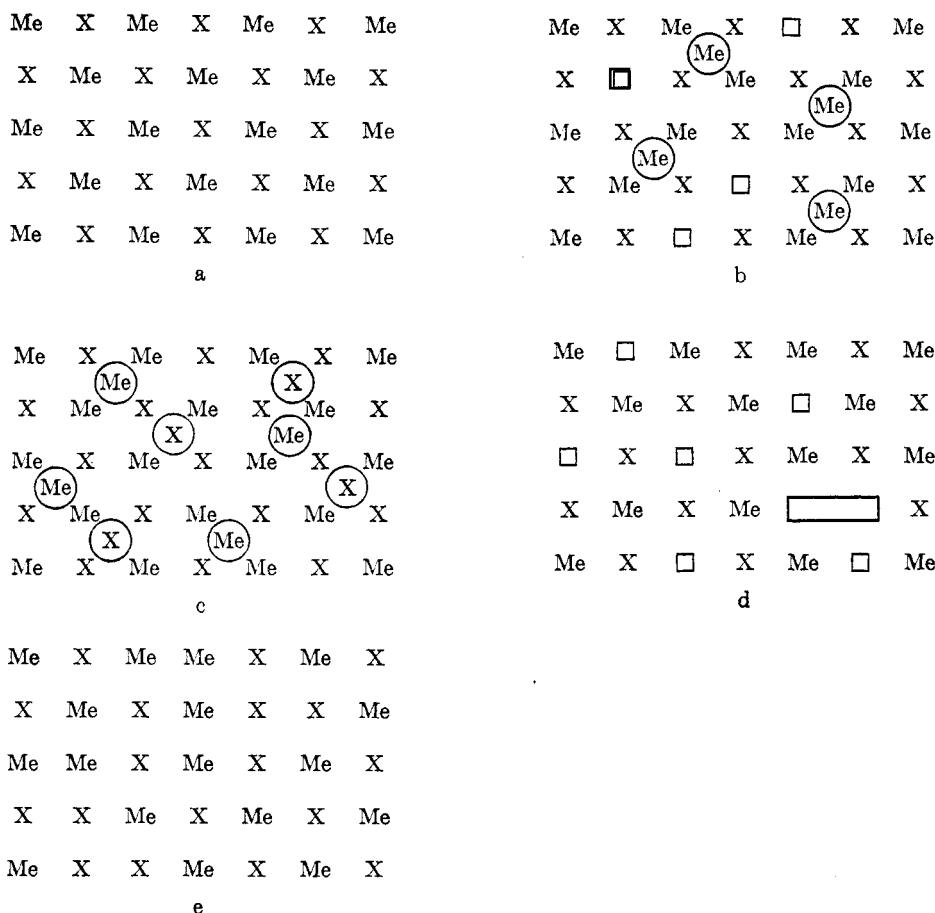
FIG. 6. Disorder models for a binary solid

is small, and the interaction between disordered particles can be neglected. Then the number of disordered ions (n) is, in a first approximation:

$$\text{For Frenkel disorder: } n \sim \sqrt{N^l N^0}\, \exp\left(-\tfrac{1}{2}E_F/kT\right) \qquad (4a)$$

and

$$\text{For Schottky disorder: } n \sim N^l \exp\left(-\tfrac{1}{2}E_S/kT\right) \qquad (4b)$$

where N^l = number of normal lattice positions,

N^0 = number of possible interstitial sites,

E_F = energy required to transfer an ion from its lattice position to an interstitial position, and

E_S = energy required to remove an ion pair from the interior of the crystal and to attach it at the outside as regular new lattice points.

It is to be noted that E_F and E_S represent heats of reaction. The thermodynamic lattice disorder is analogous, for instance, to the dissociation of a weak electrolyte

in solution; every process of disorder creates two positions of disorder,—either an interstitial ion and a lattice hole, or two lattice holes. To give an idea of the degrees of disorder which may occur, the following tabulation has been compiled, assuming the reasonable value of 1 e.v. for the disorder energy and also that the number of interstitial positions available equals the number of normal lattice positions. With these assumptions the degree of disorder is the same for Frenkel and for Schottky disorder.

ENERGY OF DISORDER	DEGREE OF DISORDER: n/N^l AT						
	100°C.	200°C.	250°C.	300°C.	350°C.	400°C.	500°C.
1 e.v.	2×10^{-7}	5×10^{-6}	1.5×10^{-5}	4×10^{-5}	9×10^{-5}	2×10^{-4}	6×10^{-4}
For AgCl~0.8 e.v.		7×10^{-5}	2.2×10^{-4}	5.5×10^{-4}	1.5×10^{-3}		
For AgBr~0.8 e.v.		6×10^{-4}	1.8×10^{-4}	4.0×10^{-3}			

For comparison purposes values for the degree of disorder of silver chloride and silver bromide as determined by Koch and Wagner in an indirect way (104) are added. Obviously the approximations (4a, 4b) yield values of reasonable magnitude. A complete calculation of the lattice disorder is not as yet possible (100, 111), mainly because of the difficulty of deriving the disorder energy from lattice data. Mott and Gurney (110) have considerably improved the approximation by taking into account the temperature dependence of the disorder energy and the disturbance of the lattice vibrations by the positions of disorder. They obtained for the number of disordered ions:

$$\text{For Frenkel disorder: } n \cong \sqrt{N^l N^0}/B\gamma_F \exp\left(-\tfrac{1}{2}E_{0_F}/kT\right) \qquad (5a)$$

and

$$\text{For Schottky disorder: } n \cong N^l B\gamma_S \exp\left(-\tfrac{1}{2}E_{0_S}/kT\right) \qquad (5b)$$

where E_{0_F} and E_{0_S} = the respective disorder energies at absolute zero temperature,

B = a factor with a numerical value of about 100,

γ_F and γ_S = factors which in case of a cubic crystal are of the order of 1, and 10–100, respectively.

The improvement introduced by expressions 5a and 5b is such that an approximate calculation of the pre-exponential factor in the temperature function of the ionic conductivity was possible.

There are a few compounds with a special form of Frenkel disorder. They include the high-temperature modifications of silver iodide (141), silver sulfide (121), and silver mercuric iodide Ag_2HgI_4 (101). There the anions possess a normal lattice, whereas the cations are distributed completely at random in the interstices of the anion lattice. The general theory outlined above is, of course, not applicable to these cases of disorder.

C. Mechanism of diffusion and conductivity

The particle motion in crystals giving rise to the establishment of internal equilibrium, or to diffusion, or to ionic conductivity is carried out by the disordered fraction of lattice particles. The possible modes of transport of matter in a crystal of the composition MeX are indicated by figure 7: (a) ions in interstitial positions move through the interstices; (b) ions move from normal lattice positions into the interstices while an equal number of vacant lattice sites are filled with ions leaving interstitial positions; (c) ions move from normal lattice positions into adjacent vacant sites eliminating the original holes and creating new holes. This process represents a migration of holes in the opposite direction.

In modes (b) and (c) there is a continuous exchange of moving particles, making possible a transfer of matter over distances much larger than the mean free path of the moving particles. In solids with Frenkel disorder all three modes of migration may occur simultaneously, whereas in substances with Schottky disorder only mode (c) is possible.
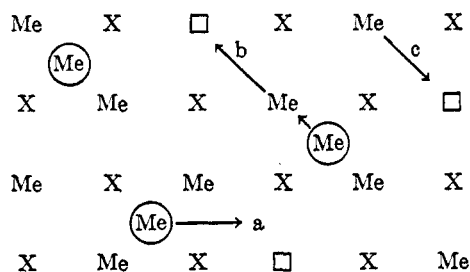

FIG. 7. Possibilities for ionic motion in a binary solid

The movement of ions within the interstices, from lattice positions to positions of disorder, or *vice versa*, requires activation energy. Only that fraction of the total number of disordered ions having the required activation energy (U) can overcome the potential barrier and move from one equilibrium position to the next one. Assuming, for the sake of simplicity, the same U-value for the different modes of migration of a given ion, the number of mobile particles becomes proportional to $\exp\left(-(\tfrac{1}{2}E + U)/kT\right)$; the term $(\tfrac{1}{2}E + U)$ obviously equals the previously mentioned energy term Q appearing in the empirical temperature function of diffusion or conduction. The number of mobile particles given by $\exp\left(-(\tfrac{1}{2}E + U)/kT\right)$ represents an equilibrium value, and processes depending on this number must be found to be reproducible. This holds for the high-temperature branch of ionic conductivity or diffusion which is often well reproducible. The low-temperature branch which is irregular and poorly reproducible must be ascribed to non-equilibrium caused by external conditions. The latter type of migration is discussed below.

A number of attempts have been made to derive theoretically or semiempirically the structure-insensitive part of the temperature function of diffusion or conductivity (11, 22, 98, 100, 139). A fruitful application of the disorder models

has been made by Mott and Gurney (110), who calculated approximately the pre-exponential factor of ionic conductivity. In electric conduction the potential barrier for particle motion is decreased in the direction of the applied external field, and it is increased in the opposite direction. The net result is a drift of ions in the direction of the field which in the case of a binary cubic crystal is given by:

$$\kappa = N \frac{\epsilon^2 a^2}{kT} \nu C B \gamma \exp\left(-[\tfrac{1}{2}E_0 + U_0]/kT\right) \tag{6}$$

where the newly appearing symbols have the following meanings:

N = Avogadro's number,
ϵ = electronic charge,
a = lattice parameter (approximately),
ν = frequency of lattice vibrations,
C = factor with a numerical value of about 10, and
U_0 = activation energy of motion at absolute zero temperature.

Accordingly, the pre-exponential factor of the temperature function of conductivity is temperature dependent, which seems to be compatible with the experimental data available. For a temperature of 600°K. the pre-exponential factors for Frenkel disorder and for Schottky disorder can be estimated to be 3×10^5 and $3 \times 10^6 - 3 \times 10^7$, respectively. Actually, substances with Schottky disorder appear to possess larger pre-exponential factors than substances with Frenkel disorder. For instance, the pre-exponential in the empirical conductivity expression for sodium ions in sodium chloride having Schottky disorder is 1.4×10^6 (135), whereas that of silver ions in silver bromide having probably Frenkel disorder is 2×10^5 (104).

D. Extension of disorder models for non-stoichiometric composition and for electronic disorder

So far crystals of stoichiometric composition have been discussed. In reality the composition of solids is never strictly stoichiometric nor is it rigorously defined. The deviations are usually minute, but may reach substantial proportions in a number of substances (2). Particularly the products of reactions in the solid state must necessarily be of non-stoichiometric and of variable composition. For the diffusion of reactants through the product layers a gradient of the chemical potential is required, i.e., a variable composition of the product layers. The variation of the composition is made possible by a relative excess of the diffusing components which is largest at the phase boundary at which each component enters and which decreases towards the opposite phase boundary.

An excess of a component can be accommodated in two ways: by incorporating particles in a number greater than the number of regular lattice sites available, or in the form of a deficiency of some other constituent whose lattice, then, is incompletely occupied. The models by which the disorder states of stoichio-

metric compounds were described can readily be adapted for non-stoichiometric crystals. This is illustrated in figure 8, again for the binary crystal of over-all composition MeX. In Figure 8a the excess metal is contained in the crystal in interstitial solution, and the metal lattice may or may not still contain holes, which at any rate are less numerous than the interstitial cations. Figure 8b refers to the case where the excess metal occupies regular lattice positions of the anion lattice. As in the case of stoichiometric crystals this type of disorder is energetically improbable because of the strong repulsion of charges of equal sign

```
Me   X   Me   X   □    X              Me   X   Me   X   Me   X
        (Me)        (Me)                     (Me)        (Me)
  X  Me   X  Me   X   Me      or         X  Me   X  Me   X   Me
              (Me)                                  (Me)
Me   X   Me   X   Me   X              Me   X   Me   X   Me   X
        (Me)                                 (Me)
  X  Me   X   □    X   Me               X  Me   X   Me   X   Me

                                 a


Me   X   Me   X   Me   X

  X  Me   Me   Me   X   Me

Me   X   Me   X   Me   Me

  X  Me   Me   Me   X   Me

                 b


Me   X   Me   □    Me   X              Me   X   Me   □    Me   X

  X   □   X   Me   □    Me      or       X  Me   X   Me   □    Me
                                 or
Me   □   Me   X   Me   X              Me   □    Me   X   Me   X

  X  Me   □   Me   □    □               X  Me   □    Me   □    Me

                                 c
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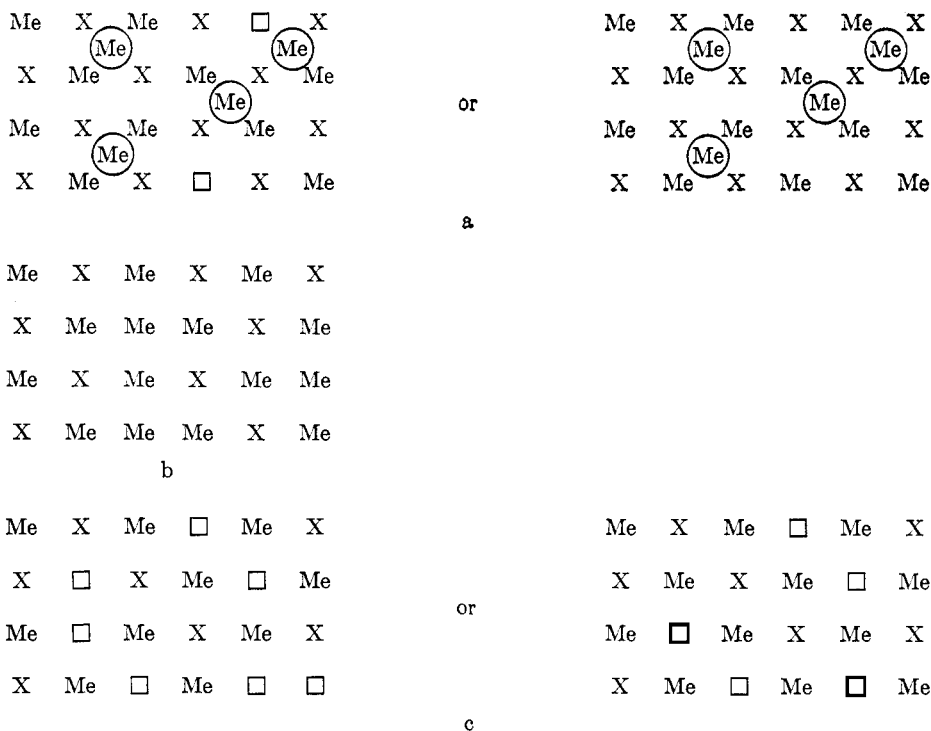
FIG. 8. Disorder models for a binary solid of non-stoichiometric composition

in the lattice. Finally the excess metal may be present as an anion deficiency, which means holes in the anion lattice (figure 8c). In this case the cation lattice need not necessarily be completely occupied, but the number of cation holes, if any, is smaller than the equivalent number of anion holes.

In principle, continuous transition is possible from non-stoichiometric to stoichiometric composition. The disorder models permit a continuous transition from the case of figure 8a to pure Frenkel disorder, or from the case of figure 8c to pure Schottky disorder. Therefore, no discontinuous change of the properties of a solid is observed when the composition undergoes such transition. The only differentiation is that in stoichiometrically composed substances one kind

of disordered particles must be balanced by an equivalent number of another kind of disorder, for instance, interstitial ions by lattice holes of the same sign, whereas such a condition does not apply to non-stoichiometric substances.

Electronic disorder: For the interpretation of electronic conductivity a mechanism can be formulated analogous to that of ionic conductivity based on the assumption of disordered electrons, which may be present as semi-free "interstitial" electrons or as missing electrons, "electron holes" which are equivalent to positive charges.[3] For a stoichiometric substance an equilibrium reaction:

$$\text{Ordered lattice} \rightleftharpoons \text{semi-free electron} + \text{electron hole}$$

may be postulated. Figure 9a shows schematically how such electronic disorder might be realized in the case of cuprous oxide. Interstitial, semi-free electrons are symbolized by (e) and electron holes by $\boxed{\varepsilon}$. Electron holes could

```
Cu+     Cu+     Cu+   Cu++       Cu+       □      Cu+    Cu++
                 (ε)
     O-      O-     O-                O-      O-     O-

Cu+    Cu++    Cu+    Cu+        Cu++    Cu+      □     Cu+
   (ε)
     O-     O-      O-                  O-      O-     O-
                    (ε)
Cu++   Cu+     Cu+    Cu+        Cu+    Cu++    Cu+            □

          a                                  b
```
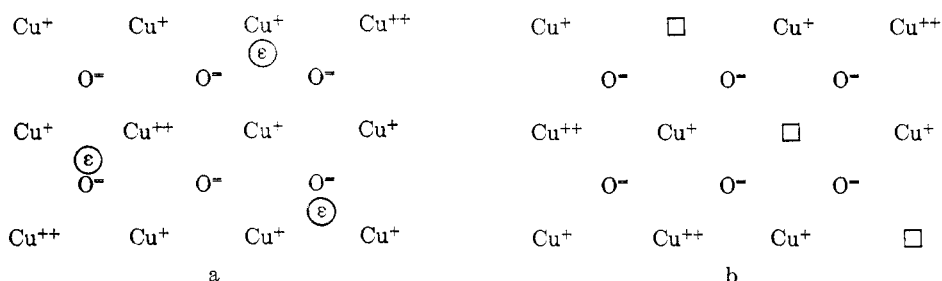
FIG. 9. Disorder model for cuprous oxide (Dünwald and Wagner (18))

be assumed to be present as doubly charged copper ions. Electronic conduction is accomplished by the motion of interstitial electrons, or by electron transfer from neighboring ions to electron holes filling the original holes and creating new holes. It is this hole migration which gives rise to the positive Hall effect. Actually, appreciable electronic disorder of stoichiometric compounds is very rare and would usually be realized only at high temperatures. Since, however, solids are never of entirely stoichiometric composition, electronic disorder must occur at all temperatures in order to neutralize the excess charge introduced into the lattice by the excess, or by the deficiency, of one of the constituent ions. Thus an accompanying electron excess conductivity, or electron hole conductivity, is made possible which is discussed in more detail in a subsequent section. In figure 9b the actual conditions are shown schematically for cuprous oxide. Cuprous oxide contains an excess of oxygen ions in the form of an incompletely occupied lattice of cuprous ions (18). The charges of oxygen ions which are not balanced by cuprous ions are neutralized by the electron holes.

[3] In the present discussion of the electronic states in crystals the band approximation (109, 110, 130) is not introduced. It has been shown, particularly by Wagner (157b, 160), that corpuscular electronic models are satisfactory for the description of reactions in the solid state. For finer details and for an understanding of processes like photoconductivity, photoelectricity, photochemistry, etc., the band approximation would be required.

Owing to this state of affairs the electronic conductivity of cuprous oxide takes place as electron hole migration, and the ionic conductivity as migration of holes of cuprous ions.

The amount of excess oxygen taken up by cuprous oxide is determined by temperature and pressure. At constant temperature the equilibrium between gaseous oxygen and cuprous oxide is expressed by the equation:

$$O_{2(gas.)} + 4Cu^+_{lattice} + 4\epsilon_{lattice} \rightleftharpoons 2Cu_2O_{lattice} + 4\boxed{Cu^+} + 4\boxed{\epsilon}$$
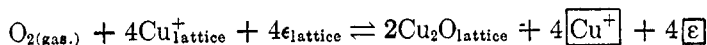
Dünwald and Wagner (18) have shown that the law of mass action can be applied to reactions of this kind:

$$K_T = \frac{(Cu_2O_{lattice})^2 \times (\boxed{Cu^+})^4 \times (\boxed{\epsilon})^4}{p_{O_2} \times (Cu^+_{lattice})^4 \times (\epsilon_{lattice})^4} \tag{7}$$

where p_{O_2} = partial pressure of oxygen. Since the concentrations of ordered cuprous ions, and also of ordered cuprous oxide, and of ordered electrons remain practically unchanged in the reaction, equation 7 reduces to:

$$K'_T = \frac{(\boxed{Cu^+})^4 \times (\boxed{\epsilon})^4}{p_{O_2}} \tag{7a}$$

E. Experimental methods for determining the types of disorder

In cases of gross deviations from the stoichiometric composition the type of disorder can be found directly. The excess constituent is determined analytically. Comparison of the measured density with that calculated from x-ray data shows whether the excess constituent is incorporated interstitially, is present in the form of holes of the other constituent, or has entered by substitution. For instance ferrous oxide, which has the sodium chloride structure, can contain excess oxygen up to the composition $FeO_{1.09}$, this oxygen being present in the form of holes in the ferrous-ion lattice (97).

In substances of closely stoichiometric composition a direct determination of the disorder type appears hardly feasible (129, 163). Indirect and rather complicated methods must be applied, and relatively few compounds have been classified so far. In the case of sodium chloride an analysis of the energy conditions by Jost (100a) showed the presence of Schottky disorder. Jost (99) has further suggested the determination of disorder types by measuring the time interval in which the equilibrium changes from one state to another upon a sudden change of the temperature of the solid. In the case of Frenkel disorder the equilibrium change involves particle motion over atomic distances only, which would take place practically instantaneously; with Schottky disorder, the equilibrium change involves diffusion of lattice particles from the interior to the surface, or vice versa, which should require measurable times when the crystals are not too small. This promising method has not yet been applied.

Wagner (157b) has devised a procedure to detect disorder types, by which conclusions are drawn from the nature of the ionic and electronic conductivities

of a given substance and from their dependence on the composition. Since the variation of the chemical composition cannot be determined directly, the substances are equilibrated with the vapor of a volatile (mostly the negative) constituent, and the dependence of the ionic and electronic conductivities on the vapor pressure is determined. The procedure may be illustrated by two examples:

(1) The substance investigated conducts predominantly electronically (transport number of electrons practically unity) and has in addition a weak cationic conductivity (transport number $\ll 1$), whereas the anions do not contribute to the conduction. With increasing partial pressure of the negative constituent, both the electronic and the ionic conductivity decrease. The substance, therefore, has the following disorder type (figure 10a). Excess cations are incorporated interstitially together with an equivalent amount of interstitial electrons. Current is conducted by these excess particles. The anions, being unable to move, have a perfectly ordered lattice. With increasing partial pressure of the
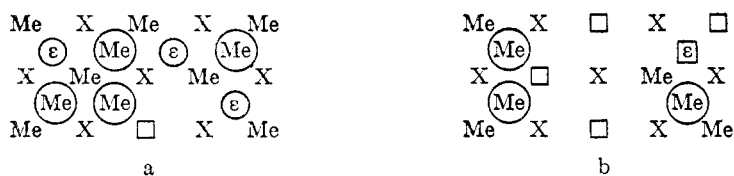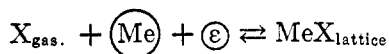

FIG. 10. Illustration of Wagner's method to determine types of disorder

negative component the excess cations and the interstitial electrons are increasingly used up to form a regular lattice owing to the equilibrium:

$$X_{gas.} + \text{(Me)} + \text{(ε)} \rightleftarrows MeX_{lattice}$$

This reaction conforms to the observed pressure dependence of the conductivity. Zinc oxide and cadmium oxide at elevated temperatures are examples of this type of disorder (5).

(2) The substance in question is predominantly an ionic conductor, the cations being the mobile constituent (transport number practically unity). Besides, there is a weak electronic conductivity (transport number $\ll 1$), but no anionic conductivity. The electronic conductivity increases markedly with increasing partial pressure of the non-metallic component, whereas the ionic conductivity is practically pressure-independent. From these facts the following disorder type is derived (figure 10b). The substance possesses Frenkel disorder of the cations containing a slight excess of the non-metallic component which is accommodated in the form of extra cation holes together with the equivalent number of electron holes. Conduction is carried out by the disordered fraction of cations (interstitial cations and cation holes) and by the electron holes. If the substance were of stoichiometric composition, the number of interstitial ions would equal the number of ion holes: $\text{(Me)} \rightleftarrows \boxed{\text{Me}}$ This is also approximately

true in the actual non-stoichiometric compound, since it conducts predominantly ionically; this shows that the deviations from the stoichiometric composition are small compared with the total degree of disorder. Therefore, the ionic conductivity is practically independent of the slight changes of composition resulting from changes of the partial pressure of the negative component. The electronic conductivity, however, increases strongly under these conditions because the number of unbalanced cation holes and electron holes is increased by the reaction:

$$X_{gas.} + \text{(Me)} + \boxed{Me} \rightleftarrows MeX_{lattice} + \boxed{Me} + \boxed{\varepsilon} \quad .$$
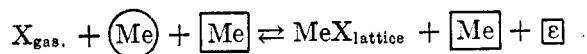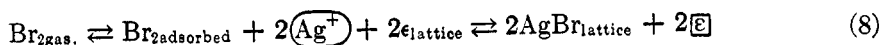
This type of disorder probably occurs in silver chloride and silver bromide and is discussed in a subsequent section.

Using the same reasoning, types of disorder other than those discussed may be identified. It also becomes evident from the examples described that an excess constituent is not necessarily the mobile component in a given compound or the vehicle for diffusion and reaction.

Another method for detecting the type of electronic disorder from the sign of the thermoelectric force of a couple made from the same bulk material but with different conductivity values has been devised by Wagner (159).

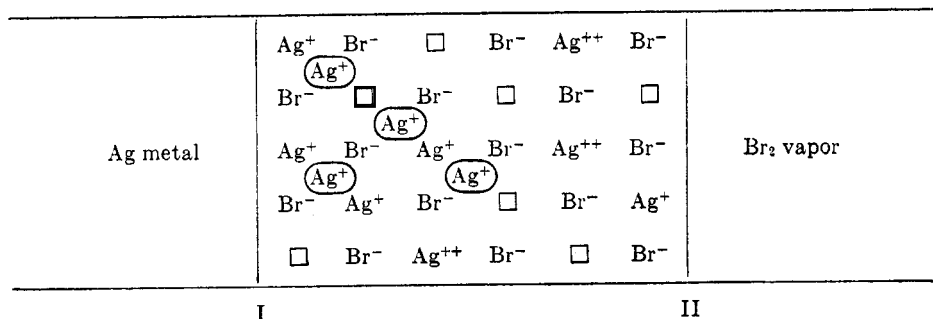### F. Application of the disorder theory to reactions in the solid state

A good example of the applicability of the disorder theory may be found in the tarnishing of silver by chlorine or by bromine. Upon exposure to the halogen vapors, silver becomes covered with a coherent halide layer which steadily increases at elevated temperatures by diffusion of reactants through the layer. It was just stated that silver chloride and bromide show Frenkel disorder of the cations and may take up excess halogen with formation of ordered silver halide and electron holes. From this disorder type the following mechanism of tarnishing is derived. Assume that a crystal of silver bromide (or chloride) is exposed at one of its surfaces to bromine (or chlorine) vapor of such pressure that the crystal is not in equilibrium with the halogen vapor; under these conditions bromine vapor reacts with interstitial silver ions with the formation of fresh layers of silver halide and of electron holes, according to the equation:

$$Br_{2gas.} \rightleftarrows Br_{2adsorbed} + 2\text{(Ag}^+\text{)} + 2\varepsilon_{lattice} \rightleftarrows 2AgBr_{lattice} + 2\boxed{\varepsilon} \tag{8}$$
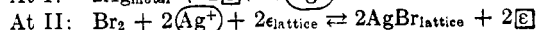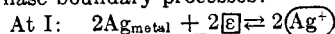
The electron holes may reasonably be assumed to be present in the form of doubly charged silver ions. Interstitial silver ions, being depleted near the exposed surface owing to the reaction, are replaced by interstitial silver ions diffusing from the interior towards the exposed surface, whereas the resulting electron holes diffuse away from the reaction zone into the interior. The reaction proceeds until equilibrium of the entire crystal with halogen vapor at given temperature and pressure is established. Analysis of different sections of the crystal

—if it were feasible—would reveal throughout the crystal a uniformly distributed excess of halide ions as a result of the migration of silver ions and of electron holes.

This state of equilibrium is not established when the face of the halide crystal opposite to the surface exposed to halogen vapor is in contact with metallic silver, as is the case in tarnishing. Then, silver atoms from the metal phase cross the phase boundary and enter the halide phase in the form of interstitial silver ions and of semi-free electrons. The latter are immediately used up in neutralizing the electron holes arriving from the exposed surface layer, whereas the newly incorporated interstitial silver ions diffuse toward the exposed surface, there to continue the reaction. In this way the concentration gradients

Ag metal	Ag^+ Br^- □ Br^- Ag^{++} Br^- (Ag$^+$) Br^- □ Br^- □ Br^- □ (Ag$^+$) Ag^+ Br^- Ag^+ Br^- Ag^{++} Br^- (Ag$^+$) (Ag$^+$) Br^- Ag^+ Br^- □ Br^- Ag^+ □ Br^- Ag^{++} Br^- □ Br^-	Br_2 vapor

I   II

Phase boundary processes:
   At I: $2Ag_{metal} + 2\boxed{\varepsilon} \rightleftarrows 2\widehat{Ag^+}$
   At II: $Br_2 + 2\widehat{Ag^+} + 2\varepsilon_{lattice} \rightleftarrows 2AgBr_{lattice} + 2\boxed{\varepsilon}$
Diffusion processes:
   $\widehat{Ag^+}$ from I to II
   $\boxed{\varepsilon}$ from II to I
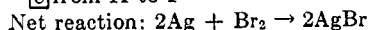Net reaction: $2Ag + Br_2 \rightarrow 2AgBr$

FIG. 11. Schematic mechanism of the reaction between silver and bromine

required for the diffusion of interstitial cations and for the motion of electron holes are continuously maintained so that the tarnishing reaction proceeds. This mechanism is illustrated in figure 11.

The mechanism[4] described is supported by the following quantitative relations developed by Wagner (158). Wagner has treated the tarnishing of metals in a general way. His basic assumption was that in a tarnishing system anions, cations, and electrons may be encountered as moving particles depending on the specific disorder type of the salt formed. In the silver halides migration of anions is not possible, but such might occur in other cases, for instance, in substances with Schottky disorder. The reaction rate is given by the absolute values of the flow (f) of particles through the diffusion layer:

$$dn/dt = |f_{anion}| + |f_{cation}| = |f_{electron}|$$

[4] A fairly direct proof for such a mechanism has recently been given by Bardeen, Brattain, and Shockley (3) for the high-temperature oxidation of copper by means of radioactive copper tracers.

With the condition that space charges are not allowed to be formed in the salt by the motion of charged particles, and with the assumption that the phase boundary processes are so rapid that equilibrium is continuously established at the interfaces between metal and salt and between salt and non-metal, the reaction rate becomes:

$$\frac{\mathrm{d}n}{\mathrm{d}t} = \frac{A}{\xi} \times \frac{300}{96,500} \times \frac{1}{N\epsilon} \times \int_{\text{Interface MeX/X}}^{\text{Interface Me/MeX}} \frac{(t_\text{cation} + t_\text{anion}) \times t_\text{electron}}{\mid z_\text{cation} \mid} \kappa \, \mathrm{d}\mu_\text{Me}$$

$$= \frac{A}{\xi} \times \frac{300}{96,000} \times \frac{1}{N\epsilon} \times \int_{\text{Interface MeX/Me}}^{\text{Interface X/MeX}} \frac{(t_\text{cation} + t_\text{anion}) \times t_\text{electron}}{\mid z_\text{anion} \mid} \kappa \, \mathrm{d}\mu_\text{X} \quad (9a)$$

where the newly appearing symbols are:

$\mathrm{d}n/\mathrm{d}t$ = particle flow (in equivalents per centimeters per second),
A = cross section of diffusion layer (in cm.^{2}),
ξ = thickness of diffusion layer (in centimeters),
z = valence of ion in question, and
μ = chemical potential (per gram-equivalent).

Comparison with the previously given rate equation (1b, page 537), $\mathrm{d}n/\mathrm{d}t = A/\xi \times k$, shows that the rate constant (k) is given by the last three terms of equation 9a.

For an integration of equation 9a it is necessary to derive the relationship between the partial conductivities (i.e., the number of mobile particles) and the chemical potential in the crystal. However, since the deviations from the stoichiometric composition are usually minute, average values for the partial conductivities may be taken:

$$\frac{\mathrm{d}n}{\mathrm{d}t} = \frac{A}{\xi} \times \frac{300}{96,500} \times \frac{1}{N\epsilon} \times \frac{(\bar{t}_\text{cation} + \bar{t}_\text{anion}) \times \bar{t}_\text{electron}}{\mid z_\text{cation} \mid} \bar{\kappa} \big[\mu_\text{Me}^{\text{Me/MeX}} - \mu_\text{Me}^{\text{MeX/X}}\big]$$

$$= \frac{A}{\xi} \times \frac{300}{96,500} \times \frac{1}{N\epsilon} \times \frac{(\bar{t}_\text{cation} + \bar{t}_\text{anion}) \times \bar{t}_\text{electron}}{\mid z_\text{anion} \mid} \bar{\kappa} \big[\mu_\text{X}^{\text{X/MeX}} - \mu_\text{X}^{\text{MeX/Me}}\big] \quad (9b)$$

The bars over the symbols denote the average values. This relation is most conveniently applied when the difference of the chemical potential across the diffusion layer is measured as the E.M.F. (E_0) of a suitable galvanic element, for instance, in the chain

Me/MeX–suitable electrolyte (borax)–X (of the same pressure as in
                                    tarnishing)/suitable electrode (Pt)

The following equation is obtained:

$$\frac{\mathrm{d}n}{\mathrm{d}t} = \frac{A}{\xi} \times \frac{(\bar{t}_\text{cation} + \bar{t}_\text{anion})\bar{t}_\text{electron}}{F} \bar{\kappa} E_0 = \frac{A}{\xi} \times k \quad (9c)$$

where F = Faraday's constant.

Before continuing with the discussion of the tarnishing of silver by chlorine or bromine, the applicability of equation 9c may be shown by the results obtained in other systems, as summarized in table 3.

It should be noted that equations 9 contain an expression for the product of ionic and electronic conductivities of the salt formed; tarnishing, therefore, is not possible when either kind of conductivity is missing in the reaction product. This explains the resistance of aluminum or beryllium or alloys containing aluminum or beryllium to oxidation (72), the ionic conductivity in aluminum oxide and in beryllium oxide being exceedingly small.

It is worth noting that the rate of tarnishing may be employed to determine electronic conductivities which are too small to be measured directly. This is illustrated by the last example of table 3, namely, the tarnishing of silver by iodine. Precise measurements of the conductivity of silver iodide yielded a transport number of unity for the cations within 1 per mille (148); the transport

TABLE 3

Rate of tarnishing reactions

SYSTEM	TEM-PERATURE	RATE CONSTANT (EQUIV./CM.SEC.)		REFERENCES
		Observed	Calculated	
$Ag + S_{liquid} \rightarrow \alpha\text{-}Ag_2S$	220	1.6×10^{-6}	$2\text{-}4 \times 10^{-6}$*	(158)
$Cu + I_2 \rightarrow \gamma\text{-}CuI$	195	3.4×10^{-10}	3.8×10^{-10}	(113)
$Cu + O_2 \rightarrow Cu_2O$	1000	7×10^{-9}	6×10^{-9}	(18)
$Ag + I_2 \rightarrow \alpha\text{-}AgI$	200	1.13×10^{-9}	$t_{electron}: \sim 10^{-4}$	(124)

* Variation due to different values given for the conductivity of Ag_2S.

number of electrons, therefore, must be smaller than 10^{-3}, a figure which is confirmed by the value of about 10^{-4} calculated from the measured rate of tarnishing.

In most tarnishing reactions the mechanism is more complex, so that the rate expressions 9 no longer apply quantitatively, one of the reasons being that the rate of phase boundary processes might contribute to the over-all rate. This seems to be the case in the tarnishing of silver by gaseous sulfur or by hydrogen sulfide (124). Other reasons are mentioned below.

So far the derivation of the tarnishing rate was merely based on the assumption of ions and electrons as the moving particles, without involving any of the specific models of the disorder theory. Wagner (160) has shown with the example of the tarnishing of silver by chlorine or bromine that the integral in equation 9a can be evaluated to a better approximation by making use of the individual models of the disorder theory.

Each volume element of the layer of silver halide can be considered as being in equilibrium with gaseous halogen at a certain pressure (p_X). Assuming ideal behavior, equation 9a changes to:

$$\frac{dn}{dt} = \frac{A}{\xi} \times \frac{300}{96,500} \times \frac{RT}{N\epsilon} \times \int_{\text{Interface MeX/Me}}^{\text{Interface X/MeX}} \frac{(t_{cation} + t_{anion})t_{electron}}{|z_{anion}|} \kappa \, d \ln p_X \qquad (9d)$$

According to the probable disorder model of silver chloride and bromide, the cationic conductivity is practically independent of the halogen pressure (transport number approximately unity), the anionic conductivity is zero, and the dependence of the electronic conductivity on the halogen pressure can be obtained from the equilibrium constant (K) of the phase boundary reaction (equation 8, page 554):

$$K = \frac{(\boxed{\epsilon})^2}{(\widehat{Ag^+})^2 \times p_X} \tag{10}$$

The lattice particles which partake in the reaction do not appear in the equilibrium relation, since their concentrations remain practically constant in the reaction. The concentration of electron holes is:

$$(\boxed{\epsilon}) = K'(\widehat{Ag^+}) \times p_X^{1/2}$$

Because the ionic conductivity is independent of the halogen pressure, the total disorder is much greater than the disorder caused by excess halogen $(\boxed{\epsilon}) \ll (\widehat{Ag^+})$, so that:

$$(\boxed{\epsilon}) \sim K'' \times p_X^{1/2}$$

The electronic conductivity is proportional to the concentration of electron holes:

$$\kappa_\epsilon = C \times p_X^{1/2}$$

respectively:

$$\kappa_\epsilon = \kappa_{\epsilon \text{ at } p_X=1} \times p_X^{1/2}$$

Thus the reaction rate is given by:

$$\frac{dn}{dt} = \frac{A}{\xi} \times \frac{300}{96,500} \times \frac{RT}{N\epsilon} \kappa_{\epsilon \text{ at } p_X=1} \int_{\text{Interface MeX/Me}}^{\text{Interface X/MeX}} p_X^{1/2}\, d \ln p_X$$
$$= \frac{A}{\xi} \times \frac{600}{96,500} \times \frac{RT}{N\epsilon} \kappa_{\epsilon \text{ at } p_X=1} \left(\overset{X/MeX}{p_X^{1/2}} - \overset{MeX/Me}{p_X^{1/2}} \right) \tag{9e}$$

The halogen pressure with which the reaction product is in equilibrium at the contact zone with silver is negligibly small, therefore equation 9e reduces to:

$$\frac{dn}{dt} = \frac{A}{\xi} \times \frac{600}{96,500} \times \frac{RT}{N\epsilon} \kappa_{\epsilon \text{ at } p_X=1} \times p_X^{1/2} = \frac{A}{\xi} \times k \tag{9f}$$

A complete evaluation of equation 9f is not yet possible, since the electronic conductivity of silver chloride and bromide has not yet been measured directly at any halogen pressure. But the validity of equation 9f was demonstrated by

Wagner, who measured the tarnishing rate of silver by bromine and chlorine at various halogen pressures. The results, given in table 4, show satisfactory agreement between the observed ratios of rate constants with the theoretical ratios. It is to be expected that deviations increase with increasing temperatures because equation 9f, based on concentrations rather than on activities, must fail at the greater degrees of disorder which exist at higher temperatures. The total conductivity of silver bromide in equilibrium with bromine of 0.23 atm. at 200°C. was found to be 12 per cent larger than in an atmosphere of pure nitrogen. It is of interest to compare this figure with the value of the electronic conductivity

TABLE 4

*Tarnishing of silver by chlorine and bromine*

Silver and chlorine

TEMPERATURE	$k_{observed} \times 10^{10}$			$\dfrac{k_{0.04}}{k_{1.00}}$	$\dfrac{k_{0.17}}{k_{1.00}}$
	p_{Cl_2} (atm.)			THEORETICAL, 0.2	THEORETICAL, 0.41
	0.04	0.17	1.00		
°C.					
300			0.19		
350	0.16	0.34	0.82	0.20	0.41
400	0.35	0.70	2.06	0.17	0.34

Silver and bromine

TEMPERATURE	$k_{observed} \times 10^{10}$		$\dfrac{k_{0.09}}{k_{0.23}}$	
	p_{Br_2} (atm.)		THEORETICAL, 0.62	
	0.09	0.23		
°C.				
200	0.23	0.38	0.61	
250	0.53	0.91	0.58	
300	0.96	1.78	0.54	
350	1.21	2.32	0.52	
400	1.15	2.27	0.50	

calculated by Wagner from the observed rate constants and from the conductivity values determined by Tubandt and Lorenz (149) in an atmosphere of nitrogen. The data are given in table 5; at a temperature of 200°C. an electronic contribution of 17 per cent to the total conductivity is obtained. All evidence, therefore, points to the disorder type described for silver chloride and bromide.

The tarnishing of metals has been discussed in some detail in order to demonstrate that reactions in the solid state may require the migration of ions and electrons. When reactions take place between ionic compounds and not between metals and non-metals, a movement of ions alone may suffice to make the reaction possible. As an example of such a mechanism we may consider the reaction:

$$MeX_m + Me'X_n \rightarrow MeMe'X_{m+n}$$
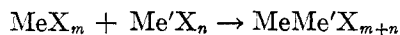
which can proceed by movement of ions of one kind only: namely, the cations moving through the product layer in opposite directions and reacting at the phase boundaries with the further formation of new product. The over-all mechanism is illustrated in figure 12. The mechanism by which the cations actually travel is, of course, given by the specific disorder type of the reaction product. The concentration gradients required for the diffusion are maintained by the continuous flow of cations from the reactants into the product layer.

TABLE 5

Electronic conductivity in silver bromide

TEMPERATURE	$\kappa_{AgBr\ IN\ N_2}$	$\kappa_{ELECTRON\ FROM\ k\ IN\ 0.23\ ATM.\ OF\ Br_2}$	$t_{ELECTRON}$
°C.			
200	5.2×10^{-4}	9.0×10^{-5}	0.17
250	3.2×10^{-3}	2.0×10^{-4}	0.06
300	1.8×10^{-2}	3.5×10^{-4}	0.02
350	$8 \ \ \times 10^{-2}$	4.2×10^{-4}	0.005
400	3.8×10^{-1}	3.8×10^{-4}	0.001

nMe $\rightarrow$ nMe $+ (m + n)$Me'X$_n -$
mMe' $\rightarrow n$MeMe'X$_{m+n}$

MeX$_m$	MeMe'X$_{m+n}$	Me'X$_n$

mMe' $+ (m + n)$MeX$_m - n$Me $\leftarrow m$Me'
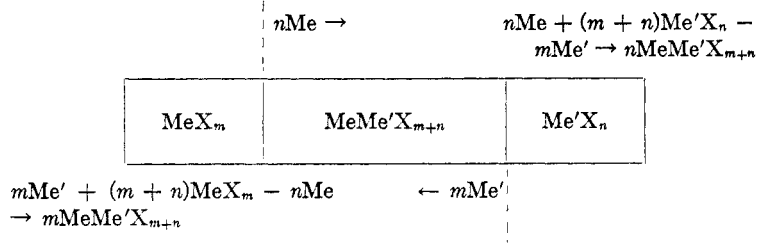$\rightarrow m$MeMe'X$_{m+n}$

FIG. 12. Schematic mechanism of double salt formation from two cationically conducting salts (Wagner (161)).

The reaction rate has been calculated by Wagner (161), comparable to his treatment of tarnishing reactions, by deriving the total flow of particles through the diffusion layer:

$$\frac{dn}{dt} = \frac{A}{\xi} \times \frac{300}{96,500} \times \frac{1}{N\epsilon} \int_{\text{Interface MeMe'X}_{m+n}/\text{Me'X}_n}^{\text{Interface MeX}_m/\text{MeMe'X}_{m+n}} \frac{t_{Me} \times t_{Me'}}{t_{Me} + t_{Me'}} \kappa \frac{(Me) + (Me')}{(Me')} d\mu_{MeX_m} \qquad (11a)$$

where the concentrations of cations (( )) in the diffusion layer are expressed in equivalents per cm.[3] In nearly stoichiometric compounds average values may again be taken for the partial conductivities and the concentrations. Expressing the free energy of formation by the E.M.F. (E_0) measured with a suitable galvanic chain, equation 11a becomes:

$$\frac{dn}{dt} = \frac{A}{\xi} \times \frac{\bar{t}_{Me} \times \bar{t}_{Me'}}{\bar{t}_{Me} + \bar{t}_{Me'}} \times \frac{\bar{\kappa}}{F} \times \frac{(\overline{Me}) + (\overline{Me'})}{(\overline{Me'})} \times E_0 = \frac{A}{\xi} \times k \qquad (11b)$$

Equation 11b has been verified by Koch and Wagner (103) for the reaction:

$$2AgI + HgI_2 \rightarrow Ag_2HgI_4$$
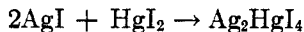
which takes place by diffusion of silver ions and mercuric ions. The observed rate constant of 2.1×10^{-11} equiv./cm. $\times$ sec. agreed well with the calculated value of 1.9×10^{-11}.

Similarly, the rates of other reactions between ionically conducting compounds may be calculated.

VII. STRUCTURE-SENSITIVE REACTIONS

A. Limitations of the applicability of the disorder theory

While the basic principle that diffusion and reaction in the solid state are performed by the disordered fraction of lattice particles in the system apparently applies to all cases, the quantitative applicability of the disorder theory is limited, and experimental proofs have so far been established only for the reactions given in the preceding section. One or more of the following reasons may be responsible for this state of affairs.

(1) *Influence of phase boundary processes:* Theoretically the influence of phase boundary processes might always be eliminated by proper selection of the dimensions of the reacting systems. In many practical and technically important cases, however, where the diffusion is sluggish the reactions have to be carried out with fine powder mixes in which the diffusion layers are very thin, so that phase boundary processes may become important or even predominant.

(2) *Structure-sensitive factors:* It has been mentioned previously that the reproducible branch of the temperature function of conduction or diffusion frequently changes rather abruptly at some lower temperature into a poorly reproducible structure-sensitive branch (figure 5). The reason for this is that solids can easily change into thermodynamically unstable states in which the solids are imperfect and are in an abnormally energy-rich (active) state. Various kinds of imperfections may occur. They may, for example, be identical with the thermodynamic lattice disorder, but be present in a number larger than is required by the equilibrium. Or the imperfections may occur in the form of unstable modifications or unstable solid solutions, expanded or deformed lattices, holes or cracks of atomic dimensions, irregular displacement of lattice particles, crystallite sizes of colloidal dimensions, amorphous state. Despite their instability, such imperfections may exist for long periods of time, indeed sometimes indefinitely when the particle motion leading to internal equilibrium (thermal aging) is completely frozen. The probability of a removal of the faulty state by rearrangement increases exponentially with increasing temperature; therefore the transition from the migration of lattice imperfections to the thermodynamic lattice diffusion may frequently be observed as a sharp break in the temperature function of diffusion or conductivity. But on the other hand it is possible that the imperfect state of the solid persists at all temperatures to such an extent that the thermodynamic diffusion remains obscured.

The presence of an excess of one or more constituents in the products of reactions in the solid state may further increase and also stabilize the lattice imperfections.

The slope of the low-temperature branch of conduction and diffusion is smaller than the slope of the high-temperature branch, since for the motion of lattice imperfections along cracks, through holes, and at any internal surface activation energy alone is required, whereas the energy requirements of the high-temperature motion include both activation energy and disorder energy ($\frac{1}{2}E + U$, cf. page 548). The lattice imperfections are thus able to move with a mechanism somewhat similar to zeolithic diffusion, but their thermal energy is not sufficient for an interaction with ordered lattice particles which would gradually eliminate the imperfections. The concentration, and probably also the qualitative nature, of the imperfections are sensitive to external and frequently uncontrolled conditions and may vary from specimen to specimen. For this reason the low-temperature motion is poorly reproducible.
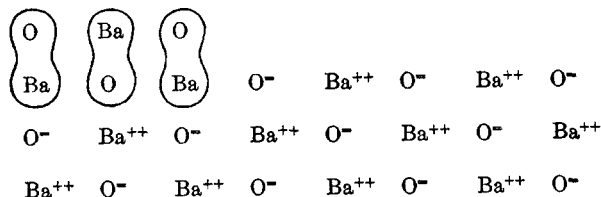

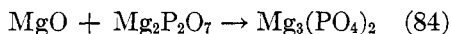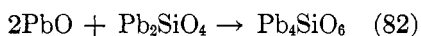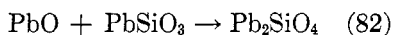FIG. 13. Schematic picture of formation of surface molecules on barium oxide (De Boer (9))

Imperfect solids may be formed in other ways than by reactions in the solid state, for instance, by precipitation from solution, by rapid quenching of melts, by preparation at relatively low temperatures (decomposition), by electrochemical processes, by incorporation of small amounts of impurities, and by mechanical treatment.

(3) *Uncharged particles as vehicle of reaction:* Many reactions have been observed to occur with great intensity at temperatures at which the reacting system does not possess an ionic conductivity adequate to explain the mechanism as a motion of ions. A detailed mechanism of the motion of uncharged particles on the basis of the general disorder theory has not yet been developed and certainly would be very difficult to prove experimentally. There is also some likelihood that the motion of uncharged particles does not proceed by a thermodynamically determined mechanism, but rather by diffusion through lattice imperfections, since neutral atoms or neutral combination of atoms may be too large to diffuse interstitially or through lattice holes of the reaction product.

Mobile uncharged particles may be formed in solids whose building stones are ions, but which do not exhibit ionic conductivity. It appears possible that the ionic character of such solids shifts towards atomic bonds at elevated temperatures (68) at which reactions take place. The formation of atoms or atom-molecules is at any rate favored at surfaces and other lattice disturbances in ionic lattices because of the asymmetry of charges there (cf. 9). Figure 13 illustrates

the trend towards molecule formation at a surface of barium oxide. According to a hypothesis by Hedvall (53) a state of anomalous polarization which may be produced locally in the interior by thermal fluctuations of the lattice vibrations may be transmitted from neighbor to neighbor until it reaches an internal or external surface at which it materializes as a reactive surface molecule.

In some reactions it has been shown experimentally that the migrating particles consist of entire groups. It was found early that the reaction $MgO + ZnWO_4 \rightarrow ZnO + MgWO_4$ appeared to proceed by migration of WO_3 groups (87). Recently, careful experiments by Jagitsch have shown that the reactions:

$$PbO + PbSiO_3 \rightarrow Pb_2SiO_4 \quad (82)$$

$$2PbO + Pb_2SiO_4 \rightarrow Pb_4SiO_6 \quad (82)$$

$$MgO + Mg_2P_2O_7 \rightarrow Mg_3(PO_4)_2 \quad (84)$$

are performed by migration of PbO and P_2O_5, respectively. At the present time this migration of uncharged particles is only sketchily understood.

Since lattice imperfections can always be present in newly formed phases, the concentration of mobile particles in the reaction products may be greater than required thermodynamically, and high reaction rates are therefore to be expected. This was actually the case in several systems investigated by Wagner (162), in which the observed rates were several times larger than the calculated ones. It is indeed rather surprising that the kinetics of some reacting systems are controlled by the thermodynamic disorder. This is possible because most of the reaction products in these systems possess a completely disordered cation lattice. Since the degree of thermodynamic cation disorder is 100 per cent, no appreciable contribution of additional lattice imperfections to the reaction rate is observed. The bulk of reactions in the solid state, however, has to be characterized empirically.

B. Characterization of lattice imperfections

In order to gain an insight into the reaction possibilities of a solid it is desirable to ascertain in as great detail as possible the particular states in which the solid can be obtained. The characterization is empirical and is obtained by combining the results of measurements of various properties of the substance in question. Some properties frequently investigated for this purpose are the following:

(1) The structural or textural state

(a) *Lattice expansion:* Occasionally a solid may occur with an anomalously expanded lattice instead of with normal dimensions. This is illustrated in table 6 on tricalcium silicate prepared by the solid-phase reaction (89): $CaCO_3 + Ca_2SiO_4 \rightarrow Ca_3SiO_5 + CO_2$. The stretching of the lattice is evident by comparing the angles of reflection of powder photographs with those of the normal compound.

(b) *Average particle displacement and partially amorphous state:* More frequently occurring than the stretching of the entire lattice are irregular disloca-

tions of lattice particles without change of the over-all parameters. Part of the compound may even be present in the form of x-ray amorphous aggregates. In table 7 these conditions are shown for ZnO and α-Fe$_2$O$_3$ prepared by dehydration of their hydroxides (33, 34, 36). The average distortion is greatest at the lowest temperature of preparation; at higher temperatures, the thermal motion causes the lattice particles to approach their normal positions. The crystallites

TABLE 6

Expanded lattice of fresh reaction product

STATE OF Ca$_2$SiO$_4$	REFLECTION ANGLES OF POWDER PHOTOGRAPHS						
Normal lattice....................	15.10	16.50	17.50	21.00	26.30	28.50	31.60
Freshly formed lattice............	14.90	16.40	17.40	20.90	26.10	28.40	31.40

TABLE 7

Effect of thermal treatment on lattice imperfections

HEAT TREATMENT			AVERAGE SIZE OF GRAIN (ZnO) OR CRYSTALLITE (Fe$_2$O$_3$)		AVERAGE PARTICLE DISPLACEMENT	FRACTION OF AMORPHOUS SUBSTANCE	MOLAR HEAT OF SOLUTION CORRECTED FOR WATER CONTENT
Temperature	Time	Water content					
°C.	hours	per cent	Å.		Å.	per cent	kg.-cal.
Vacuum heated			ZnO				
100	13	3.07	8,000		0.12	10–20	23.6
82	33	3.14	4– 8,000		0.11	10–20	23.0
300	5	0.66	8–12,000		0.08	0	22.45
Heated in N$_2$							
600	6	0.03	8–16,000		0	0	22.3
			α-Fe$_2$O$_3$				
Vacuum heated			Hexagonal axes				
			a	c			
240	1	1.68	181	100	0.21	0	54.0
Heated in air							
300	1	1.45	191	103	0.18	0	51.5
410	1	0.89	191	151	0.11	0	50.7
600	1	0.36	204	180	0	0	49.3

grow, whilst the lattice distortion and the content of amorphous compound diminish.

(c) *True and apparent density, grain size, porosity, and specific surface:* The degree of dispersion, the surface development, and the details of the surface structure can be ascertained by numerous direct or indirect methods which have been thoroughly discussed in recent reviews (cf. 1, 42, 168), and to these, therefore, no further space is devoted in this article. An interesting method may be noted, introduced by O. Hahn (40, 41), in which a radioactive tracer is incorporated within the solid generating emanation. From measurements of the amount of emanation escaping from the solid, valuable information on the textural state may be obtained (30, 80, 81, 167).

2. The energy state

(a) *Energy content:* The excess energy content caused by the occurrence of non-equilibrium imperfections or by a large surface development has been determined from measurements of the heat of solution. Examples of such measurements are included in table 7. In the case of α-Fe_2O_3 specimens with an excess energy up to 10 per cent of the normal value are reported, an excess which may influence the reactivity tremendously.

(b) *Magnetic susceptibility:* In general the different lattice states of a substance do not appear to alter the magnetic susceptibility, in particular not that of diamagnetic substances (169). In some instances, however, a dependence of the susceptibility on lattice imperfections has been reported (*cf.* 131); for instance, ZnO prepared by decomposition of the oxalate showed after heating for 6 hr. at 300°C. a susceptibility of -0.29×10^{-6}, whereas after heating for 6 hr. at 550°C. the susceptibility was -0.43×10^{-6} (76).

A distinct correlation between the magnetic state and catalytic surface activity has been observed with ferromagnetic substances (58, 59). In at least one case it was established that both the activation energy and the pre-exponential factor in the Arrhenius equation of the reaction rate constant are greater in the paramagnetic state than in the ferromagnetic state (16).

(c) *Surface activity:* It is well known that the surface activity of a solid, as expressed by sorptive and catalytic action, varies with different states of a compound and may, therefore, be employed for a characterization. Considerable work from this standpoint has been carried out and has recently been surveyed by Fricke (32) and by Hüttig (75).

The dependence of the surface activity on the energy state of the lattice is further indicated by observations of the discontinuous change of the rate of dissolution of seignette salt at the electrical Curie point (65), and of the change in the adsorption equilibrium of phenolphthalein on cadmium sulfide upon irradiation (55).

C. Significance of lattice state for reactivity

The increase in chemical potential due to structural or textural disturbances exerts an accelerating influence on reactions of solids which may be illustrated by a few examples.

The difference in reactivity of a compound when it is rich in internal defects or when it is in a comparatively perfect state is brought out by figure 14, which refers to the reaction between calcium oxide and ferric oxide (66). Two different types of ferric oxide were prepared by decomposition of ferric sulfate and ferric oxalate, the former being heavily defective. Despite its greater grain size, the "sulfate" oxide reacts much faster with calcium oxide than does the "oxalate" oxide. At higher temperatures the differences in activity are eliminated.

An instance of differential activity produced by special pretreatment of one of the reacting components is found in the formation of calcium silicate from calcium oxide and silica (figure 15) (54). The silica had been preheated in the presence of gases which cannot interact chemically with silica in the usual sense,

such as oxygen, sulfur dioxide, and sulfur trioxide, but which nevertheless affect the lattice state by penetration or dissolution. Quartz preheated in sulfur trioxide was least active; heating in air increased the reactivity and still more did heating in oxygen or sulfur dioxide.

A reacting component has a greater reactivity when it is formed in contact with its partner. This is shown by figure 16 for the formation of magnesium chromite from ferrous chromite and magnesia or magnesium carbonate (64). Magnesium carbonate decomposes at the temperatures of the reaction and is more reactive than is magnesium oxide.
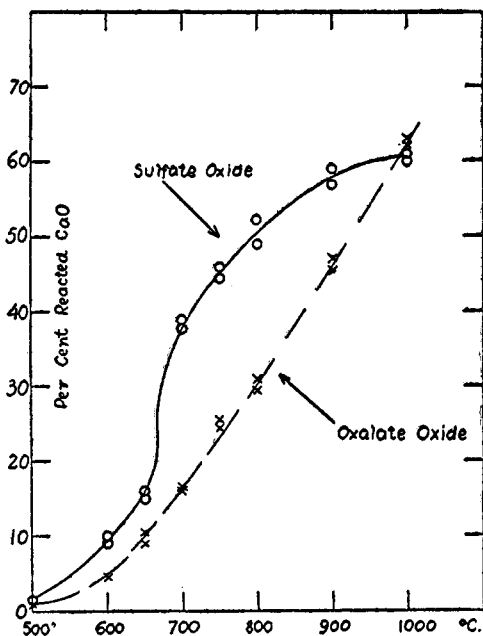
FIG. 14. Significance of parent substance on reactivity of ferric oxide (Hedvall and Sandberg (66)).

An especially active state exists during the course of a crystallographic transformation, because the bonds between lattice particles are weakened or even broken during the transition. While the transition proceeds, the crystal has a maximum activity in reactions with surrounding phases (Hedvall's rule). Figure 17 shows the relative rate maximum for the reaction between barium oxide and silver iodide, yielding barium iodide and silver oxide at the transition point of silver iodide (145°C.) (57). This relative rate maximum is, of course, observed only when the time of reaction is of the same order of magnitude as the time within which the transition occurs. Correspondingly, the "reaction temperatures" of exchange reactions involving oxygen-containing acid groups, which were found constant and independent of the nature of the salt-component (cf. table 2), are lowered to approximately the transformation temperature

provided this temperature lies below the normal reaction temperature of the basic oxide. Examples are given in table 8 (60c).

D. Qualitative picture of reaction mechanism

By means of such criteria, an interpretation of the various stages of a reaction between solids may be arrived at. However, unless a general validity can be proved experimentally, the mechanism observed and the nature of the products formed apply only to the specific reaction conditions and may vary with the
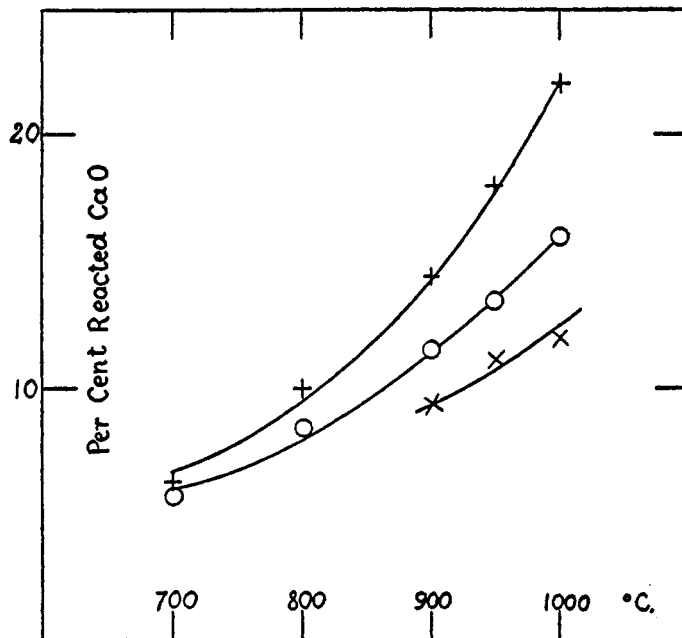

FIG. 15. Dependence of reactivity of silica on pretreatment (Hedvall *et al.* (54))

state of the reactants, composition of the reaction mixture, reaction temperature and time, and with other conditions.

Figure 18 shows the sequence of compound formation with an equimolar mixture of silica and calcium oxide at 1200°C. (94). In this mixture the metasilicate is the only stable product; nevertheless the orthosilicate and tricalcium disilicate are formed first and become gradually converted into the metasilicate.

The dependence of the nature of the product on the composition of the reaction mixture and on the reaction temperature under conditions otherwise identical is illustrated by figure 19, which exhibits the reaction between barium carbonate and ferric oxide (25). In this system the following products have so far been identified: $BaO \cdot 2Fe_2O_3$; $BaO \cdot 6Fe_2O_3$; $Ba_3Fe_8O_{21}$. The regions of existence for the last two compounds are given by the contour lines of figure 19, the numbers of the contour lines indicating the relative proportions to which the compounds were formed under the existing conditions.
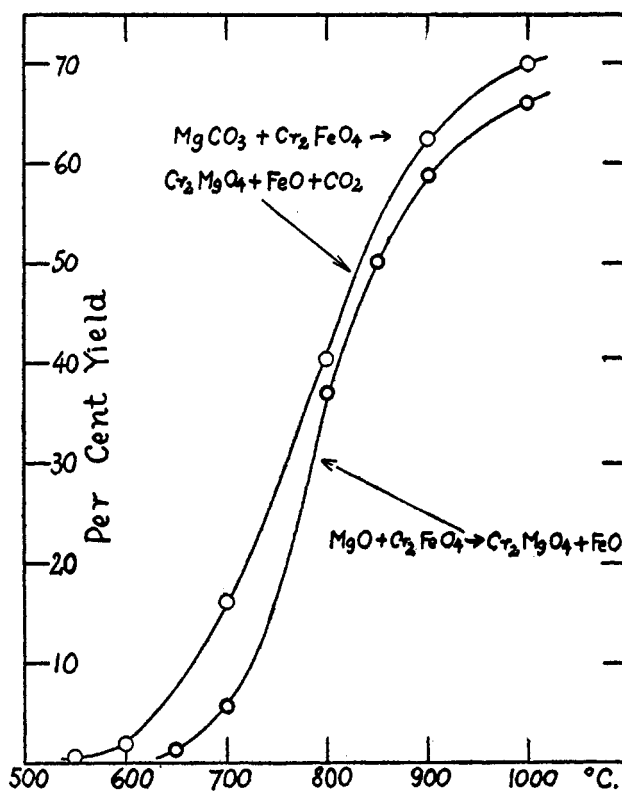
FIG. 16. Increased reactivity of nascent reactant (Hedvall and Ny (64))
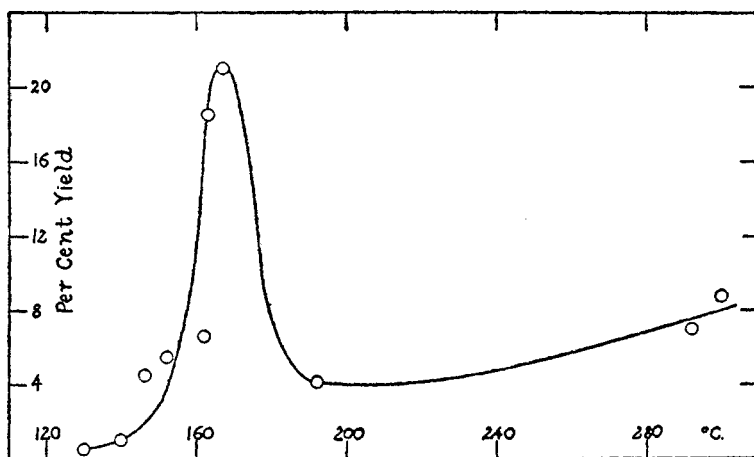

FIG. 17. Relative reactivity maximum of silver iodide at crystallographic transition point (Hedvall et al. (57)).

With other systems, however, it was found that, under all conditions studied, a given primary product was formed which subsequently may have been converted into more stable compounds, depending on the composition of the reaction

TABLE 8

Induction of reaction by crystallographic transition

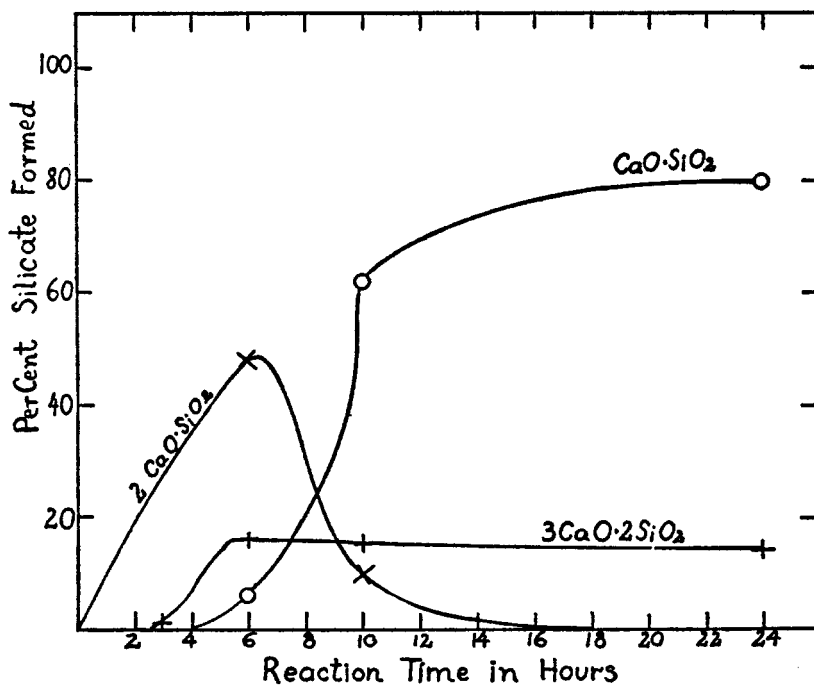| BASIC OXIDE	REACTANT			
	AgNO₃		Ag₂SO₄	
	Transition	Reaction	Transition	Reaction
	°C.	°C.	°C.	°C.
BaO................		170		342
SrO................	160	172	411	422
CaO................		164		422

FIG. 18. Sequence of compound formation in system CaO + SiO₂ (Jander and Hoffmann (94)).

mixture and on the temperature. In table 9 are listed the primary products for a number of reactions as compiled by Jander (88). This behavior can be utilized for the preparation of pure compounds by solid-phase reaction from the appropriate reaction mixture, which might not be possible of preparation by fusion.

The preferred initial formation of a given compound appears to depend on the relation of the diffusion rate to the rate of nucleation. For instance, it was found that in equimolar mixtures of calcium oxide and silica the orthosilicate stage was passed more quickly the finer the grain size of the powder mixture (70), and in equimolar mixtures of magnesium oxide and silica the orthosilicate stage was completely omitted when the mixture was prepared in "molecular dispersion" by precipitation (146).

In simple additive reactions yielding only one product (A + B → AB), a certain pattern for the various stages of the reaction has been brought out by numerous investigations which seems to hold in principle either for different temperatures and constant reaction times or for constant temperature and different times. As illustration of this pattern, the formation of zinc iron spinel
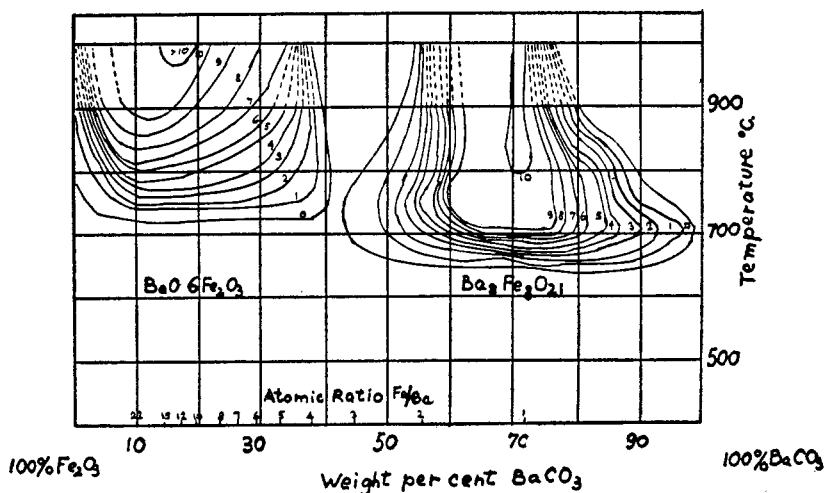

FIG. 19. Formation of $BaO \cdot 6Fe_2O_3$ and $Ba_3Fe_8O_{21}$ in system $BaCO_3 + Fe_2O_3$ (Erchak, Fankuchen, and Ward (26)).

from zinc oxide and ferric oxide may be described. Powder mixtures of zinc oxide and iron oxide were kept for given times at given temperatures, and the changes in certain physical and chemical properties were determined. Some of these measurements are shown in figure 20, in which are plotted the densities of the reacting system (77), the catalytic action on the oxidation of carbon monoxide by oxygen at 250°C. (78), the intensity of one characteristic powder diffraction line for each component (93), the average particle displacement in the freshly formed spinel lattice, and the molar heat of solution (35). At each temperature of observation, a certain step in the reaction has occurred. The intermediate stages are pictured schematically in figure 21, and the same sequence of steps may be expected to take place at other temperatures and times.

(1) *Period of primary interaction:* Even upon mixing the reactants (designated in the following as A and B) at ordinary temperature, an interaction is observed unless the substances have been thoroughly aged. This interaction may appre-

ciably increase the number of adsorbing centers at the surface. Figure 22 shows that the adsorption of lead nitrate is increased about sixfold upon mixing the oxides (138). The increase in adsorptive power is apparently connected with the chemical affinity between zinc oxide and ferric oxide; it is not observed, for instance, in mixtures of ferric oxide and chromic oxide.

Slight heating of the reaction mixture, however, causes the surfaces of the reactants to become more closely attached to each other, with the result that

TABLE 9

Primary products of reactions in the solid state

REACTING SYSTEM	COMPOUNDS FORMED BY SOLIDIFICATION OF MELTS (MOLAR RATIO)	PRIMARY COMPOUND FORMED BY REACTION IN SOLID STATE
$MgO–Al_2O_3$	1:1	$MgO \cdot Al_2O_3$
$CaO–Al_2O_3$	3:1; 5:3; 1:1; 3:5	$CaO \cdot Al_2O_3$
$BaO–Al_2O_3$	3:1; 2:1; 1:1	$BaO \cdot Al_2O_3$
$CaO–Fe_2O_3$	2:1; 1:1	$CaO \cdot Fe_2O_3$
$MgO–TiO_2$	2:1; 1:1; 1:2*	$MgO \cdot TiO_2$*
$MgO–SiO_2$	2:1; 1:1	$2MgO \cdot SiO_2$
$CaO–SiO_2$	3:1; 2:1; 3:2; 1:1	$2CaO \cdot SiO_2$
$SrO–SiO_2$	2:1; 1:1	$2SrO \cdot SiO_2$
$BaO–SiO_2$	2:1; 1:1; 2:3; 1:2	$2BaO \cdot SiO_2$
$PbO–MoO_3$	2:1; 1:1	$PbO \cdot MoO_3$
$PbO–WO_3$	2:1; 1:1	$PbO \cdot WO_3$
$CaO–MoO_3$		$CaO \cdot MoO_3$
$CaO–WO_3$	Constitution diagram incompletely known; identified 1:1	$CaO \cdot WO_3$
$BaO–MoO_3$		$BaO \cdot MoO_3$
$BaO–WO_3$		$BaO \cdot WO_3$
$MeO–UO_3$ (Me = Mg, Ca, Sr, Ba, Zn, Cd, Hg, Pb, Ni)	Constitution diagram incompletely known; identified 1:1; 1:2	$MeO \cdot UO_3$

* According to reference 91.

the specific surface, as determined by the amount of organic dyes adsorbed, decreases, and the density increases.

(2) *Formation of surface molecules (period of first activation):* At relatively low temperature, some surface particles of A or B become mobile enough to leave their original positions and to become attached to the surface of the other component. A surface molecule of AB is thus formed, without any diffusion into the other lattice and without the formation of the normal AB structure. The surface film so formed is not coherent and is loosely bound. In this stage the reaction mixture shows a relative maximum of the catalytic action. There is apparently not only a maximum yield of the catalytic reaction, but also a maximum of the number of active centers on the catalyst surface. This phe-
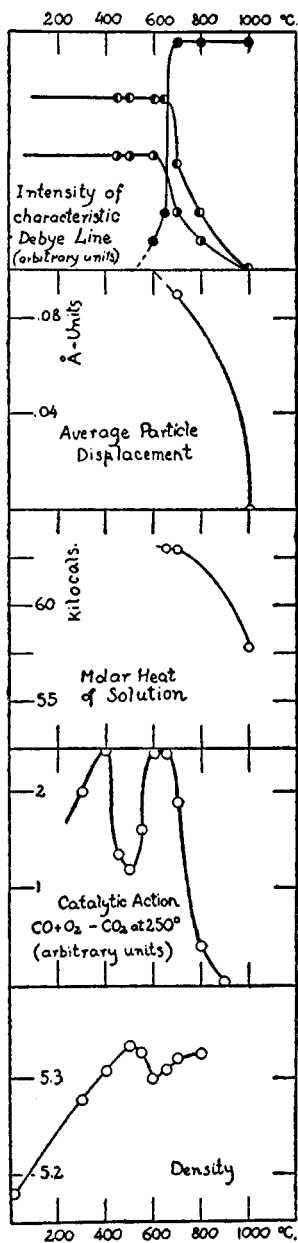
FIG. 20. Properties of reaction system ZnO + Fe₂O₃

nomenon has been observed during the formation of zinc aluminum spinel from zinc oxide and alumina (90).

(3) *Completion of molecular surface film (period of first deactivation):* By increasing the reaction temperature somewhat more, a complete layer of AB

molecules is formed by surface diffusion of the mobile component. The film is relatively stable and the molecular forces between the AB molecules are
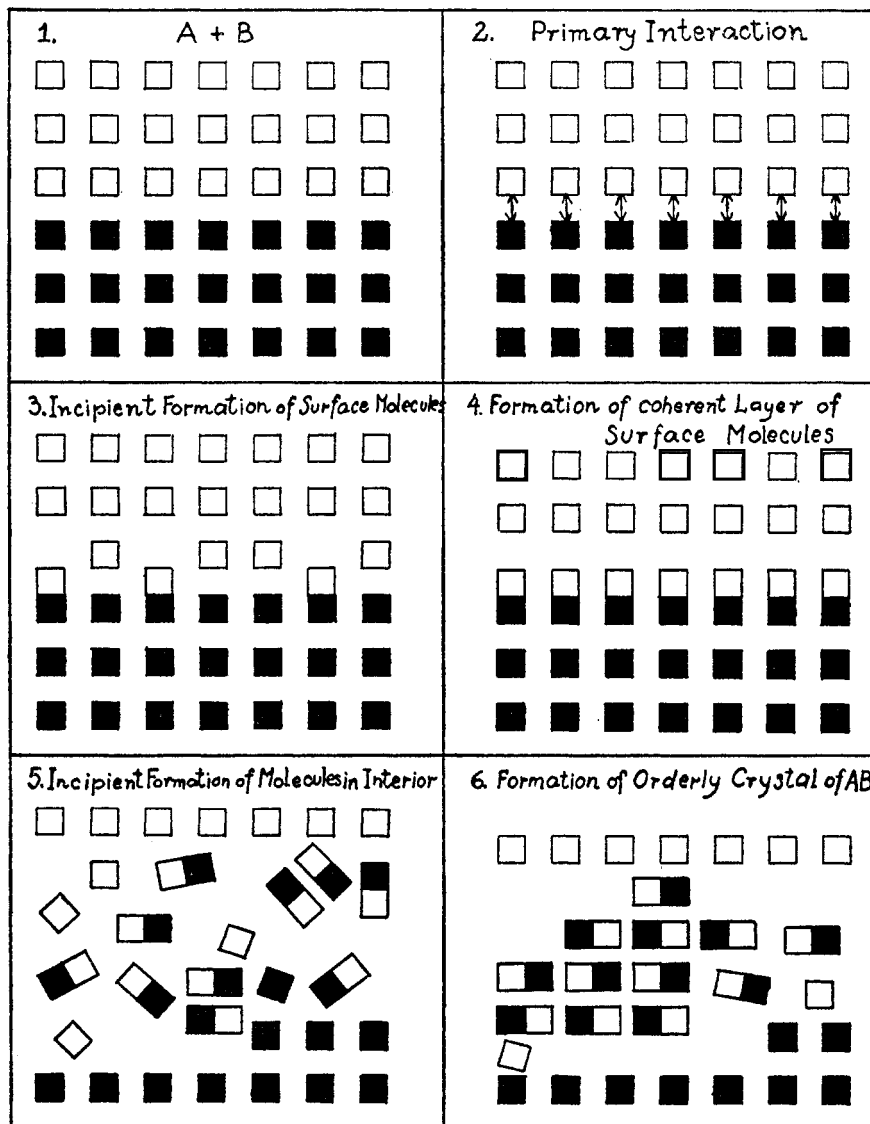

FIG. 21. Intermediate stages of spinel formation (ZnO + Fe$_2$O$_3$)

balanced. The catalytic activity, therefore, is markedly lower, while the density of the reaction mixture has increased further.

So far, the interaction between A and B has involved only a motion of surface particles possessing excess energy. These stages are, therefore, especially

structure-sensitive, and the interaction between A and B is not detectable by chemical analysis or by x-ray measurements.

(4) *Formation of molecules of AB by diffusion into the interior (period of second activation):* At still higher temperatures particles may diffuse through the first layer of the reaction product into the interior of the other lattice. An unstoichiometric layer of AB in A or B is formed, the boundary of which moves gradually
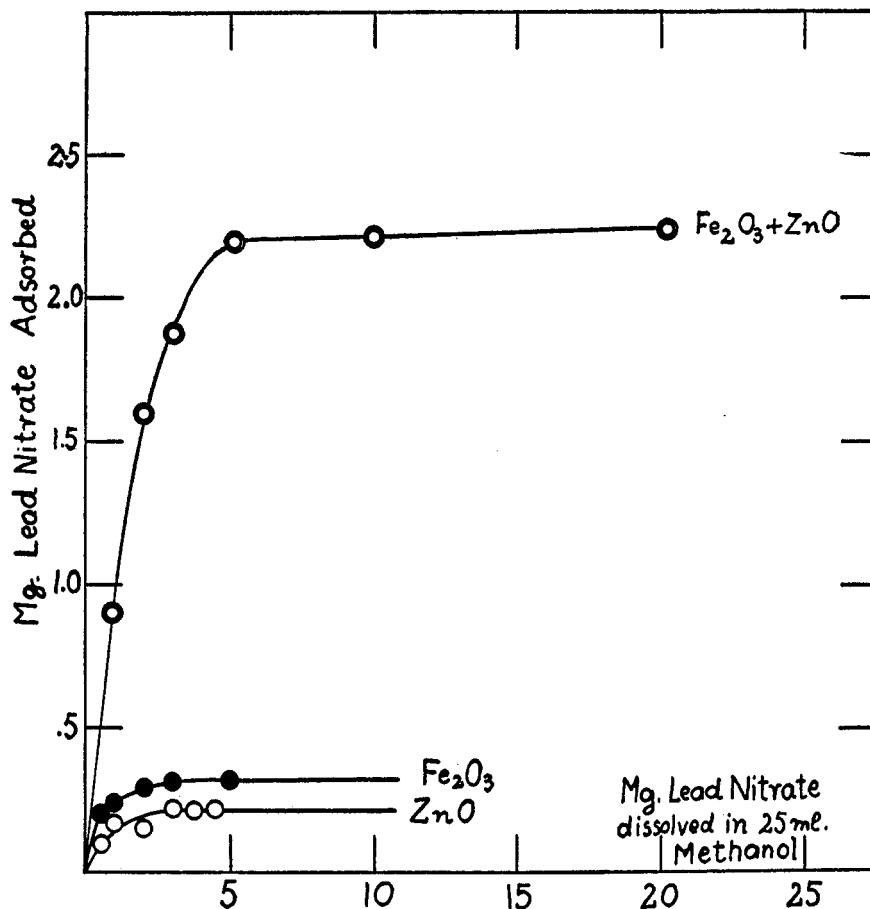

FIG. 22. Increased adsorption of mixture of ZnO and Fe₂O₃ (Starke (138))

into A or B. Initially the reaction product is formed in a very imperfect state; the catalytic activity, therefore, is again at a maximum, whereas the diffuse state of the reaction product causes a minimum of the density. It is worth noting that in the zinc iron spinel formation the reaction product immediately shows the correct, though very imperfect, crystal structure. The initial, practically amorphous layer can be only a few molecules thick, since the diffraction lines of the spinel appear as soon as the intensities of the lines of zinc oxide and

iron oxide begin to decrease. In this stage, however, some extra lines were observed indicating a possible deviation from the normal spinel structure (93). The spinel lines were quite sharp from the beginning, indicating that the number of nuclei of the new phase must be very small (35). Initially, the size of the spinel crystals must be very small, and therefore the diffraction lines should have considerable breadth; however such lines are not observed, so the number of crystals must be small and can be detected only after a certain growth. In other cases, however, appreciable amounts of amorphous reaction product may be formed in this period if the crystallization is sluggish.

(5) *Formation of orderly crystallized* AB (*period of second deactivation*): The freshly formed product has an imperfect lattice, as indicated by the average particle displacement and by the anomalously large heat of solution. The distorted state makes possible a relatively rapid diffusion through the layer of reaction product, that is, a relatively high reaction rate. With rising temperature the lattice imperfections disappear and increasing amounts of normal reaction products are formed; the catalytic activity, therefore, decreases and the density again increases. As the reaction product approaches perfection, the diffusion, i.e., the reaction rate, slows down. Nevertheless the reaction may be practically completed before the product has become free from all non-thermodynamic disorder, and no stage of the reaction may be governed by the thermodynamic disorder.

It should be emphasized that the picture just described is based on circumstantial evidence. Despite this limitation it seems possible for the present to reach a qualitative understanding of solid-phase reactions by charting the changes of a sufficient variety of properties of the reacting system, even when more than one reaction product is formed from the reacting components. An interesting beginning in this direction has recently been made by Ward and coworkers with the system $BaCO_3$–Fe_2O_3 (25, 26).

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