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MECHANISM AND KINETICS OF TOPOCHEMICAL REACTIONS TAKING PLACE WITH DECREASE IN THE VOLUME OF THE SOLID PHASES

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I. INTRODUCTION

There is a large class of reactions which can be described by the equations:

$$A(solid) = B(solid) + D(gas), \quad (1)$$

$$A(solid) + C(gas) = B(solid) + D(gas), \quad (2)$$

in which the volume of the newly formed solid phase B is less than the volume of phase A which is undergoing the conversion. This very important condition, which brings about the distinctive features of the mechanism and kinetics of the process, can be expressed by the inequality:

$$V_B < V_A. \quad (3)$$

Such reactions include: the dissociation of carbonates, oxides, sulphates; the reduction of most commercially important metals from their oxides by gaseous reductants; the dehydration of crystal hydrates; and many other processes.

Relation (3) usually leads to the appearance of a finely disperse, very porous, new solid phase. It is well-known that the dissociation of massive calcite yields calcium oxide with a very porous, finely disperse structure, and in the production of iron by the reduction of crystals of its oxides "sponge" iron is produced. Metals reduced at moderate temperatures can be pyrophoric. These facts already suggest that in processes (1) and (2) the formation of the new phase B is accompanied by its continuous breaking-away or scaling off from the initial material.

The general theory of the nucleation and growth of a new phase from an old one was created by Gibbs and developed in the works of Fol'mer, Frenkel', Stranskii, Danilov, Roginskii, and others[1-5].

It must be noted that this theory starts from the existence of ideal contact between the disappearing and the growing phases. It is completely applicable, for example, to the simplest interaction of two phases in a one-component system, that is, to the changes of state and phase transformations when drops of liquid or crystallites are formed in supersaturated vapour, crystallites or bubbles of vapour in a liquid, and so forth:

$$A_{\Phi.I} \rightarrow A_{\Phi.II}. \quad (4)$$

Here the symbol $A_{\Phi.I}$ denotes the existence of a component in a certain phase state, and $A_{\Phi.II}$ that in another phase state.

Certain general features of this theory are also correct for reactions of types (1) and (2), as is usually stressed in contemporary literature[6-9]. However, the unusualness of these processes necessitates considerable modification of the theory in analysing their mechanism. Jacobs and Tompkins[10] attempted to develop the theory applicable to this class of change.

To make more precise current views about the mechanism and kinetics of formation of a new phase in topochemical reactions of types (1) and (2), we will attempt to systematise the principal differences between the features of the reactions now being considered and those of processes (4). These differences impose certain features on the thermodynamic analysis and particular attention must be paid to them in the kinetic analysis of the changes being compared (see Table 1).

The extension of Gibbs' theory to the class of topochemical reactions now under consideration led to the conclusion that a peculiarity of these crystal chemical transformations is the existence of two crystalline phases with a boundary surface, which acts as a reaction surface. The development of the process is shown in the growth and changes of this surface.

It must also be remembered that the extension of the theory of the nucleation and growth of a new phase,

TABLE 1. Most characteristic differences between processes (1), (2), and (4).

(4)	(1) and (2)
Reaction of two phases in a one-component system. Ideal contact is maintained between the phases.	Three phases take part in the process. Forced formation of product B is brought about during contact of phases A and D or A and C.
Accumulation of the product does not hinder the course of the process, which takes place at the phase separation boundary, but, on the contrary, facilitates its development.	Accumulation of the product can spatially separate phase A from the gas and retard the process.
The formation of heterofacial fluctuations, which are nuclei of a new phase, is connected with the movement of the particles, bringing about consolidation and rarefaction in micro-volumes.	The formation of heterofacial fluctuations, leading to the appearance of new phase B, is linked with the removal of material from the bulk of the initial phase.
With the same temperature throughout the whole volume of the initial phase the fluctuations are distributed in it according to statistical laws.	With the same temperature throughout the whole volume of the initial phase the distribution of the fluctuations depends on the rate at which the gaseous substance leaves them.
The formation of nuclei of a new phase leads to the appearance of an interfacial surface. Work must be expended in the creation of this surface.	The formation of nuclei of a new phase can, by virtue of relation (3), lead to breaking-away from the old phase from separate parts of the surface. Work is required for the deformation of the crystal lattices at the point at which the phases meet and for their breaking away, that is, work on the reproduction of another two separation surfaces: A – gas and B – gas.
The growth of the new phase is connected with the supply to it of material from the initial feed medium.	The disappearance of the old phase is accompanied by the accumulation of material in the two growing phases.
The growth of the new phase is not accompanied by breaking of its contact with the old.	The growth of the new phase can bring about its rupture from the old.
The newly formed, growing, solid phase is usually compact and free from porosity.	The growth of phase B is usually accompanied by the great development of porosity in its bulk. Subsequent recrystallisation and sintering can complicate the course of the process.

loped mainly for processes (4), to reactions (1) and (2) without essential modifications to it can be considered unjustified in the light of the differences given in Table 1.

Let us consider in more detail some aspects of the mechanism and kinetics of reactions of interest to us.

II. DIFFUSION INSIDE THE CRYSTAL LATTICE OF THE INITIAL PHASE

The essence of processes (1) and (2) is the removal of material from the crystal lattice of the old phase and its subsequent reconstruction into a new phase. Therefore there is great interest in explaining the problems of the diffusion of CO_2 in carbonates, of O^{2-} and S^{2-} ions in oxides and sulphides during their decomposition, and also of O^{2-} ions in oxides during the reduction of the metals, etc.

1. Diffusion of CO_2 in the Calcite Lattice

The appearance of CaO nuclei in the depths of the $CaCO_3$ phase precedes the formation of a supersaturated solution of B in A. Its formation is linked with the departure of CO_2 molecules from the crystal lattice of the carbonate. Therefore the investigation of the diffusion of CO_2 in $CaCO_3$ is of considerable practical interest. Such an investigation[11] was made using the carbon isotope ^{13}C. From the decrease in the concentration of "labelled" carbon in the gas phase in contact with the calcite the coefficient of self-diffusion of CO_2 in $CaCO_3$ at 692–848° was found. The temperature dependence:

$$D = D_0 \exp\left(-\frac{58\,000}{RT}\right),$$

was determined and the entropy of activation of the self-diffusion of CO_2 was calculated:

$$\Delta S^* = R \ln\left(\frac{D_0}{d^2\nu}\right) = 4.7 \text{ cal deg}^{-1} \text{ mole}^{-1},$$

where $D_0 = 4.5 \times 10^{-4}$ cm^2 s^{-1}, $d = 4.04$ Å is the distance between the carbon atoms in the calcite lattice, and $\nu = 3 \times 10^{-12}$ s^{-1} is the frequency of their vibration.

But it must be noted that there is a substantial difference between the self-diffusion of CO_2 in the stable $CaCO_3$ lattice and diffusion under the conditions of dissociation of the carbonate. The first process can be hindered by an absence (or insignificant proportion) of CO_2 vacancies in the crystal lattice. In the surface layers of calcite the second process can be greatly facilitated by the disintegration of the anionic sublattice. The elimination of molecules of CO_2 and the formation of O^{2-} ions instead of CO_3^{2-} can be considered as the production of vacancies for the diffusion of CO_2 in the lattice of the carbonate. These vacancies can be propagated into the depth of the crystal lattice.

Hence the diffusion media for both types of migration will be different and the energy characteristic obtained (E = 58 000 cal mole^{-1}) and the value of ΔS^* scarcely give a correct representation of the difficulty of carrying out the removal of CO_2 from the $CaCO_3$ lattice during the dissociation of the carbonate.

2. Diffusion of Oxygen in an Oxide Lattice

The removal of oxygen from the crystal lattice of the oxides is the main aim in the reduction of metals. Moreover, the part played by oxygen diffusion in such processes is still uncertain.

Many oxides of commercially important metals (Zn, Cu, Fe, Ni, etc.) are either reduction semiconductors (ZnO) or oxidation semiconductors (Cu_2O, FeO, NiO) in which the cations have a higher mobility than the anions. This experimental fact, together with the results from investigations of the transport numbers of ions in oxide crystals, gives basis for considering the process of scale formation often as a preferential transfer of cations in the presence of a rigid network of the oxygen (or in the more general case, anion) sublattice.

Actually, in many experiments neutral particles on the surface of copper, nickel, or iron form a scale during high-temperature oxidation, by appearing closer to the metal–oxide boundary and not the oxide–gas boundary. Experiments on the sulphiding of silver[12] and copper[13] showed the incommensurably greater mobility of the metal cations compared with the sulphur anions.

All this provided a basis for some investigators to carry too far the analogy in the mechanisms of high-temperature oxidation and reduction. For example, in an analysis of the mechanism of reduction of iron[14,15] the preferential diffusion of the cations is considered in detail and no attention is paid to the possible movement of the anions, although without a corresponding removal (departure) of oxygen atoms it is difficult to understand the formation of three-dimensional metallic nuclei, the zonality of the process, the reconstruction of the oxygen sublattice in phase transformations, and other phenomena. In this, the preferential diffusion of the cations is "confirmed" by such experimental results as could equally well be explained by two-way diffusion of the cations and anions and even by the preferential motion of the latter.

Direct reduction of iron from oxides[16] is also treated as a process in which the diffusion of oxygen does not take place. But in addition the authors had to suggest that after the filling of the last cationic vacancies in the wüstite lattice and the formation of three-dimensional metallic nuclei further reduction proceeds by diffusion of oxygen along the metal–oxide interface. The problem of how three-dimensional metallic nuclei can appear without the corresponding exit of oxygen atoms, why these atoms should "await" the complete filling of all the cationic vacancies in the wüstite, why the reductant should invariably react with the oxygen which is diffusing from the deep zones along the metal–oxide interface and not react with the oxygen atoms which are nearer and more accessible for reaction, etc. was left completely unresolved.

Such a biased treatment of the mechanism of the reduction processes was due, evidently, to the fact that until quite recently nothing was known about the diffusion of oxygen in oxides. However, many recent studies have established the diffusion of oxygen in various oxides. For example, Barzakovskii and Volkov's review[17] gave the data in Table 2.

Calculation of the diffusion coefficients for oxygen by the formula:

$$D = D_0 \exp\left(-\frac{E}{RT}\right),$$

TABLE 2. Diffusion of oxygen in oxides†.

Oxide	Temperature range	D_0, $cm^2 s^{-1}$	E, kcal $mole^{-1}$	ΔS^*, cal × × $mole^{-1}$ deg^{-1}
BeO	1600—1900	$5.2 \cdot 10^{-7}$	4.29	—
Cu_2O	1030—1120	$6.5 \cdot 10^{-3}$	39.3	−3.4
UO_2	550— 800	$1.2 \cdot 10^{+3}$	65.3	—
TiO_2	860—1030	1.1	73	+12
CdO	640— 820	$8 \cdot 10^6$	93	+43
ZnO	1100—1300	$6.5 \cdot 10^{11}$	165	+59

† D_0 is the pre-exponential factor in the equation for the temperature dependence of the diffusion coefficient D, E the activation energy, and ΔS^* the entropy of activation of the process.

from the results of Table 2 suggests that at high temperatures (800–1400°) the rate of motion of the oxygen often becomes close to the similar quantity for the cations of the metals. Barzakovskii and Volkov[17] concluded that it may be necessary to take into account the mass transfer of oxygen in reactions between solid oxides.

It must be specially emphasised that these results were obtained under conditions where the oxides are stable. The usual method of studying self-diffusion of oxygen in oxides involves the observation of the isotopic exchange between the gaseous oxygen labelled with the isotope ^{18}O and the oxide crystal. Knowing the surface area of the powder and the fall in concentration of the isotope, the diffusion coefficient can be calculated.

The data in Table 2 are not readily comparable with one another, since the experiments for different oxides were performed in different temperature ranges. However, it is evident that the quantities D and E vary within very wide limits, which, finally, depend on the nature of the oxide, the presence of lattice defects (in particular, oxygen vacancies), the diffusion mechanism, and other factors.

In this connection, attention must be paid to the fact that in high-temperature reductions which take place with irreversible disordering of the oxygen sublattice, the conditions for the diffusion of oxygen from the deep layers of the crystal to its surface should be incomparably more favourable than for the stable existence of the oxides. Here the analogy with the destruction of the anionic sublattice during the dissociation of carbonates is completely relevant.

In a conductimetric investigation[18] it was concluded that during the reduction of metals by diffusion of oxygen, in the surface layers of the oxides at least, the process can be preferred to the migration of cations in a positive direction both from the thermodynamic and from the molecular-kinetic points of view.

It has been noted[19,20] that in the reduction of wüstite a dense film of iron can be formed on its surface. Examination of this film under the electron microscope showed the complete absence of pores. Moreover, the reduction of wüstite continues, although very slowly. It can proceed here only by diffusion of oxygen through the compact layer of iron. The calculated[20] activation energy for this diffusion is 53 000 ± 4000 cal per g-atom of oxygen.

Hence, when the diffusion of oxygen through a compact film of iron in the reduction of wüstite is considered, then the possibility of the movement of oxygen in oxides with breakdown of the oxygen sublattice in process (2) cannot be doubted.

Evidently the time has come to reconsider the part played by diffusion of oxygen in the reduction of iron and other metals from their crystalline oxides. The theoretical or experimental evaluation of the rates of diffusion of anions under the conditions of breakdown of the anionic sublattice would be a considerable achievement.

III. MECHANISM OF THE FORMATION OF A NEW PHASE

1. Nature of a Solid Solution of B in A

It must be assumed that the production of nuclei of a new phase precedes the formation of a solid solution of component B in A. Whereas from a thermodynamic viewpoint such a solution can be considered as an excess of MO in MCO_3 or of M in MO and MS as compared with the stoichiometric formulae of the carbonates, oxides, and sulphides, from the viewpoint of its formation mechanism two treatments are possible.

On the one hand the formation of the solution can be considered as the introduction of metal cations and oxide anions during the dissociation of carbonates or of metal cations during the reduction and dissociation of oxides and sulphides into the crystal lattice of the initial phase.

On the other hand, the departure of CO_2 molecules, oxygen atoms, or sulphur atoms from the initial substance A in the processes under consideration creates an unstable transition structure in the surface layer, which can be considered to be a solid solution. It is completely clear, however, that its nature will be quite different in comparison with the solution which is obtained by contact saturation of the carbonate with oxide, or of the oxide and sulphide with the metal.

The solubility of oxides in carbonates is apparently negligible. Thus, Gel'd and coworkers[21] could not detect it, and concluded that the solubility of the components could not exceed 0.06%, that is, the accuracy of the measurements.

As regards the solubility of metals, such a definite conclusion cannot be drawn for even the lower oxides and sulphides. The oxide and sulphide phases can have an excess of the metal or the non-metal[22] and their homogeneity region can be rather broad. Metals can be dissolved in the oxide by introduction between the sites of the crystal lattice. The filling of vacancies is evidently more correctly considered as chemical reaction, and not as dissolution, because this act is connected with the redistribution of electrons in the crystal.

A feature of the reactions we are considering is that the appearance of a new phase is associated with the loss of material from the old, and therefore here the greatest interest will relate to unstable transition structures arising during processes (1) and (2) and not to solutions formed by contact saturation of phases A and B.

The instability of the transition structure is linked with the degree of departure of the system from equilibrium and from the thermodynamic standpoint can be treated as chemical supersaturation of the solid solution of B in A. The onset of this supersaturation in the surface layer, in some of, or in the whole volume will evidently depend (at a

temperature) on the rate of removal of material from the initial phase.

For example, the very rapid removal of CO_2 from the carbonate lattice and the replacement of CO_3^{2-} anions by O^{2-} can comparatively easily bring about the formation of oxide in the micro-volumes of the surface layer. On the other hand, it can be thought that the removal of some CO_2 molecules still does not bring about the reorganisation of the old lattice into the new and when conditions for the equilibrium redistribution of particles throughout the whole volume are created by withdrawing negligible amounts of CO_2, then supersaturation can be attained throughout the whole piece of carbonate. Hence the smaller the piece the easier it is to reach supersaturation throughout it (less time is required for this). From this viewpoint it is understandable why the stepwise nature of the process during the reduction of oxides can be followed more easily the smaller the dimensions of the grains being reduced and the lower the rate of conversion.

A thermodynamically necessary condition for the supersaturation is that the chemical potential of the substance in the new phase should be less than its value in the solid solution:

$$\mu_2 < \mu_1, \tag{5}$$

Esin and Gel'd[8] proposed that for the dissociation of carbonates μ_2 should be considered to be the chemical potential of the pure oxide and μ_1 that of the oxide in the solid solution. By analogy with this it can be assumed that in the dissociation of oxides and their reduction μ_2 will be the potential of the pure metal and μ_1 that of the metal dissolved in the oxide. For a thermodynamic evaluation of the supersaturation it does not matter how this difference in chemical potentials arises: by the dissociation of an oxide or its reduction. But from the standpoint of the practical realisation of the process, it is known how difficult it is to create chemical supersaturation in order to bring about dissociation, for example, of the lower oxides of copper, iron, nickel, chromium, and other metals (at least, at the temperatures of ordinary pyrometallurgical processes), and how it is reached comparatively easily in the high-temperature reduction of these metals.

The magnitude of the chemical supersaturation expresses the probability of formation of a new phase, and with the aid of the latter, the rate of the process, thus connecting in this way a thermodynamic quantity with a kinetic characteristic.

A feature of the transformations being considered is that the supersaturation of the solid solution is connected in a definite way with the extent of the departure from equilibrium of the system as a whole. The way of writing:

$$\Delta G = \mu_2 - \mu_1 \tag{6}$$

ignores the thermodynamic properties of the gas which actively participates in the process of establishing the new condensed phase. Therefore it is evidently more correct to take for the characteristic of the method of reaching supersaturation in the "solution" the probability of the formation of nuclei, not the difference (6) but the magnitude of ΔG_i based on the occurrence of reactions (1) and (2):

$$\Delta G_1 = \mu_D + \mu_B - \mu_A \tag{7}$$

or

$$\Delta G_2 = \mu_D + \mu_B - \mu_C - \mu_A. \tag{8}$$

In Eqn. (6) ΔG is the change in free energy of the system due to the appearance of the new solid phase B, and ΔG_1 and ΔG_2 are the changes in potential of the system brought about by the course of reactions (1) and (2); μ_i are the chemical potentials of each of the substances taking part in the reaction.

When D is absent from system (1), then $\mu = \infty$, so that:

$$\mu_D = \mu_D^0 + RT \ln P_D, \tag{9}$$

where P_D is the pressure of gas D in the system and $\Delta G_1 = -\infty$. The thermodynamic probability of the formation of phase B in this system should be very great.

From these relations, in a comparative investigation of the rates of oxidation of iron and of its reduction from oxides[23] the probability of formation of nuclei of a new phase was linked with the quantity ΔG_2.

2. Heterofacial Fluctuations

Variations in density exist in carbonates, oxides, and sulphides, as in all other thermodynamic systems. However, the heterofacial fluctuations which can become the stable nuclei of new phase B also arise as the result of a chemical process — the essential difference in the mechanism of formation of a new phase in changes (1) and (2) as compared with processes of type (4).

Thus, in the dissociation of carbonates the chemical act of detachment of CO_2 from the complex anion CO_3^{2-} and also the diffusion of CO_2 lead to the replacement of the CO_3^{2-} anions by the monatomic O^{2-}. This destroys the symmetry of the force fields and distorts the carbonate crystal lattice, creating an unstable transition structure, within which the formation of heterofacial fluctuations is possible — the nuclei of the new phase MO.

In the dissociation or reduction of oxides or sulphides the chemical act is the transfer of electrons to the metal cations, which, together with the departure of oxygen or sulphur from the crystal lattice, also leads to the appearance of a transition structure, a "solid solution".

When the oxides or sulphides have cationic vacancies, then during the course of the reaction it is possible for monatomic particles of metal to migrate to the unfilled lattice sites[24]. But when the rate of production of anionic vacancies is so great that the rate of diffusion of oxygen or sulphur surpasses the intensity of movement of metal in the bulk of the oxide or sulphide, which is evidently so in real technological processes, then the "solution" will be none other than unfilled anionic places in the lattice of phase A. Its supersaturation provokes the appearance of stable heterofacial fluctuations which can become the nuclei of the new phase.

The instability of the transition structures is also connected with the replacement of the pair $M^{2+}-CO_3^{2-}$ by $M^{2+}-O^{2-}$ or $M^{2+}-O^{2-}$ by M–M, which are characterised by a lesser distance between the particles and a tendency to approach one another.

From this position it is easy to explain the appearance of three-dimensional nuclei of product B and also the appearance of zonality during the reduction of an oxide. Rostovtsev and Rudenko[25] discussed the problem of whether atomised iron is present at the interfacial surface. Each iron ion is in an environment of oxygen anions. In the defect sites of the oxide surface there are evidently almost

"gaseous" metal atoms, which can easily be reduced to the metallic state. But such atoms can hardly become stable nuclei of the new phase.

A heterofacial fluctuation can appear in any part of the volume of phase A, but its appearance in the surface layer is the most probable. When the process is proceeding intensively the fluctuations arising on the surface do not extend through the whole volume of the initial phase; their "concentration" in the surface layer becomes high. Under such conditions the coagulation (merging) of small fluctuations into coarser and more stable ones is even possible. The formation of nuclei of a new phase on the surface, but not in the volume, becomes predominant.

It is assumed that the processes of dissociation and reduction start from active centres, which are the most distorted sites of the crystal lattice, surface defects of the crystals: here the bond between particles can be weakened and the initial act of removal of oxygen or carbon dioxide is more probable [26]. In this connection it should be noted that the origination of heterofacial fluctuations (the three-dimensional nuclei of a new phase) is not only connected with the removal of individual oxygen atoms of oxygen, sulphur, or molecules of carbon dioxide from the crystal surface, but also with the probability of their departure from the bulk of the external layer of phase A.

From the diagram (Fig. 1) it is easy to see that this probability is quite dissimilar for particles situated on the protuberances and in the depressions. Points *a* and *b* are equally removed from the crystal surface, but whereas the first has more than one shortest path to the surface, the second has only one. Therefore the probability of fluctuations arising at the vertices of a cube will be greater than on an edge; at the latter, greater than around a face, and at a face greater than around the corner of a depression.

If it is assumed that the crystal surface is ideal and does not have defect sites, then again the probability of the occurrence of the elementary act of removal of a particle at its individual points will be unequal, because of the different energetic states of the ions. There will always be individual particles which are energetically more prepared for the completion of the elementary chemical act than the others.

3. The Formation of Nuclei of a New Phase

In phase transformations (4) at least one of the phases is mobile and this ensures ideal contact between the phases. When in a one-component system there is interaction between two solid phases with only a slight difference in specific volumes, then contact between them can also be very enduring and stable.

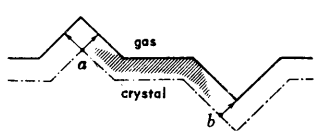


Fig. 1. Mechanism of loss of material from defect places of a crystal surface.

Relation (3) is responsible for the appearance of specific features in the mechanism of formation of nuclei of a new phase. It is clear that in processes (1) and (2) the contact between solid phases A and B can be very imperfect and in individual parts even completely destroyed. The existence of submicroscopic porosity in the products has also received direct confirmation [19,27].

Since the crystallites of the new phase should exhibit their intrinsic properties and have corresponding lattice parameters, its formation as a result of the operation of inequality (3) should be accompanied by detachment from the matrix medium A, if not along the whole interfacial surface, then at least partly. The formation, for example, of nuclei of calcium oxide in calcite should lead to the appearance in their vicinity of a "free" volume, approaching $\sim 117\%$ of the volume of the nucleus itself.

This circumstance should be reflected even in the initial equation for the change in free energy for formation of heterofacial fluctuations:

$$\Delta G = (\mu_2 - \mu_1)n + \alpha\sigma n^{2/3}, \qquad (10)$$

where the first term reflects the change in G due to the difference in the chemical potential of the particles in the new (2) and old (1) states, and the second term the work in the creation of the interfacial surface A–B.

Recently it was even noted that the quantity σ should not be treated as interfacial tension for changes (1) and (2) [10,23].

The directed action of the atomic forces at the contact surface of the two crystal lattices or the internal stresses should cause corresponding deformations or changes in the lattice parameters, which requires a definite amount of work. This was studied in a review [10] by Jacobs and Tompkins [10], where instead of σ, the quantity γ is introduced, the energy of the stress associated with unit surface of separation:

$$\Delta G = \Delta G_i n + \alpha\gamma n^{2/3}. \qquad (11)$$

It is not difficult to see that the nature of processes (1) and (2) is not reflected completely here either, since relation (3) is not obeyed.

For reactions of type (1) and (2) the second term in Eqns. (10) or (11) should also take into account the work of breaking away of the new phase from the old, which can be done by the introduction of a third term:

$$\Delta G = \Delta G_i n + x\alpha\gamma n^{2/3} + y\alpha\varepsilon n^{2/3}, \qquad (12)$$

where α is a numerical factor depending on the geometrical form of the fluctuations which arise; γ the energy of the stress, ϵ the work of adhesion (if the nuclei break away from the initial phase) or cohesion (if the nucleus itself ruptures), x the fraction of interfacial surface A–B, y the fraction of interfacial surface A–gas or B–gas, and n the number of particles.

Evidently $x + y = 1$. But it must be remembered that the areas of the A–gas and B–gas surfaces for nuclei can be somewhat different by virtue of ratio (3).

Apparently instances are possible when either x or y can be neglected and the more general Eqn. (12) takes the form of the partial equations (10) and (11).

ΔG_i can be determined by Eqns. (7) and (8). It must then be remembered that in Eqn. (12) it relates to a single elementary particle; in the formation of a metallic nucleus, to one atom of the metal; in the formation of oxide from carbonate, to one pair of ions M^{2+}–O^{2-}.

IV. DEVELOPMENT OF THE PROCESS AND PECULIARITIES OF ITS MECHANISM AND KINETICS

1. Role of the Gaseous Phase

In reactions (1) and (2) the new phase can appear only as a result of the interaction of the initial phase and the gas. Therefore the process always starts at the A–D or A–C boundary. The appearance of reaction product B complicates the course of the process, since it separates the reagents spatially.

This is well evident from the following examples. Almost all the metals (with the exception of palladium, iridium, platinum, and gold) are unstable under ordinary atmospheric conditions and should be changed into the ionic state[28]. But it is well known that most of them do not oxidise under these conditions, since the very thin oxide film formed separates the metal from the oxygen of the air. According to current views[29] the time for the formation of the film on iron in an atmosphere of air is 0.05 s. Often the reaction of carbonation also ceases almost completely because of the formation of a compact film of carbonate on the crystalline oxide.

These two examples relate to the reverse course of reactions (1) and (2), in which a relation opposite to inequality (3) holds. The direct course of these processes is usually aided by the new phase being very porous. This leads to the conclusion[19,30] that the formation of the product does not lead to the breaking of the A–gas contact between the reagents. But in the very investigations, on the basis of which these conclusions were made, it was observed that when a dense and pore-free product is obtained the process is sharply retarded. It is still possible only owing to the diffusion of elementary particles through the crystal lattice of the reaction product. In this the operation of the chemical reaction no longer takes place at the (initial phase)–gas boundary, but at the (new phase)–gas boundary or the surface of separation of the solid phases.

Thus in the oxidation of a metal the initial reaction proceeds owing to its contact with the oxidant gas, and then (after the formation of a film) is continued either owing to the movement of cations to the oxide surface, where they react with oxygen, or by diffusion of oxygen through the oxide layer to the metal surface.

In the reduction of oxides with the formation on them of a compact film of metal, the place of that reaction also moves from the oxide–gas-reductant boundary to the metal–gas separation surface, to which oxygen diffuses, there reacting with the reductant[19,20].

Hence the chemical reaction and the phase transformation can be spatially separated. This shows that the mechanism of changes (1) and (2) is more complicated than that for transformations (4).

Consequently, in these reactions the formation of products which block the surface of reagent A can sharply retard the course of the process. On the other hand, the breakdown of this blockade owing, for example, to cracking of the scale during the high-temperature oxidation of metals, or the formation of pores and cracks in the product during the dissociation of carbonates and the reduction of oxides can greatly accelerate the process, both as a result of the renewal of the (phase A)–gas contact, and also as a result of the great shortening of the diffusion paths of the elementary particles.

Note that in many investigations the rate of reactions (1) and (2) are usually considerably greater than the rate of the back reactions, when they relate to the same physical and geometrical conditions of the experiment. For example conductimetric investigation of the rates of oxidation and reduction of copper and iron wires[18] showed that under the same conditions reduction requires ten times less time than oxidation. The dissociation of carbonate is incomparably more rapid and more complete than carbonation[31].

2. Rate of Formation of Nuclei and Their Growth

The thermodynamic stability of the heterofacial fluctuations — the nuclei of the new phase — is determined by Eqn. (12), from which it is evident that even when the first term is negative the positive values of the last two terms can affect the absolute magnitude more than the first term, and the fluctuations then become unstable.

Since for a given degree of departure of the system from equilibrium (or for a definite chemical supersaturation) the first term in Eqn. (12) grows more rapidly than the sum of the second and third terms with increase in the number of particles n, ΔG, as a function of n, has a maximum. The value of ΔG_{max} corresponds to that critical value of n at which the growth of the nucleus can occur spontaneously, because it is accompanied by a fall in ΔG.

$$\frac{\partial(\Delta G)}{\partial n}=\Delta G_i+\frac{2}{3}\varkappa\alpha\gamma n^{-\frac{1}{3}}+\frac{2}{3}y\alpha\varepsilon n^{-\frac{1}{3}}. \qquad (13)$$

Equating this derivative to zero, we find n_{crit}:

$$n_{crit}=\frac{8}{27}\alpha^3\frac{(x\gamma+y\varepsilon)^3}{(-\Delta G_i)^3}. \qquad (14)$$

An analysis of this equation shows that not only the energy of deformation of the crystal lattice, but also the work of formation of the primary submicroscopic particles should affect the value of n. From Eqn. (14) it follows that the necessary condition for the formation of critical nuclei is the inequality:

$$\Delta G_i<0, \qquad (15)$$

since if the reverse of (15) holds we obtain $n_{crit}<0$, which has no physical significance. For reactions (1) and (2) it is very important to emphasise that when, during its formation, the crystallite of the new phase is separated from the initial phase and the possibility of its further growth is excluded, then it can be thermodynamically stable only under the condition $\Delta G<0$. Note that if the nuclei in reactions (1) and (2) cannot grow at their points of detachment from phase A by the addition of elementary particles, the possibility of their growth by mutual cohesion is obviously not excluded (especially when there is great chemical supersaturation in the system).

The probability (p) of the formation of the nuclei depends not only on ΔG, but also on the mobility of the atoms, since the formation of the new phase requires the reconstruction of the crystal lattice, which is impossible without corresponding movement of the particles. Starting from this consideration, p is determined by the relation:

$$p=C\exp\left(-\frac{U+\Delta G}{KT}\right), \qquad (16)$$

and the rate of formation of nuclei (v):

$$v=A\exp\left(-\frac{U+\Delta G}{KT}\right), \qquad (17)$$

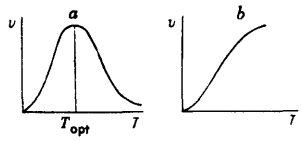


Fig. 2. Rate of formation of three-dimensional nuclei (v) as a function of temperature (T): a) for crystallisation from a melt; b) for the dissociation of carbonates, oxides, and sulphides.

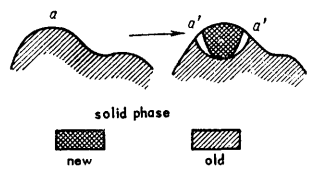


Fig. 3. Scheme for the reproduction of "defect" places — active centres of reaction.

where the energy factor U is identified with the activation energy of diffusion, A and C are proportionality coefficients, and K is Boltzmann's constant.

During crystallisation from the melt, ΔG increases with temperature but U falls. There is therefore a temperature at which the rate of formation of the nuclei will be maximal (Fig. 2a).

For dissociations (1), there may not be an optimal temperature. At constant pressure, increase in T should decrease both ΔG and U. Therefore the rate of formation of the nuclei will be an increasing function of temperature (Fig. 2b). It is necessary to mention this because in recent monographs[7,8], in discussing the above mechanism and kinetics of the dissociation of carbonates in terms of the theory of the formation and growth of a new phase and in fixing the position of the optimal temperature on the $v-T$ curve, for some reason it was not observed that there could not be one for the processes considered.

As regards reduction processes, there is evidently always a decrease in U and rise in temperature affects ΔG differently. For example, in the reduction of magnetite and wüstite to iron by hydrogen, ΔG, as well as U, is a decreasing function of temperature and therefore extremal values cannot be expected on the $v-T$ curve. But in the reduction of the same compounds with carbon monoxide there is one, for ΔG is an increasing function of temperature.

In real technological processes changes (1) and (2) are carried out at great degrees of chemical supersaturation and high rates. Under such conditions the rate of nucleation of the new phase is extremely high and the conditions for their growth can appear very unfavourable. The following features of the reactions being considered hinder the growth of the nuclei.

1. Whereas in processes (4) the supply of material is effected comparatively readily, in changes (1) and (2) the growth of the nuclei of the new phase is complicated by the slowness of the diffusion of the elementary particles in the crystal lattice.

2. The formation of a crystallite of the new phase should be accompanied — if not by complete — then at least by partial detachment of it from the initial substance, because of relation (3) (see, for example, Fig. 3). The gaps formed in the neighbourhood of the crystallite will be insurmountable obstacles for the diffusion of particles to the surface of the nucleus.

3. If the attachment of the nucleus of the new phase to the old is not coherent but has a distinct boundary, then its motion should bring about movement of the nucleus, since $v_B < v_A$. But with the condition of intensive formation of nuclei, their free movement is excluded (not for a gas and not for a liquid). The crystallites press one another and even their insignificant formation at the interfacial boundary should lead to fracture of the phase.

Obviously the growth of the crystallites is strongly connected with the processes of coalescence, sintering, and recrystallisation, which will be the more successful and occur at lower temperatures the smaller, and consequently the more active and more mobile the nuclei themselves; to a lesser extent the growth occurs by the attachment of elementary particles. This obviously also explains the possibility of obtaining pyrophoric metals in the low-temperature reduction of the oxides[30].

What has been stated agrees well with the ease of obtaining very finely dispersed and porous products B during reactions (1) and (2), which is observable in practice.

It is worth noting that very few results of investigations of the physical and chemical properties of the products of reactions of type (1) and (2) (for example, properties such as density, electrical conductivity, mechanical strength, adsorptivity, chemical activity, etc.) have been published. Such investigations are extremely desirable since they can give additional information about the mechanism of the process.

3. Pore Formation

In the mechanism of the changes which we are analysing, a special place is occupied by the formation of pores and their part in the development of the reaction. The origination of pores can often be considered to be the same result of a process as the formation of a product. Therefore the size of the relative porosity (the volume of pores compared with the volume of the lump of carbonate, oxide, or sulphide) can even serve as a measure of the completion of the process.

In several investigations, for example, that of Edström[30], it was noted that the dimensions of lump specimens either did not change at all or changed insignificantly during dissociation and reduction, although the difference in the volumes of phase A and B can be very considerable. If therefore the change in dimensions of single-crystal or polycrystalline specimens during the conversion be neglected, then it is not difficult to calculate the limiting value of the overall porosity (π_p, %) corresponding to complete conversion of the old phase into the new.

For example: $CaCO_3 \rightarrow CaO + CO_2 + \text{pores}$

$$\pi_p = \left(1 - \frac{2.8 \times 56}{100 \times 3.4}\right) \times 100 = 54\%,$$

where 100 and 56 are the molecular weights of $CaCO_3$ and CaO respectively, and 2.8 and 3.4 their densities in g cm^{-3}.

Similarly, it is possible to calculate that the reduction of Fe_3O_4 to FeO requires the appearance in the product of

a relative porosity of ~15%: Fe_3O_4 to Fe ~52%; FeO to Fe ~40%.

Then the ratio of porosity π corresponding to a definite stage in the process, to its limiting value π_p provides a criterion of the degree of completion of process A:

$$(\pi/\pi_p) \times 100 = A\%. \quad (18)$$

The difference between the value thus found for A and the real value is usually due to sintering or recrystallisation.

It has often[23,32-34] been observed that the sintering of a layer of products can even bring about some decrease in the rate of the process with rise in temperature, which explains why obstacles to diffusion arise with densification of the layer. In this connection, there is great interest in investigating not only the overall, but also the differential, porosity and also the true surface of the reagents.

Tatievskaya and Chufarov[27] found that from 65 to 90% of the pores formed as a result of the reduction of haematite and magnetite at temperatures up to 500° are very fine capillaries with a radius not exceeding 50×10^{-7} cm. An increase in temperature to 800° leads to the almost complete disappearance of fine pores with a radius less than 200×10^{-7} cm.

In a later investigation[19] of the reduction of wüstite at temperatures between 600 and 870° the fraction of pores with radii up to 1.3×10^{-5} cm varied accordingly from 42.8 to 56.3%. It was found that the relative surface of the products decreased from 23 540 to 13 910 $cm^2\ cm^{-3}$.

These experimental results suggest that submicropores appear in the products of reactions (1) and (2) during the formation of the crystallites of the new phase as a consequence of the inequality (3).

The formation of pores leads to the reestablishment of the contact between the initial solid and gaseous phases, considerably facilitating the course of reactions (1) and (2) in comparison with the back reactions. In the latter the products should be compact and pore-free, since its volume is greater than the volume of the solid substance entering into the reaction. True, in the processes which are the reverse of the reactions which we are analysing pores can be formed in the internal layers of the product (for example, in the high-temperature oxidation of metals) but for another reason — due to the Kirkendall effect[35].

Hence the change from the oxidation of metals to their reduction significantly changes the mechanism of the process: the transport of the reagents in oxidative reactions is realised almost exclusively by mass transfer of them through the crystal lattice of the product, but in reductions, by motion along the micropores, that is, by Knudsen diffusion.

4. "Autocatalysis"

The following feature is characteristic for changes (1) and (2): there is a maximum on many rate–time graphs. This phenomenon is termed autocatalysis, since as the reaction develops it accelerates itself. The explanation is that the main place at which the reactions proceed is the surface separating phases A and B. The interfacial boundary grows during the process, but since the reaction is heterogeneous and its rate is proportional to the surface, this rate must also increase and reach a maximal value.

The many investigations of Chufarov, of Rostovtsev, and others[36-39] provide an experimental basis for the autocatalytic theory applicable to the processes we are considering.

Chufarov developed the adsorption-autocatalytic theory for the reduction of a metal; this theory has been widely recognised and extended. It is the leading theory in the contemporary educational literature on the theory of metallurgical processes.

Many papers have considered in detail the adsorption nature of reduction processes[40-42].

However, it must be noted that some aspects of the adsorption-autocatalytic theory are not satisfactory. Thus in Lyuban's monograph[43] it is stated that as the temperature is raised the role of adsorption in the reduction processes must necessarily be diminished. But here it must be remembered that chemical adsorption of gases can occur at comparatively high temperatures. Thus, oxygen is adsorbed on graphite even at 1200°.

The adsorption side of the theory was criticised in Manchinskii and Shkodin's review[44], where it was shown that in many experiments which provide an experimental basis for the theory and from which quite important conclusions were drawn about the nature and mechanism of the reactions being studied, the use of a vacuum could change the process in the diffusion, but not in the kinetic, region, notwithstanding the opinions of their authors.

It is noted that from the standpoint of the adsorption theory, in criticising the baseless analogies between equilibrium and kinetic characteristics in the "two-stage" hypothesis on the mechanism of the reduction of metals, they themselves tolerate a similar error, by explaining the difference in the rates of reaction of metals with hydrogen and carbon monoxide in terms of the equilibrium values of adsorption of these gases. These values are extrapolated into the region of high temperatures without sufficient reason. Furthermore, adsorption relates not to unit volume of the adsorbent but to its unit surface and the true surface of the solid phases in the experiments was not estimated. The authors unfortunately did not discuss the question of how the adsorption in real processes departs from its equilibrium values.

The "autocatalytic" mechanism for the processes being analysed also needs considerable refinement.

It is now thought[7-9] that, after the formation of the nuclei of the new phase, reactions (1) and (2) are localised on the surface of separation A–B, that is, in those places where their operation is complicated by the above three circumstances. This starts from the fact that the process of building up a new phase is easier (from the energetic point of view) than its initial formation.

Here, evidently, the difficulties of the reactions proceeding on the surface of separation between two solid phases are partly understated and the difficulties of formation of three-dimensional nuclei (which cannot be so great at high chemical supersaturations) are exaggerated to a certain extent.

As a sharp separation surface between the solid phases is necessary for catalysis, first of all it is necessary to settle the question as to whether such a surface is always present in the changes being studied.

Starting from the analysis given above of the nature of the "solid solution" it is expected that there can also be

continuous — coherent change between A and B. It is interesting in this connection to note that some authors confirm the accelerating action of the reaction product[45,46] whereas others do not[47-49].

Furthermore, if reaction (3) is obeyed, then both the initiation and the growth of the new phase can lead to the disappearance of the A–B surface of separation and to the production of A–D and A–C contacts. Then the main place for the reaction to take place can become the surface of separation of the initial solid phase from the gas. But then the explanation of the maximum on the atuocatalytic curves in terms of the growth of the A–B interfacial surface does not seem very convincing.

With the exception, for example, of such processes as the formation of a condensed phase from saturated vapour, of a crystallite from a melt, etc., the mechanism of which can prove to be quite different from that in reactions (1) and (2), where three phases interact, the genesis of an interfacial surface, which brings about the separation of the reagents, may not only accelerate but also complicate and retard the change. The essence of the latter is that loss of material from initial reagent A is hindered by the appearance of the product and boundaries separating the solid phases.

Hence the phenomenon of "autocatalysis" can be explained by the change in the A–B interfacial surface only when good contact is maintained between the phases which are interacting and there is a distinct separation surface between them.

In accordance with what has been stated other possible reasons for the appearance of a maximum on the rate–time curves must be considered.

1. When as a result of inequality (3) there is detachment of the new phase from the old, then this can bring about extensive renewal of an A–gas separation surface. This has a limit. As reagent A is consumed a moment is reached after which the occurrence of the reaction is accompanied by a decrease in this surface.

At high degrees of chemical supersaturation and almost continuous covering of phase A by the nuclei of phase B the surface of contact between the initial substance and the gas very rapidly reaches a maximal value and subsequently can only decrease, which agrees well with experiment.

2. The nuclei of the new phase are formed mainly in defect sites on the surface of the crystallites. Even partial rupture of a crystallite of B from the initial substance A signifies renewal of the defect sites, which can also accelerate the process. This can be represented, for example, by the scheme shown in Fig. 3. Here it is evident that instead of one active centre a, the sharp edge a'–a' of a crater is formed and on this there will be many defect sites.

The appearance of the descending branch of the autocatalytic curve is due not only to the decrease in the reaction surface and the number of defects but also the growth in the thickness of the layer of product, which hinders the supply or removal of gaseous reagents and the heat exchange.

Hence the advances in general and physical chemistry in the investigation of the processes analysed in the present review make it possible to build up a mechanism for them from new points of view. These advances also enable us to hope that in the near future essential modifications will be made to the theory of nucleation and growth of a new phase in topochemical changes of the type considered here.

We think that the following are the most interesting features of the mechanism and kinetics of these reactions.

1. Processes (1) and (2) are complex heterogeneous interactions which include at least six stages: (a) the chemical reaction itself; (b) reconstruction of the crystal lattice of the initial phase A into that of the new phase B; (c) transport of the gaseous reagents and products between the reaction surface and the centre of the gas stream; (d) diffusion of the gases into the pores of the initial crystalline phase; (e) the diffusion of gases into the pores (capillaries) of the solid reaction products; and (f) the diffusion of particles (atoms, ions, molecules) in the crystal lattices of the solid phases.

Each of these stages can be rate-limiting — it depends on the particular conditions under which the process is carried out.

2. The formation of the solid product B leads to spatial separation of the reagents and to difficulties in carrying out the process.

3. The difference (3) between the volumes of the solid phases originating and disappearing during the course of the interaction leads to the development of porosity, to the spatial drawing together of the reagents, and even to renewal of their contact, which in turn facilitates the course of the reaction, in distinction, for example, from the back reaction.

4. The interaction of these two tendencies (those mentioned in paragraphs 2 and 3) bring about the peculiar features of the kinetics of the processes analysed here, sometimes causing their acceleration and sometimes their retardation.

The reaction rate at a given temperature and degree of chemical supersaturation can be affected by: (a) the topography of the surfaces of the solid phases and the renewal of defect places; (b) the disordering of the crystal lattices and the formation of transition structures during the transformation; (c) the formation of electrical fields and the possibility of their penetration in connection with the development of porosity in the depth of the crystal of the solid phase; (d) the sintering (recrystallisation) of the reaction products and the hindering (or facilitation) of capillary diffusion of the gaseous reagents, and also the supply or removal of heat necessary for the course of the reaction.

5. Many experimental results show that the solid product of reactions of the type considered are usually obtained finely disperse with a strongly developed surface and consequently high chemical activity. The production of coarsely crystalline and single-crystal products is greatly hindered by the operation of inequality (3). Crystal growth is evidently mainly brought about by their sintering and to a lesser extent by the addition of elementary particles.

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