CHANGES IN CRYSTAL STRUCTURE AND THEIR INFLUENCE ON THE REACTIVITY AND CATALYTIC EFFECT OF SOLIDS[1]

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Without a certain measure of mobility in the structural elements of matter, no measurable reaction between reactive particles can take place. In the gaseous and liquid states this condition is fulfilled at common temperatures, and the mobility of the particles, due to the relative independence of their individual spheres of attraction, forms the very foundation for the peculiarities of these states in several physical and chemical aspects. In most cases it is comparatively simple to define the qualities of particles with mobility of their own in these states of matter. It is possible to use a statistical kinetic treatment, and this, combined with the fact that the experimental work of observing the processes occurring is not especially complicated, makes it natural that the equilibria and velocities of reactions in gases and liquids were investigated first. As for crystals, even their regular external boundaries show that in them we must take into account an inner cohesion caused by fields of force, which of course makes it more difficult to attack them whether by mechanical or by chemical means. An overestimate of these difficulties led to the generalization *corpora non agunt nisi fluida*, which slogan prevented for a remarkably long period interest in the chemistry of the solid state.

A large number of technical processes furnish clear evidence that under favorable conditions solid bodies also possess no small reactivity, provided the other component of the reaction is fluid or gaseous. Such cases are, for instance, the combustion of solid carbon and the reduction of oxide ores; furthermore, such processes as solution or thermal decomposition no doubt indicate reactive solid phases. A typical case of this kind is the combustion of the diamond in oxygen; no one will here imagine either a fused or a gaseous carbon phase as an intermediate reactive body.

At the end of the last century a series of instances were published in which solid phases exclusively were in reaction. I mention the well-known experiments of Roberts-Austen, Violle, Marsden, and several others, who

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showed the diffusibility of metals and carbon at relatively low temperatures (23). The contemporaneous discovery of solid solutions and their theoretical treatment by van't Hoff (64) incited increased interest in the chemistry of solid bodies.

At the beginning of this century the rapidly growing work on metallographic problems gave still further impulse in this direction; the pioneer researches of Tammann and his coworkers in particular added many instances of processes in or between entirely solid metal phases.

Omitting the researches of Spring on the reaction between sodium carbonate and barium sulfate, which have been criticized by Tammann (57), the experiments of Cobb (6) on the reaction of calcium carbonate with silicon dioxide may be considered as the first study of a real chemical reaction between non-metallic solid substances; Endell (12) shows foresight when he points out the importance of the study of such reactions for the development of the chemistry of silicate technology.

ADDITIVE REACTIONS; EFFECT OF PARTICLE SIZE, ORIGIN OF PREPARATIONS, THEIR HEAT TREATMENT AND CRYSTALLOGRAPHIC CONDITION

When heating cobaltous oxide with a great number of other metallic oxides, it was found that solid solutions of CoO–MgO, CoO–MnO, and CoO–ZnO, as well as the compounds $CoO \cdot Al_2O_3$, $2CoO \cdot SnO_2$, $CoO \cdot Cr_2O_3$, and others could form with considerable velocity and completeness even without a flux and at as low a temperature as 800°C. (19).

These researches were probably the first systematic work on non-metallic additive reactions in the solid state, and showed beyond a doubt that there existed at relatively low temperatures a diffusibility in and between non-metallic solids which at that time had not been expected. The results then obtained by purely chemical means have lately been confirmed through x-ray analyses by Natta and Passerini (53) and by Holgersson (44). During this early work it already was noticed that the previous treatment or origin of the reagents and also their particle size, of course, influenced the intensity or the yield of the reaction. In a series of related researches it was shown both that increased particle size delayed the reaction or necessitated a higher reaction temperature in order to reach a certain yield, and that different primary materials or maximum temperatures in the preparation of the reagents could give products in which various crystal surfaces with different reactivities dominated (22). Modifications of different crystal symmetry are probably very seldom obtained when preparing a substance in different ways (24), but the different atomic spacing in the surfaces has a certain importance. For really different modifications of one substance it was possible to show that those which were richer in energy were the most reactive (21).

This became evident in reactions between silica of different modifications and oxides or carbonates of the alkaline earth metals. The reaction of silica with the oxides is already noticeable after some minutes of heating to about 950°C., and silica can displace carbon dioxide in the carbonates mentioned, below their dissociation temperature at normal pressure. About ten years later Dyckerhoff (10) made a closer examination of the reaction products, viz., the possibility of the formation of different silicates of calcium oxide. The cement and ceramic industries have, as might be expected, also shown a great interest in these and similar reactions. It must be remembered that even though the yield of a reaction between solids has no direct importance, these reactions are nevertheless very important indirectly, because through them the substance changes its composition and therefore also its fusion and sintering temperatures (27).

NON-ADDITIVE REACTIONS

The aforesaid reactions were either of the additive type or else, as in the case of silica acting on carbonates, were reactions corresponding to the displacement in fluid phases of a volatile substance by a less volatile one, although the comparison is rather far-fetched with respect to volatility. These latter reactions, however, were the immediate cause of attempts to transfer the "acid anhydride group" in a salt to an added oxide with a stronger affinity for the anhydride, without the anhydride in the interim leaving the solid state. The first experiment in this direction was the heating of barium oxide with calcium carbonate, and the time–temperature curve showed clearly that the reaction had taken the expected turn and resulted in the formation of barium carbonate and calcium oxide. From about 350°C. the curve showed a strong and rather rapid rise of temperature corresponding to a considerable heat of reaction; the horizontal line a little above 900°C. corresponding to the thermal dissociation of calcium carbonate had almost entirely disappeared and was instead found at a higher temperature corresponding to the decomposition of barium carbonate. The reaction was therefore as follows: $BaO + CaCO_3 = BaCO_3 + CaO$. Continued investigations soon showed that this reaction was only an instance of a general but formerly unnoticed type:

$$M^{I}O + M^{II}AO_n = M^{II}O + M^{I}AO_n + Q$$

or

$$M^{I}O + M^{II}X = M^{I}X + M^{II}O + Q$$

where $M^{I}O$ and $M^{II}O$ are two oxides, AO_n and X are the negative parts of a salt of an oxy acid or other acid, respectively (i.e., CO_3, SO_4, SiO_3, Cl, S, and so on), and Q is the liberated heat. At first the investigation of

these processes was limited to determinations of those temperatures at which the course of the reaction could be observed on a heating curve, i.e., by observing the temperatures where the reactions set in with greater intensity. Even in the first experiments some peculiarities had been observed which showed that the study of these "reaction temperatures"—which, of course, are not definite temperature constants in the usual sense, but only indicate the more or less marked increase in yield of a reaction which has started at considerably lower temperature—could indeed also lead to an explanation of the mechanism of these formerly unknown reactions. Reliable and consistent results were obtained (32) after developing the method of using heating curves for the study of reactions and of other changes in non-metallic systems. This method had previously been developed for the investigation of thermal dissociations (20) and of exothermic addition reactions involving small evolution of heat. It was now applied to these new reactions, which often were accompanied by a strong evolution of heat (37). Table 1 presents the above-mentioned characteristics of these reactions.

The completeness of these reactions, which happen in a few seconds or less, is attested by the fact that the reactions

$$BaO + CuSO_4 = BaSO_4 + CuO$$
$$SrO + CuSO_4 = SrSO_4 + CuO$$
$$CaO + CuSO_4 = CaSO_4 + CuO$$
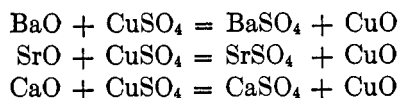
gave yields of 87.8, 88.2, and 61.1 per cent, respectively, without regrinding, when an equimolecular reaction mixture was used.

The table shows strikingly that the reaction temperatures are divided into three groups which are well separated. Barium oxide reacts at the lowest and calcium oxide at the highest temperature, as would be expected from their general chemical, thermal, and crystallographic character and as also agrees with the results obtained by Biltz (3). It is also remarkable that the difference between the reaction temperatures of the individual salts of the same kind, e.g., sulfates, is so very small. The influence of the metallic ion is noticeable but not very strong. Nor does the anion of the salt seem to influence the reaction temperature to any great extent *in the salts of the oxy acids used here*, for phosphates, carbonates, silicates, and sulfates react with the same oxide within narrow temperature limits.

It was pointed out in the very first publications that there could be no question of anything but reactions between solids (33). For the reactions with barium oxide, but only for this one oxide, the question might be asked, whether the fusion of the hydroxide or its eutectic could possibly act as an intermediate in the reaction. Balarew (2) put this forward as

TABLE 1

Reactions of salts with oxides

SALT	REACTION WITH BARIUM OXIDE		REACTION WITH STRONTIUM OXIDE		REACTION WITH CALCIUM OXIDE	
	Reaction temperature	Reaction product	Reaction temperature	Reaction product	Reaction temperature	Reaction product
	degrees C.		*degrees C.*		*degrees C.*	
Carbonates						
$SrCO_3$	398 ± 5	$BaCO_3 + SrO$	—	—	—	—
$CaCO_3$	344 ± 2	$BaCO_3 + CaO$	464 ± 4	$SrCO_3 + CaO$	—	—
$MgCO_3$	345 ± 5	$BaCO_3 + MgO$	456 ± 4	$SrCO_3 + MgO$	523 ± 1	$CaCO_3 + MgO$
Sulfates						
$SrSO_4$	372 ± 2	$BaSO_4 + SrO$	—	—	—	—
$CaSO_4$	370 ± 6	$BaSO_4 + CaO$	451 ± 5	$SrSO_4 + CaO$	—	—
$MgSO_4$	369 ± 1	$BaSO_4 + MgO$	441 ± 3	$SrSO_4 + MgO$	ca. 540	$CaSO_4 + MgO$
$ZnSO_4$	341 ± 5	$BaSO_4 + ZnO$	424 ± 3	$SrSO_4 + ZnO$	520 ± 6	$CaSO_4 + ZnO$
$CuSO_4$	346 ± 0	$BaSO_4 + CuO$	418 ± 7	$SrSO_4 + CuO$	516 ± 5	$CaSO_4 + CuO$
$CoSO_4$	328 ± 14	$BaSO_4 + CoO$	431 ± 1	$SrSO_4 + CoO$	533 ± 4	$CaSO_4 + CoO$
Phosphates						
$Sr_3(PO_4)_2$	ca. 350	$Ba_3(PO_4)_2 + SrO$	—	—	—	—
$Ca_3(PO_4)_2$	340 ± 5	$Ba_3(PO_4)_2 + CaO$	ca. 450	$Sr_3(PO_4)_2 + CaO$	—	—
$Pb_3(PO_4)_2$	335 ± 3	$Ba_3(PO_4)_2 + PbO$	453 ± 1	$Sr_3(PO_4)_2 + PbO$	524 ± 3	$Ca_3(PO_4)_2 + PbO$
$Co_3(PO_4)_2$	354 ± 3	$Ba_3(PO_4)_2 + CoO$	466 ± 2	$Sr_3(PO_4)_2 + CoO$	ca. 520	$Ca_3(PO_4)_2 + CoO$
$CrPO_4$	342 ± 1	$Ba_3(PO_4)_2 + Cr_2O_3$	464 ± 4	$Sr_3(PO_4)_2 + Cr_2O_3$	517 ± 4	$Ca_3(PO_4)_2 + Cr_2O_3$
Ag_3PO_4	306 ± 1	$Ba_3(PO_4)_2 + Ag + O_2$	461 ± 1	$Sr_3(PO_4)_2 + Ag + O_2$	516 ± 4	$Ca_3(PO_4)_2 + Ag + O_2$
Silicates						
$CaSiO_3$ (Wollastonite)	354 ± 1	$BaSiO_3 + CaO$	454 ± 1	$SrSiO_3 + CaO$	—	—
$MgSiO_3$ (Enstatite)	354 ± 1	$BaSiO_3 + MgO$	453 ± 1	$SrSiO_3 + MgO$	562 ± 1	$CaSiO_3 + MgO$
$MnSiO_3$ (Rhodonite)	355 ± 0	$BaSiO_3 + MnO$	467 ± 2	$SrSiO_3 + MnO$	563 ± 1	$CaSiO_3 + MnO$
Al_2SiO_6 (Sillimanite)	357 ± 1	$BaSiO_3 + Al_2O_3$	429 ± 2	$SrSiO_3 + Al_2O_3$	532 ± 1	$CaSiO_3 + Al_2O_3$

his opinion, based on some experiments in which the necessary care for obtaining reliable temperature measurements had in no way been exercised. Without mentioning here all the evidence for the defects in Balarew's working arrangements and the consequent errors in his conclusions, which were immediately pointed out by several authors (36, 47, 59), it may be mentioned here that barium hydroxide reacts less intensively and often at higher temperatures than does barium oxide. This might be expected because the attraction of the oxide to the acid constituent of the salt indubitably depends on the same affinity for it as for acid anhydrides in the gaseous state, e.g., carbon dioxide; and this attraction ought to have a certain connection with the degree of unsaturation of the attracted substance.

Nor, as was also shown, could a gaseous anhydride, such as carbon dioxide or sulfur trioxide, be the cause of the reaction. A comparison between the reaction temperatures and the vapor tension showed the impossibility of this. Indeed in several cases it was possible to determine the relatively unimportant rôle that was played by the gaseous phase at the higher temperatures which were a consequence of the exothermic reactions in the solid state (41). In such systems as mixtures containing silicates or some phosphates (cf. table 1), it is of course just as nonsensical to talk about a reactive gaseous phase as it is to try to find a liquid phase in the reaction mixtures containing strontium oxide or calcium oxide, where strontium hydroxide or calcium hydroxide decompose without previous fusion. It may be added that only on the assumption that these reactions occur in the solid state can they be explained from a common point of view. This ought *a priori* to have given less appeal to the search for other explanations, conceivable in some special case, perhaps, but not generally possible. Continued research in this field has not been promoted by these opinions in any way other than by compelling us to increase the accuracy of our experiments still more. They have been mentioned in their historical relation, because at the very start they were questions that craved an answer.

Of course, a fusion when caused by impurities or by the reaching of a fusion point or a eutectic temperature through the heat of reaction may in some cases increase the yield of the reaction. According to what has been said before, this can also occur through the liberation of a gas during the heating. This increase in yield which can be caused by direct reaction with a liquid or gaseous phase can also be caused by these phases in destroying or decreasing the thickness of the diffusion layer of the reaction product, thus producing new contact surfaces. At first considerable attention was given to these phenomena (35). Recently we have published the results of experiments intended to determine what quantities of a fusion caused by

added impurities were necessary to increase the yield of the reaction to any appreciable extent. The quantities so found considerably exceeded the amount of impurities which can be expected in preparations of high quality (28). It was also found that it is not necessary that the appearance of fusion should always help a certain reaction (26). In reaction mixtures such that low fusing compounds or eutectics are formed on account of the original composition, or through the reaction, it is always easy to determine from which temperature the influence of a liquid phase has to be taken into consideration; for even in cases where the eutectic or polyeutectic conditions are not known it is always possible to find when fusion starts by determining the electrical conductivity (26, 60).

No doubt the results from a new field of science should be met with healthy doubt, but it is interesting to see how in certain quarters there was an extreme unwillingness to believe in the possibility of reactions between solid substances only. Although not mentioned in the chemical literature by anybody except by Balarew it was commonly thought that something like a catalytic action of extremely thin liquid surface films was required, and even that those small traces of gas which correspond to the extremely small vapor tensions of substances at temperatures several hundred degrees below their dissociation point, could cause this reactivity. Everybody who has worked with these reactions and has studied their high velocity must consider the possibility of a gaseous phase as the reaction medium as practically impossible. Certainly this is so at the beginning and in the first stages of the reaction, even when only sulfates or carbonates are considered and when no consideration is given to the absolutely impossible case of a gaseous phase in the reaction with the silicates. Tammann, who together with his coworkers gave a number of instances of this type some years ago, has found one such reaction which is particularly favorable, viz., $PbO + CuSO_4 = PbSO_4 + CuO$ at about 500°C., where the sulfate has a vapor tension of 37 mm. Even here the gas phase had very little influence on the reaction yield (59).

It seems that these attempts to make a gaseous phase act as a medium for the reaction were based on a conception which was borrowed from the well-known hypothesis put forward by Nernst after Debray's researches on the thermal equilibria of solids, and which was intended to make possible the application of the Guldberg-Waage law to heterogeneous equilibria. But it has been overlooked that this conception is entirely incapable of explaining rapid reactions. Against the assumption of the existence of thin active liquid layers it is of course not sufficient to show that absolutely dry materials have been used. It must rather be shown *that the courses of the reactions are connected with and vary with factors which evidently are characteristic of the solid state.* Such a working plan was, indeed, used

from the very beginning of this investigation. It had to be, because any other attempt to use *one* explanation for these reactions was found to be impossible. The results obtained have also fully proved the truth of the hypothesis that *every interference with the crystal lattice which sufficiently decreases its interior stability,* increases the mobility of the units of the lattice, and therefore more or less stimulates the crystal to react with another crystal.

THE INFLUENCE OF WEAKENING THE COHESION OF THE LATTICE

1. Heating and deformation

Factors which widen or weaken the crystal lattice are: above all, heating; changes in the symmetry of the lattice; and the introduction of foreign substances into it. Already in our first publication (31) it was assumed that the ionic lattice which salts of some oxy acids contain at low temperatures could partly change when heated to an anhydride lattice, hence in a sulfate to metallic oxide and sulfur trioxide, the extent of change being dependent on the temperature. This should be an intermediate state between the low temperature ionic lattice and thermal dissociation at high temperature. Such a change must be regarded as extremely probable, considering what precedes the thermal decomposition of the lattice, and has lately been verified by measurements of the conductivity and diffusion made by W. Jander (49). X-ray photographs at different temperatures, which should give interesting results in this case, do not, as far as I know, exist.

In subsequent publications on non-additive reactions, the fact that barium oxide reacts at the lowest temperature, being followed by strontium oxide, calcium oxide, and so on (25), was explained on the basis of the above-mentioned working hypothesis. It need only be mentioned here that it seems quite natural that barium oxide, having a stronger affinity to acid anhydrides, ought to cause a reaction at a lower temperature and a correspondingly lesser deformation of the ion group (e.g. SO_4) or a smaller number of free or loose anhydride complexes per unit volume than do strontium oxide or calcium oxide. It was also shown that the very small influence of the metallic ion of the salt of an oxy acid on the reaction temperature was in good agreement with the great independence of anions of this kind revealed by Schäfer and Schubert (56) through measuring their infra-red absorption. Further confirmation of this conception was given by Fajans (13), working on the anions of oxy acids, who showed that these anions are very non-susceptible to the deforming action of cations. Taking into account the dominating importance of the atoms of oxygen in building up the crystal lattices of the silicates and oxides, as

pointed out by W. L. Bragg, it seems possible that this is also responsible for the independence of the anions in the salts of oxy acids (5). Such a connection might possibly be able to explain the similar reactivity of salts of different oxy acids.

On further study of reactions of this or similar types, diagrams were made showing the reaction yields at different temperatures but with constant time of reaction. It was then found, as expected, that a slow reaction started at considerably lower temperature than the rapid progress indicated by the heating curves. Curves were obtained of the same type as those for other properties which depend on the inner mobility of the lattice, such as conductivity, vapor tension, etc. With properly selected reaction periods these curves showed discontinuities at the same temperatures as do the corresponding heating curves. It was consequently evident that the thermal expansion of the lattice, by increasing kinetic energy of the particles and their consequent momentary opportunities for moving outside their mutual fields of attraction, had caused the expected increase in reactivity.

If the crystal lattice of the salt in question contains ions which can exert deforming or polarizing action, it can be expected that the above-mentioned purely thermal expansion at lower or higher temperatures ought to be changed by deformation effects. In an ionic lattice a partial de-ionizing at various points in the lattice could thus occur to a certain extent. Such changes of course imply disturbances in the homogeneity of the field of force in the ideal lattice, which cause a local weakening and facilitate mobility of the particles or transport of matter. These consequences of the action of the ions on one another should be observed most readily in ionic lattices with strongly deforming cations (small and of non-rare gas type) and easily deformable anions (as already stated, not anions of oxy acids but halide ions, and especially the larger ones).

One must consider the incomplete extent to which it is possible to survey the phenomena of deformation, the thermal data of the crystal lattices (lattice energy, heat of formation) and the degree of ionization as functions of the temperature, and must also keep in mind the probable difference in action between ions and uncharged particles as reaction partners, not only for different crystal combinations but also for the same mixture at different temperatures. Hence it cannot be expected that heating curves alone should give any *quantitative* information even of a relative nature about the inner condition of the lattices or about the character of the reacting particles. Even the simple and approximate heating-curve method, however, gives *qualitative* results which are evidence for the correctness of the above-mentioned opinions. Thus the sulfates whose SO_4 groups, according to Fajans, are very resistant to the action of deforming cations,

form a reaction system much more homogeneous in reaction temperatures than the halides, the ions of which are much more sensitive to deforming influences (table 2).

In the case of the sulfates the temperatures are grouped, as would be expected from lattice energy data and from the possibility of deformation of the sulfate ion, which, as aforesaid, is very small and therefore *a priori* makes a stronger influen 'e of the cation of the salt improbable. On the other hand, within the halide group there is strong individuality in the reacting salt, caused by a closer influence of the ions on one another.

TABLE 2

Reaction temperatures of sulfates and halides

SALT	REACTION TEMPERATURE WITH		
	BaO	SrO	CaO
	degrees C.	degrees C.	degrees C.
$SrSO_4$....................................	372	—	—
$CaSO_4$....................................	370	451	—
$MgSO_4$....................................	369	441	540
$ZnSO_4$....................................	341	424	520
$CoSO_4$....................................	328	431	533
$CuSO_4$....................................	346	418	516
Ag_2SO_4....................................	342	At transition point of Ag_2SO_4 (Cf. table 4)	
$CuCl$..	270		
$CuBr$..	312		
CuI...	340		
$PbCl_2$.......................................	273		
$PbBr_2$.......................................	248		
PbI_2..	ca. 200		
$NiCl_2$.......................................	312		
$NiBr_2$.......................................	272		

2. Foreign constituents in the crystal lattice

Very similar to this kind of weakening of the cohesion of the lattice *is the exchange of a small part of one or more of the units of the crystal lattice*, as is the case in isomorphous mixed crystals or in solid solutions. Differences in the radii of atoms or ions, or differences in electrical charge between the original and the foreign particles of the lattice can, when the proportion between them is favorable, cause internal changes which should produce a change in reactivity compared with that of the fully uniform crystal. Several investigations of such cases have proved the correctness of this hypothesis (26). Table 3 shows this for reactions between barium oxide and in one case pure lead chloride; in another case a mixed crystal of lead

chloride + 0.1 molar per cent of barium chloride. The foreign substance in this case being the same as the compound formed in the reaction, no complicated eutectics or reactions are obtained, and the possibility of a fusion is entirely eliminated at the temperature in question. According to Goldschmidt (18), the ionic radius of Ba^{++} is 1.43×10^{-8} cm., and of Pb^{++} 1.32×10^{-8} cm.

Continued investigations of the same kind with this and several other reaction mixtures have shown that these additions also influence such characteristics as surface formation, particle size, velocity of solution, and catalytic effect. It has also been ascertained that there exist limits for the admixture of foreign substances beyond which a contrary effect obtains, and that this is often the case at rather low percentages. These results are

TABLE 3

Reactions in pure and impure crystals

REACTION TEMPERATURE	PER CENT OF $PbCl_2$ REACTED ACCORDING TO EQUATION $BaO + PbCl_2 = BaCl_2 + PbO$	
	With pure $PbCl_2$	With $PbCl_2$ + 0.1 molar per cent of $BaCl_2$
degrees C.		
228.0	10.6	15.5
235.0	11.6	22.0
248.0	16.8	24.0
258.0	23.9	27.0
269.0	27.5	30.1
279.0	29.2	33.5
289.0	34.3	43.3
292.0	39.8	49.5
298.0	45.0	55.4

of interest in connection with the production and use of mixed catalyzers and their activity. Investigations by the writer and his coworkers have shown that even very small admixtures (0.1 molar per cent) of manganous oxide, magnesium oxide, or nickelous oxide in cobaltous oxide appreciably decrease the size of the cobaltous oxide crystals and increase their tendency to oxidize to Co_3O_4. Similar results with regard to particle size have also been obtained by Wyckoff (66) and by Edner and Schönfeld (11).

3. Different kinds of structural changes

Nearly ten years ago the first instance of a method of greatly increasing the reactivity of the solid state was published, a method which, because of its manifold applications and practical importance, seems to be of general interest (34). Starting from the same working hypothesis as before, the

supposition was made that *a crystal which at a given temperature sustains a change of phase in the form of a polymorphous transition or in any other form, ought to show, during this process when the particles have an abnormally great freedom of movement, an abnormally great reactivity when mixed with another reactive substance, whether solid, liquid, or gaseous.* Continued and still pending researches in this field have shown that the reactivity is a very sensitive indicator of every kind of such change of phase. A great number of crystallographic changes, both between different systems and classes and in the so-called secondary structure, including the fusion of a substance, magnetic transitions without change of lattice structure, and changes of phase of alloys (e.g., when a solid solution at a given temperature separates into two), all provide instances of such an effect. In what follows some of the results obtained in this field will be mentioned.

The characteristic fact has already been mentioned that when basic oxides react with salts of oxy acids the oxides react with a group of salts

TABLE 4

Reactivity and transition temperatures

OXIDE	WITH SILVER NITRATE		WITH SILVER SULFATE	
	Reaction temperature	Transition point	Reaction temperature	Transition point
	degrees C.	*degrees C.*	*degrees C.*	*degrees C.*
BaO............................	170 ± 1		342 ± 4	
SrO............................	172 ± 3	160	422 ± 1	411
CaO............................	164 ± 5		422 ± 5	

within a temperature range which is characteristic for the oxide, so that barium oxide reacts at about 350°C., strontium oxide about 100°C. higher, and calcium oxide at about 70°C. still higher. Yet the reactions in mixtures of each of these oxides with silver nitrate or silver sulfate, which have transition points at 160°C. and 411°C., respectively, showed the reaction temperatures listed in table 4.

For silver nitrate the transition point from rhombic to rhombohedral lies at 160°C. The reaction temperatures of all three oxides lie immediately above this temperature, when the change has reached the necessary velocity. The influence of the corresponding change in silver sulfate is entirely analogous, although, of course, it cannot affect the reaction temperature with barium oxide, which normally lies lower than the transition point. Similar behavior has been proved for the reaction between barium oxide and silver iodide, according to the equation $BaO + 2AgI = BaI_2 + 2Ag + \frac{1}{2}O_2$. In this case heating curves as well as yield curves have been

obtained. Figure 1 shows that the yield reaches a maximum where the change from hexagonal to regular shape is rapid, and therefore decreases with increasing temperatures (39).

To this class of changes belong also those changes of phase of silicon dioxide which have a considerable influence on its reactivity. According to Fenner (14) there occurs at 575°C. a less radical displacement of the atoms accompanied by a change of symmetry, in which silicon dioxide is rapidly changed from β-quartz to α-quartz or the reverse. On continued heating nothing happens until 870°C. when the α-quartz becomes instable, after which, in the absence of a flux, no tridymite but instead cristobalite is formed. On heating quartz with Fe_2O_3 in oxygen (to prevent reduction), the yield curve shown in figure 2 was obtained for heating periods of 2 hours each. The reaction product was rose-red and contained up to 4.5
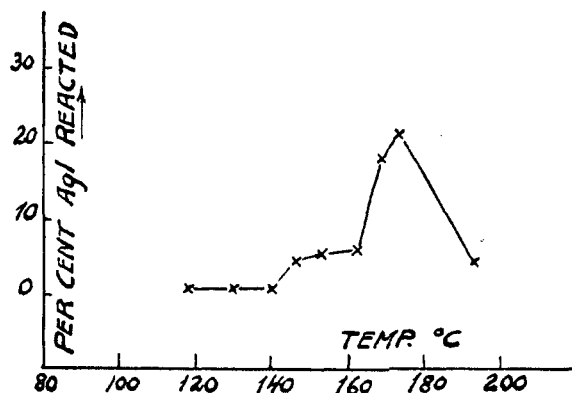

FIG. 1. REACTION VELOCITY AND TRANSITION TEMPERATURE

per cent of ferric oxide which was insoluble in acids. From the curve, it is evident that this reaction starts, though only to a slight extent, at the first rapid transition, then stops until about 900°C. when the α-quartz changes slowly to cristobalite, giving the ferric oxide plenty of time to react. The x-ray photographs showed that the penetration of ferric oxide into the silicon dioxide lattice gave a displacement of the cristobalite lines corresponding to an expansion of the lattice (43).

It is evident that this quite unexpected solid solution of ferric oxide *can only be formed in connection with transition processes,* for neither cristobalite nor tridymite, when mixed with ferric oxide, gives the red product, nor do β-quartz or α-quartz do so below their transition points (43). Besides, the rose-red product formed is of interest in itself, because this state of the iron oxide, which seems rather unnatural from a crystallo-

graphic point of view, causes widely changed characteristics both of ferric oxide (if it can be said to exist individually in the solid solution) and of the product compared with pure cristobalite, especially with respect to its catalytic activity.

From an investigation with S. Ljungkvist (30b), the following facts can be briefly stated. After a method had been devised to obtain homogeneous products containing no free ferric oxide, two solid solutions of ferric oxide in cristobalite were made, one containing 0.24 and the other 1.0 per cent of Fe_2O_3. These preparations were tested with regard to the sensitiveness of the color to change of temperature, the possibility of reducing the dissolved ferric oxide, and their catalytic activity on ethanol vapor. Whereas pure ferric oxide made from the oxalate began to darken
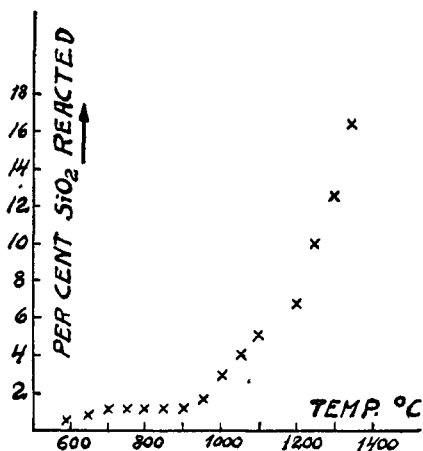

FIG. 2. REACTIVITY OF SILICA

at about 300°C., such a change already sets in with the red Fe_2O_3–SiO_2 products at 240°C. The change begins quite suddenly and reaches a grey- to brown-violet final stage at 270°C. in contrast with the behavior of pure ferric oxide, which darkens to a deeper and deeper color at far higher temperatures. These color changes are reversible in the red products. Whereas in respect to color changes the dissolved ferric oxide must consequently be considered much more sensitive to heating than is pure ferric oxide, the opposite is the case, as could be expected, as regards resistance to chemical reagents. It is neither dissolved by acids nor by solutions which could form complex ions containing iron, and it is also much more resistant to reducing gases. Hydrogen reduces free iron oxide at 300°C. but leaves the red solid solution unattacked even after heating for 1 hr.

at 400°C. Saito (54) has found that ferric oxide is reduced by a gas mixture containing 5 per cent of carbon monoxide at and above 300°C.; the red products were entirely intact, however, after heating for three-quarters of an hour in a mixture of 25 per cent carbon monoxide and 75 per cent carbon dioxide at 580°C. From a catalytic point of view the considerably increased stability in the presence of vapors of ethanol or its decomposition products are also of great interest. Pure ferric oxide is reduced below 300°C.; the solid solutions are on the contrary unchanged even at 440°C. Experiments with R. Hedin (30b) have also shown that the solid solutions have a greater reactivity in the solid state, e.g., when reacting with calcium carbonate, than does pure cristobalite (cf. figure 3).

The catalytic activity, at least in such reactions as have been investigated, is greatly changed when compared with that of ferric oxide or of cristobalite when all have had the same treatment. Thus, for instance, the breaking down of ethanol with the formation of aldehyde, ethylene, ethyl ether, and hydrogen, already occurs at about 400°C., whereas cristobalite does not act until about 60°C. higher. On the other hand free ferric oxide shows quite different behavior. As before mentioned it is reduced at a much lower temperature. For selective catalysis, especially with regard to the formation of heat-sensitive products or the stability of the catalyst, these characteristics should command interest (30b).

A similar maximum of reactivity at the transition point has been obtained for the change of rhombic to monosymmetric sulfur in an investigation with A. Floberg and P. Paulson, the results of which are in press (28a).

To reaction effects caused by structural changes can be assigned the increased intensity of reactivity of bismuth and copper at 75°C. and 70°C., respectively, as shown by a recently completed investigation by the writer with R. Hedin and S. Anderson. In the literature on measurements of the physical constants of these metals, especially of bismuth, one observes that opinions are very much divided on these "transition points," the existence of which has been found by Cohen (7, 8) and his coworkers. A tabulation of the results obtained with different measuring methods and by different investigators leads to the opinion, that here we are dealing with phenomena which certainly exist at the given temperatures, but can hardly be characteristics of the primary crystal lattice. That this is the case, we have also shown by Laue diagrams above and below the "transition point," which do not show any change of structure. The appearance or non-appearance of these "transitions" seems indeed to depend to a remarkable degree upon accidental circumstances during the formation of the crystal. As it was of interest to find out if the rule of increased reactivity during transitions could also be applied to changes of this kind, determina-

tions were made of the velocity of solution of bismuth and copper in dilute nitric acid and for bismuth also in an iodine–potassium iodide solution (figure 5). The tests were made in a thermostat at constant temperature (±0.05°C.). The reaction time was 30 minutes for bismuth and 60 min-
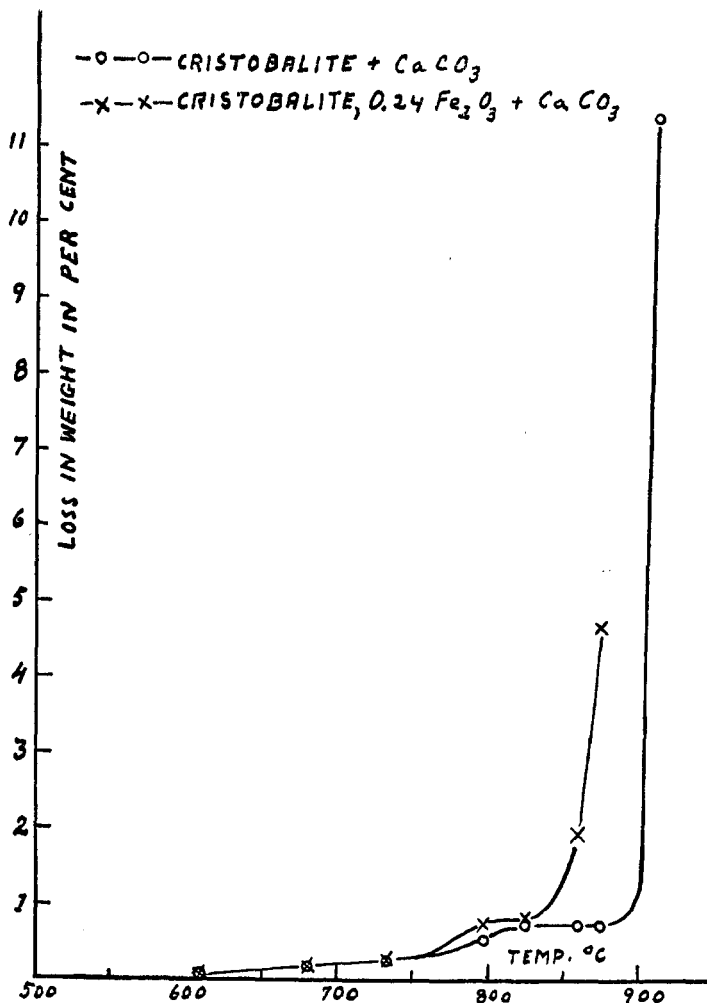
FIG. 3. REACTIVITY IN THE PRESENCE OF SOLID SOLUTION

utes for copper, and was determined after dilatometric tests had given the time of change in the test pieces used. Results were obtained which were entirely in agreement with the temperatures reported by Cohen. The transition period for bismuth was 30 minutes at rising temperature, and

90 minutes at falling temperature; for copper in both cases it was about 60 minutes. Only a brief résumé of the results of this investigation will be given here, as a fuller report will shortly be published. As can be seen from figure 4, a considerable increase of intensity in the reaction with nitric acid is found in Cohen's "transition range." In the series of tests with rising temperatures the increase begins at about 74.1°C. and reaches a maximum at 74.5°C., corresponding to the maximum between 74.9 and 73.5°C. on the curve with falling temperatures. The differences between the two curves at temperatures above the "transition point" depend upon the fact that the test pieces for the curve with rising temperatures, when heated
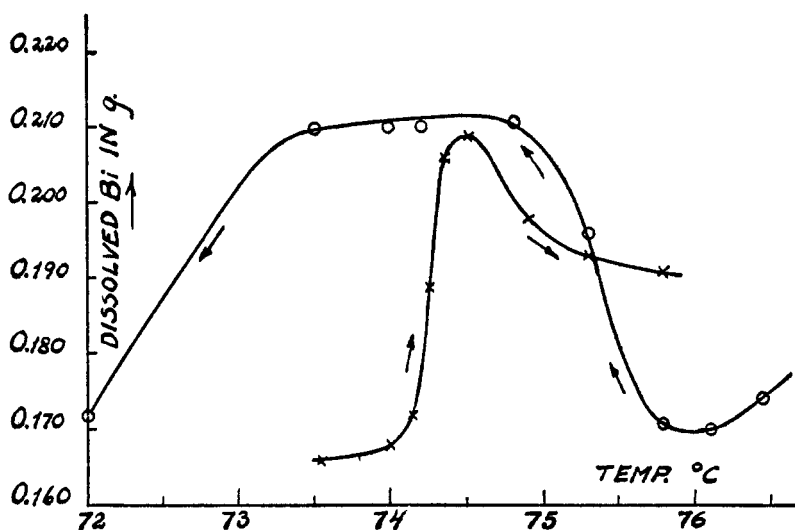

FIG. 4. RATE OF SOLUTION OF BISMUTH IN NITRIC ACID AT TRANSITION TEMPERATURE

in the acid to the test temperature, rapidly pass the "transition range," which consequently has a certain influence in this case also. The circumstances are analogous when copper dissolves in nitric acid or when iodine reacts with bismuth.

In a recent publication Goetz and Hergenrother (17) have proved that in this case it cannot be a question of transitions in the usual sense, but instead these are changes in a kind of secondary structure which does not belong to the lattice, but to the macrocrystal, and which is caused by a certain periodicity (depending on the chemical character of the crystal and its temperature) in the formation of contracting and more resistant atomic planes, which divide the crystal into a block- or mosaic system. Such phenomena, which certainly have a close connection with the forma-

tion of etching figures, have been the subject of a number of recent investigations, especially by Zwicky (68) and Goetz (16).
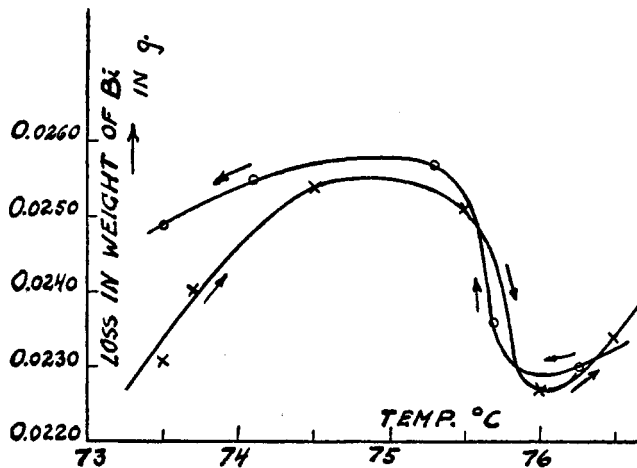

FIG. 5. RATE OF REACTION OF BISMUTH WITH IODINE AT TRANSITION TEMPERATURE
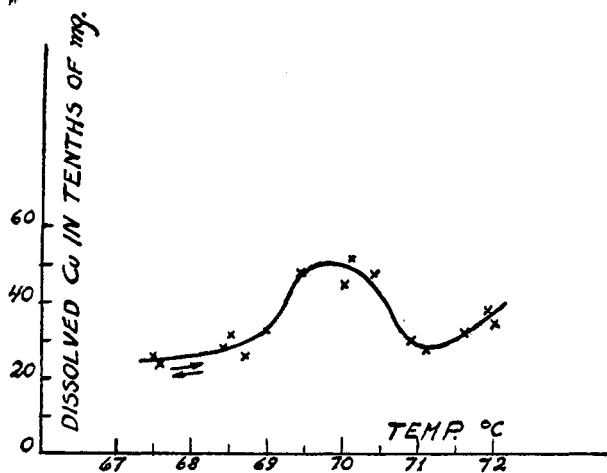

FIG. 6. RATE OF SOLUTION OF COPPER IN NITRIC ACID AT TRANSITION TEMPERATURE

4. Changes in the crystal lattice through radiation

Every absorption of energy quanta which increases the energy of an atom, an ion, or molecule, or of the crystal lattices built up of these, ought to lead to a change of reactivity in case of sufficient radiation and sufficient quantum yield. Especially in gaseous or liquid systems several instances

of such photochemical effects produced by visible or ultra-violet radiation have long been known (cf. Dhar, The Chemical Action of Light). A number of such phenomena are also known in crystals. In the first place, of course, in the silver halides used in photography, a de-ionization with formation of uncharged Ag and Br particles occurs in certain places such as in the AgBr ionic lattice. There can hardly be any doubt that such a change in the lattice of the silver bromide, being to some extent comparable to an admixture of foreign particles, ought also to change the reactivity between silver bromide and another suitably selected reactive crystal, e.g., a solid oxide as described above. *Moreover, such an effect can also be expected in those substances in which the change on irradiation does not reach the stage of ionization or de-ionization, but leads only to electron displacements which produce phenomena of phosphorescence or possibly also of fluorescence.* As far as I know, investigations of this kind have not heretofore been made, and the work in progress here has as yet not given results ready for publication. We have started, however, to make comparisons of reactivity and catalytic effect between such differently sensitized or sensitive substances in normal and in activated condition, using irradiation with visible or invisible radiation, including x-rays.

Some difference between visible and x-ray radiation seems to be probable, as it is known from the investigations of Glocker (15) that the chemical action of x-rays is connected with the formation of more or less rapid photoelectrons or in certain cases Compton-electrons, and therefore should be more of a secondary nature than the usual photochemical processes. The Einstein photochemical equivalence law cannot reasonably be expected to be valid, but there should always be some proportion between "real absorption" (photoelectron formation) and chemical action. Since a photoelectron, given a higher or lower velocity, can attack, and eventually in a certain reaction can activate or inactivate a number of particles in the lattice, thus disturbing the uniformity of the interior cohesion of the lattice, it is evident that to attain a perceptible result it is possible to take into account the change not only of that particle from which the electron has been thrown out, but of a considerably greater number. (It has been calculated that one thousand silver bromide "molecules" can be attacked for each absorbed quantum of x-ray radiation.) For the demonstration of this possibility, it should be advantageous to use substances with a strong x-ray absorption; for, contrary to the case with light, a relatively small absorption, i.e., a low efficiency, has to be counted on. Such substances do not appear to have been used.

In exothermic reactions it is also desirable to determine whether a quite small addition of energy through radiation may not be able to cause chain reactions,—at least so-called energy chains. The rigidity of the solid

system and the difficult or delayed contact between the reaction components in the solid mixture are perhaps in most cases obstacles serious enough to prevent the establishing of such an effect, even when using sources of radiation giving more energy than those which were at our disposal in the previously mentioned experiments. *A priori*, experiments with exothermic rearrangement or decomposition inside the crystal lattice of a single substance look more promising. Experiments of this kind, e.g., increasing the velocity of transition of an undercooled high-temperature modification or the decomposition of an endothermic compound, deserve closer investigation.

Endothermic reactions, as also the thermal decomposition of exothermic compounds, should, however, be capable of being affected by suitable irradiation. If the dissociation energy is supplied by heat, it should be possible to change the velocity of the decomposition. In such cases, of course, there can be no question of chain reactions, but the action of the photoelectrons on the normal electric uniformity of the lattice or on the momentary energy state of certain particles, should be able to influence the internal diffusion in the crystal, if the substance and radiation are suitably selected, and therefore affect also the velocity of thermal decomposition. Such preliminary experiments have been made with compounds of lead and barium as shown below.

For the investigations made by the writer in collaboration with L. Nelson salts of heavy metals have been selected. The objection may be raised that the velocity of the photoelectrons may decrease with increasing nuclear charge, and thus the gain through strong absorption may be compensated or overcompensated. Yet, according to Bothe (4) and to a private communication from Glocker, it does not seem permissible to postulate a simple connection between the nuclear charge and the velocity of photoelectrons of a certain radiation, nor has it been possible with x-rays to find such a selective absorption of certain frequencies as is the case with chemically active light. In preliminary experiments—and practically all experiments on the chemical action of x-rays are at present preliminary, for in this field the conceptions are still more muddled than in the rest of photochemistry—it is therefore not even possible to recommend the use of very homogeneous radiation.

In our experiments we used a Müller-metalix tube ("media") giving tungsten radiation. The voltage used was 60 to 70 kv. and the current 2.5 to 3.0 ma. The tungsten anticathode was about 17 cm. from the irradiated powder, which was kept in a small quartz flask open in the one constricted end to permit the escape of gas and the introduction of the wires of a thermocouple. During an experiment two such flasks with the same substance, one of them protected from the radiation, the other one

exposed to it, were rotated at uniform speed in the heating apparatus standing immediately below the x-ray tube. This apparatus consisted of an electrically heated furnace with a long constant-temperature space and of large heat capacity, which could be kept at a constant temperature ($\pm 1°$C.) within the space where the flasks were placed. As the time required to reach the reaction temperature is of great importance in its influence on the course of the reaction, and as this could not be the same for the irradiated and the protected substance on account of the change in heat capacity which is caused by the material designed to absorb the radiation, the rotating device was placed in the furnace inside a stationary brass tube with a wall thickness of 5 mm. This tube had an opening at the top directly over the flask to be irradiated, and to equalize the heat capacity an opening of the same size on the lower side, under the protected flask. As the radiation penetrated the brass tube to a certain extent, the non-irradiated flask was further protected by a lead pipe 2 mm. thick, or for high temperatures, by a steel pipe 5 mm. thick outside the brass tube, with an opening corresponding to that of the brass tube. Using this arrangement it was possible to obtain a synchronous and absolutely constant rate of heating during any period for both irradiated and non-irradiated samples. A series of experiments with parallel concentrated ultra-violet radiation from a mercury-arc lamp of Kromayer type was also made.

The reaction time in these experiments was varied within wide limits, because in the case of chain reactions of the above-mentioned type, positive results could possibly be expected even with rather short exposures. The radiation from the x-ray tube had to pass about 3.5 mm. of quartz in all before reaching the powder.

The results were negative throughout, possibly because of the use of too weak a source of energy. In the exothermic reaction, $CaO + NiCl_2 = CaCl_2 + NiO$, which had been the subject of an earlier research of the writer and Nelson (40), there was no distinct difference in the yield between the irradiated and the non-irradiated sample when ultra-violet radiation was used for 15 minutes at 130°C., nor with x-radiation at 61 kv. and 2.5 ma. for 15 minutes at 139°C., nor with the same x-radiation for 180 minutes at 18°C.

In the endothermic reaction, $PbCO_3 = PbO + CO_2$, x-radiation of 70 kv. and 3.0 ma. was used at 194°C., 206°C., and 269°C. without difference in yield under the radiation. The lead carbonate was made by the method of Centnerszwer and Awerbuch (9).

In another endothermic reaction, $4PbO_2 = 2Pb_2O_3 + O_2$, studied both under x-rays and under ultra-violet radiation and at temperatures between 306°C. and 315°C., with the time varied between 15 and 270 minutes, the

differences were somewhat larger, but so also were the experimental errors, so that no definite influence of the radiation was ascertainable.

Finally the reaction, $BaO_2 = BaO + \frac{1}{2}O_2$ was selected because of the strong absorption of x-rays by barium and because of the binding between the atoms of the peroxide. X-radiation of 65 kv. and 3.1 ma. was applied at 575°C. for periods up to 300 minutes but without evidence of influence by the radiation. Mixtures of barium peroxide and aluminum oxide also failed to show any such influence.

These investigations will be continued with better equipment in order to find out what really happens when x-rays act chemically. This can best be done by the study of the decomposition of solids, using simple kinds of atoms, ions, or lattices, or characteristic types of compounds. It seems unnecessarily involved to undertake this important study with solutions of complicated compounds, with complex organic substances, or by color changes in minerals, as has been done heretofore.

TRANSITION POINTS AND CATALYTIC ACTIVITY

The importance of widening the crystal lattice or of rendering it in-homogeneous, which is well-known in the use of "mixed catalysts," has been mentioned in a previous section. In certain cases, however, there should be still one more possibility, as yet not described, namely to change the activity of a catalyst by allowing it to act within the temperature range corresponding to a rapid reversible change in it. Experiments of this kind are now being made with repeated passage through the transition range in both directions. The small fluctuations of temperature can be obtained by surrounding the catalyst chamber with a heating element, the heat capacity of which is small compared with that of the furnace, and which is periodically shunted into the circuit.

It should also be mentioned that experiments by the author and E. Gustafsson indicate that magnetic transitions give similar effects (30a). Using nickel to catalyze the formation of carbon dioxide from carbon monoxide, or the decomposition of nitrous oxide, discontinuities in the yield are obtained at the magnetic transition point (358–360°C.), as shown by curve 1 in figure 7. The sudden increase in gas volume at the transition point can only be explained by a more rapid decomposition following the equation $N_2O = N_2 + \frac{1}{2}O_2$. Curve 2, where pure nitrogen is passed through the tube, shows that no discontinuity can be observed due to increase in volume of nickel at the transition point. The gas volume introduced into the tube was the same in both cases. Such an effect is, however, highly selective, as could be expected. It should be mentioned that the extended application of the law of increased reactivity during structural changes has recently been applied to catalytic reactions by Hüttig (45), who thus was able to

explain that change in catalytic activity which can be observed during the so-called aging period of the catalyst.

REACTIONS IN ORE ROASTING AND THE INFLUENCE OF THE NASCENT STATE IN SOLIDS

In connection with certain studies on roasting and other metallurgical processes, some investigations were made some years ago on those rapid reactions which take place when oxides of alkaline earths are heated with
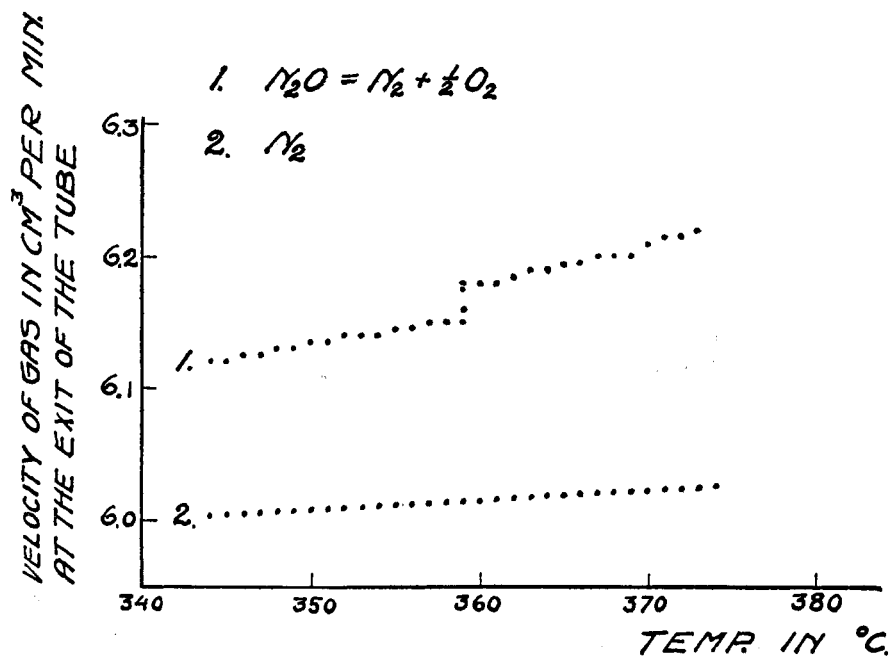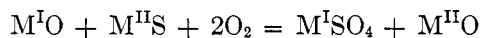

FIG. 7. CATALYTIC ACTIVITY AT THE MAGNETIC TRANSITION POINT

metal sulfides in air or oxygen.   These reactions follow the general equation

$$M^{I}O + M^{II}S + 2O_2 = M^{I}SO_4 + M^{II}O$$

and it was shown analytically that the rôle played by gaseous sulfur dioxide or sulfur trioxide was very small compared with the direct reaction between solid oxide, solid sulfide, and oxygen gas.   Continued investigations showed also that these reactions are instances of a general principle; for just as sulfides reacted to form sulfates, so phosphides give phosphates,

carbides give carbonates, and silicides give silicates of the metal of the added oxide (42). In metallurgical practice such reactions have often been used without their nature being known. The conditions of sulfating roasts, of removing carbon or silicon from metals, and the formation of slag phosphate are instances of this kind. These reactions, too, occur at remarkably low temperatures. Of the alkaline earth oxides, barium oxide reacts at the lowest temperature, followed by strontium oxide and calcium oxide; calcium oxide, like magnesium oxide, generally gives a rapid reaction at about 500°C.

As it was of theoretical interest to ascertain whether alloys of one positive and one acid-forming metal reacted in the same way, and as this question was of practical value in understanding the corroding action of alloys on the linings of crucibles or furnaces, the writer and F. Ilander (38) studied the reactions which occur when calcium oxide is heated with alloys of copper and tin or of copper and antimony in air or oxygen. These "stannides" and "antimonides" react in full analogy with sulfides, carbides, and silicides, forming stannate and antimonate. It is of no consequence whether the tin or antimony were originally present as true compounds with copper, or as solid solutions or even as fused mixtures. The reactions set in very strongly at changes of phase, as from solid to solid, or from solid to liquid state. Thus, for instance, the formation of stannate in these mixtures was found to begin several hundred degrees lower than when heating calcium oxide with stannic oxide, showing a real nascent state effect in the solid state. When homogeneous solid phases decompose or split up into other compounds or solid solutions or in certain cases when a fusion is formed, the matter in question possesses a considerably increased reactivity, in full analogy with the reactivity due to displacements in the lattice as described above. This reactivity can of course be utilized in suitable cases for the production of substances which are otherwise obtained only with difficulty. These conditions are also very clearly revealed in a research by the writer and L. Lindblad on the oxidation of cadmium–silver alloys. When alloys of the approximate composition Ag–Cd (1:1) were used, the formation of cadmium oxide showed a rapid increase at about 425°C., which is in accordance with the results of the work of Natta and Freri (52) and of Åstrand and Westgren (1), which show a change of phase from a low temperature lattice of cesium chloride type to another built with hexagonal close-packing of the atoms. A series of experiments made by the writer and O. Persson have given similar results with CoSn at 515°C., whereas Co_2Sn, in accordance with the above-mentioned rule, does not give such a discontinuous change in oxidizability.

THE MECHANISM OF THE REACTIONS

As soon as sufficient material was available in this new field to make possible a preliminary survey, it of course became a pressing problem to find an answer to questions concerning the kinetics and equilibria in these reactions. A question of the greatest interest was to ascertain the function of the lattice ions. As for the problem of the equilibria this was already solved in principle through the researches of van't Hoff (65). Exothermic reactions between solely solid phases should go to completion if solid solutions are not formed, and when the process of repeated grinding and heating was resorted to, some of the early experiments mentioned above showed this to be the case. These problems have been theoretically treated by Tammann (58) with special regard to such reactions as were not known at the time of van't Hoff. On the other hand, reactions leading to solid solutions, e.g., $Ag_2S + 2 CuI = Cu_2S + 2 AgI$, where the iodides or sulfides give solid solutions, were investigated a few years ago by Tubandt (63), who found evidence that in such systems equilibria are obtained which as usual are dependent on the temperature. After some preliminary researches by Tammann on the kinetics of reactions between solids, these problems have been taken up in connection with investigations of the equilibria in endothermic reactions, especially by W. Jander (48). Tammann had shown that after the formation of a layer of reaction product, the reactions proceed, as could be expected because one or more of the reacting particles or groups diffuses through this layer, the growth of which could be calculated from an empirical formula. In these experiments (61) with tungsten trioxide and molybdenum trioxide, that migration of acid anhydride groups which had already been adopted as the explanation in our first attempt at an interpretation of these reactions, was proved. Jander has later proceeded further and has derived from the theory of diffusion an expression for the velocity of reaction in isothermal processes which agrees very well with the observed results. He has also succeeded in calculating the change of reaction velocity with temperature, and in diffusion experiments he has directly proved that the acid anhydrides in fact possess the ability to migrate (49).

There is consequently no doubt that reactions between oxides and salts of oxy acids, (i.e., those first found and described here, such as $CaO + CuSO_4 = CaSO_4 + CuO$), can proceed exactly according to our first hypothesis, viz., by a migration of the anhydride corresponding to the acid (sulfur trioxide in the above reaction) to the added oxide. But it is of course (as mentioned by Jander) not impossible that reactions between solid substances in other cases can be ascribed to moving metallic oxides or

that they can be reactions between ions. For such processes and for the addition of oxides of alkaline earth metals, the probability of a reaction caused by moving ions is very small even if the salt in question consists of an ionic lattice at ordinary temperatures, for the inability of these oxides to transmit electric current by moving ions (46), even at very high temperatures, shows that the energy required to remove an ion is too large to permit the assumption of ionic mobility which is necessary for this kind of reaction (55). For other oxides the proportion between the energies required for removing an ion or an electron may of course be entirely different, and it must be determined in each special case from such calculations, determinations of conductivity or general chemical considerations, whether the reactions are of ionic or molecular type. Some work of this kind has lately been done by W. Jander (50). This seems to prove, in good agreement with what has been said before, that the type of reaction changes from one mixture to another according to the conditions specified. For reactions between magnesium oxide and tungstates of zinc, cadmium, nickel, and manganese there is no doubt that it is the WO_3 group which moves over to magnesium oxide. Determinations of electrical conductivity show electronic transmission within the range of experimental temperatures, and only in such cases can determinations of this kind be considered final. As has been lately shown (29) and confirmed by Jander (51), an ionic conductivity is no criterion that there is a reaction between ions.

That such is the case was shown with a high degree of probability in the first experiments with reactions between oxides of alkaline earth metals and halides, although they seem to show that a close connection could exist between ionic conductivity and yield of reaction. By dissolving the unreacted halide in organic solvents it was possible to make yield–temperature diagrams (30), which for a reaction such as $BaO + 2\,CuX = BaX_2 + CuO$ (where $X = $ Cl, Br, I) are illustrated by figure 8. If the temperature ranges for the rapid rise of the yield curves are compared with those temperatures at which Tubandt (62) found an appreciable increase of ionic conductivity, there is an obvious agreement which cannot be accidental but must imply a real connection, and which has also been observed in other reactions of this kind (29).

Taking into consideration, however, that the ionic conductivity in these salts must be ascribed to the moving copper ions, it is at least evident that it cannot very well be a possible attack of Cu^+ on barium oxide that is to be considered as the primary cause of the reaction. A contact between Cu^+ on one hand and BaO, Ba^{++}, or O^{--} on the other, can hardly matter from the point of view of reactivity, nor can this be the case with the contact between Cl or Cl^- with O^{--}. More important could be the collision

between Cl^- and Ba^{++}; but it can hardly be considered as specially probable merely because Cu^+ starts moving.   Taking into account also the fact that reactions between barium oxide or other oxides of alkaline earth metals and a number of halides, e.g., of copper, silver, lead, and nickel, yield the same chemical result, and that these also occur (though with less intensity) at temperatures where there exists only electronic conductivity, it seems natural to ascribe less primary importance to the mobility of the ions.   At least it seems more probable that the connection between increase in yield and increase in ionic conductivity is due to the fact that when at a certain temperature the mobility of the ion rapidly increases, this induces a weakening in the lattice and provides a greater possibility for the exchange of atoms.   Such a lattice ought consequently to conduct
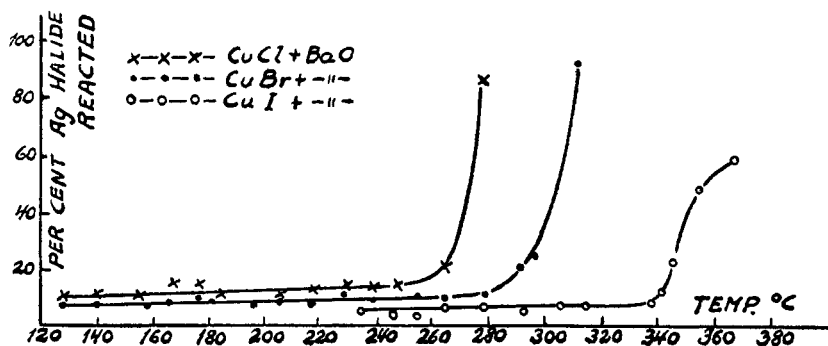

FIG. 8. REACTIVITY OF IONIC LATTICES

itself with regard to reactivity with another in about the same way as during a change of phase.

If we want to test directly the function of the ion in reactions in the solid state we meet with numerous difficulties.   First, we must of course distinguish between the influence of the degree of ionization and of the mobility of the ions, and in comparative experiments with different substances must keep one of these factors constant.   In preliminary work this has been found extremely difficult with less complicated compounds such as must be used in this case.   No doubt it would be simplest to investigate the effect of the mobility of the ions by starting with mixtures of typical ionic lattices and ascertaining whether two such salts, having markedly different conductivity, give yields which are proportionate to their conductivities when reacting with a third substance.   To escape complications from difficult diffusion through the reacting layer, the third reactant would probably have to be a gas or possibly a liquid.   Still more interest-

ing would be to test the influence of the degree of ionization (by comparing the reactivity with a third substance) in lattices of the ionic type and in lattices where the molecular type is dominant. Here we meet the difficulty, however, of finding a pair of substances with this difference in structure, but with the same internal diffusion. It is also difficult to be sure that the replacement of particles used up by the reaction proceeds with the same velocity in both reacting lattices.

This paper is an attempt to give a survey of the results and problems in a rather new field of chemical research, one which has been allowed to lie neglected for a surprisingly long time although it involves problems in one of the three states of matter, which no one can reasonably allege to be less important or less central than those which are met in the gaseous or the liquid state. In the introduction an explanation has been given for this unfavorable position of the chemistry of the solid state, but it must be remembered that the work in this field is now greatly facilitated by those fundamental earlier researches which apply also to this field, especially those which deal with the processes and laws of heterogeneous systems. It can hardly be denied that the piecing together of the results so far obtained gives the outline of the picture which eventually will appear, even though now it appears as a mosaic with many missing pieces. These results show also that purely chemical methods and reactions are convenient aids in many cases and give important evidence in investigations of crystalline materials and their changes in response to exterior or interior processes.

REFERENCES

(1) ÅSTRAND, A., AND WESTGREN, A.: Z. anorg. allgem. Chem. **175**, 90 (1928).
(2) BALAREW, D.: Z. anorg. allgem. Chem. **134**, 117 (1924); **136**, 216 (1924); **160, 92** (1927).
(3) BILTZ, W.: Naturwissenschaften **13**, 500 (1925).
(4) BOTHE, W.: Z. Physik **20**, 253 (1923).
(5) BRAGG, W. L.: Proc. Roy. Soc. London **114A**, 450 (1927).
(6) COBB, J. W.: J. Soc. Chem. Ind. **1910**, 69.
(7) COHEN, E., AND HELDERMANN, W.: Z. physik. Chem. **87A**, 419 (1914).
(8) COHEN, E., AND MOESVELD, A.: Z. physik. Chem. **85A**, 419 (1913).
(9) CENTNERSZWER, M., AND AWERBUCH, A.: Z. physik. Chem. **115**, 29 (1925).
(10) DYCKERHOFF, W.: Dissertation, Frankfurt a. M., 1925.
(11) EDNER, A., AND SCHÖNFELD, H.: Z. Physik **75**, 442 (1932).
(12) ENDELL, K.: Cf. survey in Metall u. Erz **18**, 1 (1921).
(13) FAJANS, K.: Z. Krist. **61**, 39 (1925); **66**, 321 (1928).

(14) FENNER, C. N.: Z. anorg. allgem. Chem. **85**, 133 (1914).
(15) GLOCKER, R., AND RISSE: Z. Physik **48**, 845 (1928).
(16) GOETZ, A.: Proc. Nat. Acad. Sci. **16**, 99 (1930).
(17) GOETZ, A., AND HERGENROTHER, R.: Phys. Rev. [2] **40**, 643 (1932).
(18) GOLDSCHMIDT, V. M.: Ber. **60**, 1270 (1927).
(19) HEDVALL, J. A.: Dissertation, Uppsala, 1915; Z. anorg. allgem. Chem. **96**, 71 (1916); **98**, 47 (1916); **103**, 249 (1918); **116**, 137 (1921).
(20) HEDVALL, J. A.: Z. anorg. allgem. Chem. **96**, 64 (1916).
(21) HEDVALL, J. A.: Z. anorg. allgem. Chem. **98**, 57 (1916).
(22) HEDVALL, J. A.: Z. anorg. allgem. Chem. **96**, 64, 71 (1916); **98**, 47 (1916); Z. physik. Chem. **123A**, 33 (1926).
(23) HEDVALL, J. A.: Svensk Kem. Tid. **1919**, 169.
(24) HEDVALL, J. A.: Z. anorg. allgem. Chem. **120**, 327 (1922); **121**, 217 (1922).
(25) HEDVALL, J. A.: Survey of previous work in Svensk Kem. Tid. **40**, 65 (1928).
(26) HEDVALL, J. A., AND ANDERSSON, W.: Z. anorg. allgem. Chem. **193**, 29 (1930).
(27) HEDVALL, J. A., AND ASKERLÖF, E.: Tekn. Samf:s Handl. Göteborg 1929, February, and Svensk Gasverksfören:s Årsskr. **1932**, I, 7.
(28) HEDVALL, J. A., AND BERGSTRAND, I.: Z. anorg. allgem. Chem. **205**, 251 (1932).
(28a) HEDVALL, J. A., FLOBERG, A., AND PAULSON, P.: Z. physik. Chem. In Press (1934).
(29) HEDVALL, J. A., GARPING, E., LINDEKRANTZ, N., AND NELSON, L.: Z. anorg. allgem. Chem. **197**, 399 (1931).
(30) HEDVALL, J. A., AND GUSTAFSSON, E.: Svensk Kem. Tid. **39**, 280 (1927); Z. anorg. allgem. Chem. **170**, 71, 80 (1928).
(30a) HEDVALL, J. A., AND GUSTAFSSON, E.: Svensk Kem. Tid. In Press (1934).
(30b) HEDVALL, J. A., HEDIN, R., AND LJUNGQVIST, S.: Z. Elektrochem. In Press (1934).
(31) HEDVALL, J. A., AND HEUBERGER, J.: Z. anorg. allgem. Chem. **122**, 182 (1922); see also **128**, 11 (1923).
(32) HEDVALL, J. A., AND HEUBERGER, J.: Z. anorg. allgem. Chem. **128**, 4 (1923); **135**, 49 (1924).
(33) HEDVALL, J. A., AND HEUBERGER, J.: Z. anorg. allgem. Chem. **128**, 6 (1923); **135**, 65-9 (1924); **140**, 243 (1924).
(34) HEDVALL, J. A., AND HEUBERGER, J.: Z. anorg. allgem. Chem. **135**, 65 (1924).
(35) HEDVALL, J. A., AND HEUBERGER, J.: Z. anorg. allgem. Chem. **140**, 247 (1924); J. Phys. Chem. **28**, 1316 (1924).
(36) HEDVALL, J. A., AND HEUBERGER, J.: Z. anorg. allgem. Chem. **140**, 243 (1924). Also HEDVALL, J. A.: Z. anorg. allgem. Chem. **162**, 110 (1927).
(37) HEDVALL, J. A., HEUBERGER, J., AND GUSTAFSSON, E.: Z. anorg. allgem. Chem. **135**, 70 (1924); **170**, 80 (1928).
(38) HEDVALL, J. A., AND ILANDER, F.: Z. anorg. allgem. Chem. **203**, 373 (1932).
(39) HEDVALL, J. A., AND LINDEKRANTZ, N.: Z. anorg. allgem. Chem. **197**, 414 (1931).
(40) HEDVALL, J. A., AND NELSON, L.: Z. anorg. allgem. Chem. **197**, 419 (1931).
(41) HEDVALL, J. A., AND NORSTRÖM, E.: Z. anorg. allgem. Chem. **154**, 12 (1926).
(42) HEDVALL, J. A., AND NORSTRÖM, E.: Z. anorg. allgem. Chem. **154**, 1 (1926); Svensk Kem. Tid. **1925**, 166.
(43) HEDVALL, J. A., AND SJÖMAN, P.: Z. Elektrochem. **37**, 130 (1931).
(44) HOLGERSSON, S.: Dissertation, Lund, 1927.
(45) HÜTTIG, G., AND BRÜLL, J.: Ber. **65**, 1795 (1932).
(46) HORTON, F.: Phil. Mag. [6] **11**, 505 (1906).

(47) JANDER, W.: Dissertation, Würzburg, 1927.

(48) JANDER, W.: Dissertation, Würzburg, 1927; Z. anorg. allgem. Chem. **163**, 1
        (1927); **166**, 31 (1927); **168**, 113 (1928); survey in Z. angew. Chem. **41**, 73
        (1928). Cf. also FISCHBECK, K.: Z. anorg. allgem. Chem. **165**, 46 (1927).

(49) JANDER, W.: Z. anorg. allgem. Chem. **190**, 65, 397 (1930); **191**, 171 (1930); **192**,
        286, 295 (1930); **196**, 321 (1931).

(50) JANDER, W.: Z. angew. Chem. **43**, 1057 (1930).

(51) JANDER, W., AND STAMM, W.: Z. anorg. allgem. Chem. **199**, 180 (1931).

(52) NATTA, G., AND FRERI, M.: Rend. accad. Lincei [6a] **3**, 422 (1927).

(53) NATTA, G., AND PASSERINI, L.: Gazz. chim. ital. **59**, 144, 280, 620 (1929).

(54) SAITO, H.: Science Repts. Tohoku Imp. Univ. **16**, 186 (1927).

(55) SMEKAL, A.: Z. tech. Physik **8**, 577 (1927).

(56) SCHÄFER, CL., AND SCHUBERT, M.: Wied. Ann. **1916**, 283.

(57) TAMMANN, G.: Z. anorg. allgem. Chem. **149**, 53 (1925).

(58) TAMMANN, G.: Z. anorg. allgem. Chem. **149**, 21, 89 (1925).

(59) TAMMANN, G.: Z. anorg. allgem. Chem. **160**, 101 (1927).

(60) TAMMANN, G., AND WESTERHOLD, FR.: Z. anorg. allgem. Chem. **149**, 31, 40 (1925)

(61) TAMMANN, G., AND WESTERHOLD, FR.: Z. anorg. allgem. Chem. **149**, 35 (1925).

(62) TUBANDT, C., JOST, W., RINDTORFF, E.: Z. anorg. allgem. Chem. **165**, 212 (1927);
        and private communication to the author concerning cuprous bromide and
        cuprous chloride.

(63) TUBANDT, C., AND REINHOLD, H.: Z. physik. Chem. **140A**, 291 (1929).

(64) VAN'T HOFF, J. H.: Z. physik. Chem. **5**, 322 (1890).

(65) VAN'T HOFF, J. H., AND VAN DEVENTER, CH.: Z. physik. Chem. **1A**, 166 (1887);
        5, 322 (1890).

(66) WYCKOFF, R. W. G.: J. Am. Chem. Soc. **47**, 2866 (1925).

(67) ŻEMCŻUŻNY, S. F., AND BELYNSKY, S. W.: Z. anorg. Chem. **59**, 365 (1920).

(68) ZWICKY, F.: Proc. Nat. Acad. Sci. **15**, 253 (1929); **17**, 524 (1931); Helv. Chim.
        Acta **3**, 269, 446 (1930); **6**, 49 (1931).