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Autocatalytic and Impedance Phenomena and the Effect of the Physical State of the Solid Product on the Acceleration and Retardation of Reversible Topochemical Reactions with Participation of Solid and Gaseous Reactants

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I. INTRODUCTION

During the last 2–3 decades significant advances have been made in the chemistry of solids [1–16]. However, it is noteworthy that many problems of the kinetics and mechanism of heterogeneous reactions involving solids are only in the initial stage of development. Furthermore, the development and research in this field and the accumulation of experimental data make it necessary to revise or correct the classical hypotheses in this branch of science.

The present review deals with the most important kinetic features of reactions of the type

$$A(solid) + C(gas) \rightleftarrows B(solid), \quad (1)$$

$$A(solid) + C(gas) \rightleftarrows B(solid) + D(gas). \quad (2)$$

Reactions of the first type include the formation of metal oxides, sulphides, selenides, and halides, the hydration of oxides and their conversion into carbides, and the reverse reactions. Processes of the second type include numerous reactions involving the reduction of oxides to the metals by gaseous reducing agents and the reverse reactions, as well as certain other interactions. Reactions (1) and (2) are heterogeneous and take place at an interface. Therefore the physical state and the topography of the surface of the initial solid phase A and the product B play a very important role in the kinetics of these processes.

The intrinsic chemical step is complicated by a number of physical phenomena which accompany it: the rearrangement of the crystal lattices of the interacting phases and their recrystallisation and sintering, the diffusion of the reactant C and the product B in the gaseous medium and their motion through pores and cracks in the solid phases A and B, the adsorption and desorption of gases, and the supply and removal of heat. Therefore the processes can take place both under kinetic and diffusion-dependent conditions.

In the examination of the kinetics of reactions (1) and (2) under isothermal conditions (this is the case most frequently encountered in technology), we shall distinguish two factors which have been called "autocatalysis" and "impedance".

Autocatalysis consists in the reaction, having begun after a certain induction period, developing at an increasing rate, the process gradually coming to a stop only at more advanced stages as a result of the disappearance of the initial reactant. The accumulation of the product of an autocatalytic reaction can be described graphically by an S-shaped curve and mathematically the relation between the extent of reaction α and time t can be expressed by the Kolmogorov–Erofeev equation, for example [17]:

$$\alpha = 1 - \exp(-kt^n). \quad (3)$$

The self-acceleration of the reaction and a rate maximum on the kinetic curve have been observed experimentally in numerous investigations [18–27].

Another no less interesting feature of reactions (1) and (2) is that the formation of the product B results in the separation of the reactants in space and the appearance of factors hindering the process, whose magnitude increases as the solid product accumulates. This phenomenon has been called impedance. Factors hindering the reaction can arise even at the very beginning, whereupon the rate will steadily decrease (provided, of course, that there are no abrupt changes in the nature of the process itself, the

conditions of the process, or the physical state of the interacting phases). The time-dependent inhibition of the process can be described mathematically either by a parabolic or a logarithmic relation[28,29]:

$$\delta^n = kt, \tag{4}$$

$$\delta = \ln(kt), \tag{5}$$

where δ is the thickness of the layer of product, t the time and n the exponent of the parabola.

Despite the abundance of the available experimental data, the nature and mechanism of autocatalysis have not yet been completely elucidated. In the literature there are contradictory interpretations of this phenomenon[30-33]. The occurrence of extrema on the kinetic curves can be explained in different ways[13]. The extensive experimental data on impedance have not been adequately systematised.

The aim of the present review is to reveal certain contradictions in the interpretation of the mechanisms of autocatalysis and impedance. The comparison of these phenomena in a single review should facilitate a deeper understanding of their nature and mechanisms. Analysis of the experimental data which have accumulated in this field during the last decades permits the formulation of an empirical principle broader than, for example, the Pilling–Bedworth rule[34] which has existed since 1923.

II. THE MECHANISM OF AUTOCATALYSIS

Usually the acceleration of reactions (1) and (2) is attributed to the increase during the process of the area of the A–B interface. According to the theory of the initiation and growth of a new phase developed by Gibbs, Volmer, Frenkel', Roginskii, and others, it is now believed that, after the formation of the nuclei of the new phase B, further reaction is localised at the interface between the phases A and B.[35] The process develops from the nuclei into the bulk of the specimen. Todes gave a mathematical description of this mechanism. If the particle is very small, the nucleus can completely fill it up before the second nucleus is produced—this is a case of mononuclear transformation in a chemical reaction[36].

Clearly reactions of types (1) or (2) extend into the bulk of the compact crystal, having begun on its surface. However, the theoretical foundations of the role of the A–B interface in autocatalysis, and the details of the model of this surface and its application to any type of topochemical reaction have given rise to a number of contradictions and therefore they require revision and correction. For example, Esin and Gel'd, gave the following explanation of the role of the A–B interface, on the basis of Langmuir's studies, in connection with the discussion of the mechanism of the reduction of an oxide to the metal by a gaseous reducing agent[37]. It is assumed that in the reaction

$$a\mathrm{A(solid)} + c\mathrm{C(gas)} \rightleftarrows b\mathrm{B(solid)} + d\mathrm{D(gas)} \tag{6}$$

the rates of the forward (V_1) and reverse (V_2) processes depend on the total areas of the solid phases:

$$V_1 = k_1 S_A p_C^c, \tag{7}$$

$$V_2 = k_2 S_B p_D^d. \tag{8}$$

On attainment of equilibrium, $V_1 = V_2$ and

$$k_1 S_A p_C^c = k_2 S_B p_D^d, \tag{9}$$

whence

$$K = \frac{k_1}{k_2} = \frac{S_B p_D^d}{S_A p_C^c}. \tag{10}$$

It follows from Eqn. (10) that the equilibrium constant K depends on the ratio of the total areas of the solid phases, but this is inconsistent with experiment.

To eliminate this "contradiction", Esin and Gel'd[37] conclude that the reactions of the gases C and D with the solids A and B do not take place on the entire surface of each phase but only at their contact boundary. They believe that such localisation of the process in a narrow contact zone between two solid phases has a number of advantages.

However, one should bear in mind that the appearance of a solid product can give rise to diffusion-dependent inhibition and can result in a change of the process conditions from kinetic to diffusion-dependent. Then the kinetic laws should cease to apply and should be replaced by diffusion laws. The application of the law of mass action to reactions of types (1) and (2) in its usual kinetic form is possible only when the interaction of the gas with solid phases is not complicated by either external or internal diffusion. This means that the gas phase is mixed sufficiently vigorously and has free access to the surface of the solid reactant, i.e. the supply of the molecules of C and D to the substances A and B is not rate-limiting.

Furthermore, one should bear in mind that, as equilibrium is approached, the difficulties associated with the formation of the new phase become increasingly significant. The size of the critical nucleus is inversely proportional to the degree of chemical supersaturation raised to the third power. This means that at equilibrium the fundamental forward and reverse steps (for example, oxidation and reduction) can take place on both surfaces (A and B) without the formation of a new solid phase.

This conclusion becomes particularly convincing if the following version of equilibrium is postulated. We assume that the reaction volume contains the solid phases A and B, which are separated in space, and that the gas mixture (C + D) has the equilibrium composition. Clearly in this case there is no A–B interface but a dynamic equilibrium nevertheless exists.

Therefore one can assume that at equilibrium the reaction surface is not the A–B interface but the surfaces of the phases A and B (for example an oxide and a metal) which are accessible to the gas. Since on attainment of equilibrium the number of forward reaction steps becomes equal to the number of reverse steps, it must be assumed that the reaction surface areas S_A and S_B are equal regardless of the ratio of the total areas of the phases A and B:

$$S_A = S_B \tag{11}$$

Here by S_A and S_B we understand not the macroscopic areas of the phases A and B but those surfaces of both solid phases on which the forward and reverse reaction steps can take place. It is possible to explain in this way the independence of the equilibrium constant for the topochemical reaction of the ratio of the surface areas of the solid phases. Therefore the explanation by Esin and Gel'd[37] of the role of the A–B interface in autocatalysis is not very convincing.

For processes which are the reverse of reactions of type (1) (thermal dissociation processes), Jacobs and Tompkins give the following explanation of autocatalysis[38]. The Gibbs free energy (ΔG) of formation of a nucleus of the new solid phase A must include not only the difference between the thermodynamic potentials of the products and reactants ($\Delta G'$) but also the energy γ of the strain in the crystal lattices of the solid phases at the sites where they are in contact. Accordingly, the following equation holds:

$$\Delta G = m\Delta G' + \sigma\gamma \tag{12}$$

where σ is a geometric factor (equal to $4\pi r^2$ for a spherical

interface) and m the number of molecules involved in the formation of the nucleus. Eqn. (12) can be put in a different form:

$$\Delta G = am^{2/3} - bm \,. \qquad (13)$$

Here a is proportional to the strain energy and b denotes the free energy change per molecule with the sign reversed.

If $\Delta G' < 0$, ΔG is a decreasing function of m when $\gamma = 0$ or there is a maximum when $\gamma > 0$ (Fig. 1). The maximum value of ΔG corresponds to the critical size of the nucleus (m_{cr}). Apparently as a result of the strain due to the formation of the new phase, small particles of A are unstable and tend to be reconverted into B, while large particles are more stable in relation to the reverse transition. Jacobs and Tompkins[38] believe that because of this subsequent reactions take place preferentially at the interface between the two solid phases and not via the formation of a large number of submicroscopic particles A. The phase A formed in the reaction steadily increases in size, extending from the nuclei into the bulk of the crystal.

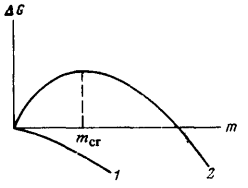


Figure 1. The ΔG–m curve for $\Delta G' < 0$: *1*) $\gamma = 0$; *2*) $\gamma > 0$.

The authors explain the autocatalytic nature of the reaction by a general hypothesis, according to which the nuclei are formed initially, this being followed by a period of their relatively rapid growth. If the activation energy for the growth at the interface is less than the activation energy for the formation of the nucleus, then the growth of the already existing nuclei predominates over the formation of new ones and the phase formed acquires the form of individual compact grains. In the opposite case a large number of very small nuclei are formed, none of which attains a size sufficient for observation with the naked eye.

The above mechanism of the development of the process differs little from the classical hypotheses of Volmer and Frenkel'[39,40]. It has the advantage that it can embrace in a general form a wide range of topochemical reactions, including reactions (1) and (2). At the same time it is readily seen that a more concrete application of the theory to reactions (1) and (2) requires the correction of some of its postulates. This applies in particular to the structural model of the A–B interface and the question of the site where the reaction takes place.

Autocatalysis due to the growth of the A–B interface requires in the first place that such an interface be present. However, it is known that, with the exception of molecular crystals, most solid crystalline chemical compounds exhibit appreciable deviations from stoichiometry (see, for example, Ref. 41). Furthermore, there is a possibility of the occurrence in the process itself of unstable transitional structures which, from the thermodynamic point of view, can be embraced by the concept of the solid solution. Therefore there may be no definite interface between the solid phases.

Furthermore, the volumes of the interacting phases are not as a rule equal. Because of this and because of the difference in the rates of migration of the elementary species through the layer of the solid products, the solid phase formed is usually very porous, amorphous, or finely dispersed. In this connection, it is interesting that as early as 1940 Erofeev examined photographs of nuclear grains and found that crystallisation processes are separated in space from the interface. An amorphous product, which becomes crystalline only at a certain distance from the contact surface, is in contact with the initial substance. In some cases the solid crystalline product is not observed at all or is observed only a considerable time after the reaction. Thus the crystallisation process is separated from the intrinsic chemical reaction both in space and in time[17].

If the volume of the new solid phase is smaller than the volume of the initial solid consumed in the formation of the former, then, if the process takes place under conditions which impede sintering and recrystallisation, the reaction usually results in the formation of a finely dispersed porous product. Thus the reduction of single-crystal and polycrystalline oxides by gaseous reducing agents can yield pyrophoric metal as the product[42]. The dissociation of calcite, $CaCO_3 \rightarrow CaO + CO_2$, leads to the formation of a product which has a bulk porosity of up to 54%.[43] A continuous growth of porosity occurs in the multistage reduction of ferric oxide to the metal, $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow \rightarrow FeO \rightarrow Fe$, in the dissociation of oxides, sulphides, oxalates, and carbonates, and also in the dehydration of hydrates. In this connection the studies of the overall and differential porosity, the size of the primary crystals, and the total surface areas of the solid phases merit attention[15,44–48].

In concrete cases various mechanisms of the formation of pores obtain. For example, the formation of metal nuclei and submicroscopic pores in oxides or oxide nuclei and pores in carbonates can be represented in two different ways: (a) an unstable transition structure is formed in the bulk of the parent phase; the formation in the latter of a three-dimensional hetero-phase fluctuation, which already has different lattice parameters and smaller distances between its constituent species, should result in its separation from the parent medium, if not over the entire surface then at least partially (Fig. 2*a*); (b) when a nucleus forms on the surface of the initial phase due to an orientation effect (epitaxy), it draws its "constructional material" from the surrounding medium. The loss of mass in the immediate vicinity of the nucleus should initiate the formation of a pore (Fig. 2*b*).

It is important to note that in both cases, regardless of mechanism, the appearance of the nucleus of the new phase is accompanied by the formation of two new interfaces: between the initial solid phase and the new solid phase and between the new solid phase and the gas. This may be accompanied by the regeneration of the interface between the initial solid phase and the gas. This factor along requires the correction of Eqn. (12), as was done in our earlier review by the present author[35].

A mechanism for the formation of pores in the dehydration of hydrates was proposed by Garner[49] (Fig. 2*c*). Wagner[50] put forward a mechanism for the development of a pore in the reduction of wustite (Fig. 2*d*). The primary defect of this mechanism is that it accounts only for the development but not the formation of the pore. It is quite clear that in the reduction of wustite to iron pores not only develop but new ones are actually formed.

Pores are not necessarily formed only when the volume of the new phase is smaller than that of the initial phase but also when the opposite relation between phase volumes holds. For example, in the conversion of copper, nickel, and iron wires into the corresponding oxides, sulphides, and selenides the cations move faster than anions. As a result, there is, as it were, a dispersal of the mass of the metal from the surface towards the periphery; pores are formed which can coagulate and give rise in the limit to a cavity with the same geometrical shape and dimensions as the initial specimen[51].

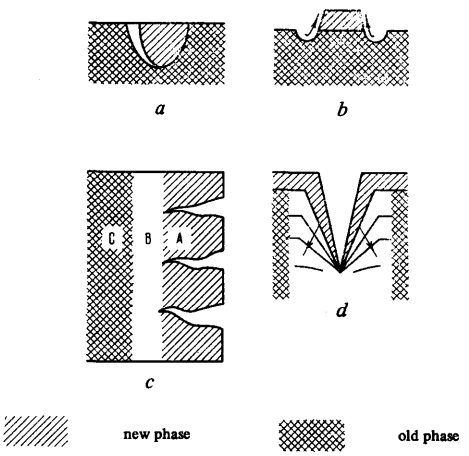


Figure 2. Mechanisms of the formation and growth of pores in topochemical processes:
a) the formation of a nucleus and pore within the parent phase[61]; *b*) the formation of the nucleus of the new phase on the surface of the old; *c*) the formation and growth of pores in the dehydration of hydrates[49] [*A*) new phase; *B*) transition layer; *C*) old phase]; *d*) the development of the pore in the reduction of wustite[50].

The formation of pores renews or maintains contact between the gaseous and solid reactants[42,52], shortens the diffusion path[42], and sets up the conditions necessary for the penetration of electric fields into the bulk of the crystal, which gives rise to the possibility, for example, of the reduction of oxides to metals at temperatures so low that the reoxidation of the latter cannot take place to a significant extent[53].

The experimental data on pore formation throw doubt on the exceptional role which has been attributed to the A–B interface in the development of autocatalysis. A typical autocatalytic reaction is the thermal decomposition of oxalates. For example, Jacobs and Kureishy[14] obtained S-shaped kinetic curves for nickel oxalate both in the powder and compressed states.

Let us consider the dissociation of oxalates:

$$Ag_2C_2O_4(\text{solid}) \rightarrow 2Ag(\text{solid}) + 2CO_2(\text{gas}), \quad (14)$$

$$PbC_2O_4(\text{solid}) \rightarrow Pb(\text{solid}) + 2CO_2(\text{gas}), \quad (15)$$

$$MgC_2O_4(\text{solid}) \rightarrow Mg(\text{solid}) + 2CO_2(\text{gas}). \quad (16)$$

It follows from the ratio of the densities of MnC_2O_4 and M that reactions (14)–(16) should be accompanied by considerable pore formation in the solid product. If one neglects the sintering effect, it is possible to calculate that the porosity of the product formed in reaction (15), for example, may reach about 67% and that of the product formed in reaction (17) may be up to 70%.

Clearly in this case the fundamental decomposition steps on the oxalate–metal surface are hindered. There is no space available for carbon dioxide molecules to desorb into and they cannot dissolve in the atomic lattice of the metal and diffuse through the latter. On the other hand, at the oxalate–gas boundary the reaction is facilitated by the fact that the carbon dioxide molecules can pass freely into the gas phase. Here the decomposition is accompanied by the regeneration of the solid phase–gas interface, breakdown of the crystal, and self-dispersion[13,35].

It is not fortuitous therefore that in recent years investigators have studied the kinetics of thermal decomposition reactions in conjunction with measurements on the changes in the total surface of the solid phase and the porosity occurring in the course of the process. This is evident in the work of Dollimore[15], Gordeeva and coworkers[47], Danes[48], and the present author and Bystrova[43].

The fundamental chemical step in the dissociation of the carbonate, $MCO_3 \rightarrow MO + CO_2$, is the breakdown of the complex anion CO_3^{2-} into a CO_2 molecule and the monatomic anion O^{2-}. It is not difficult to show that this step too is incomparably easier on the carbonate–gas interface than on the carbonate–oxide interface. On the crystal surface, carbon dioxide molecules can be desorbed freely into the gas phase. Their evolution from the outer layers gives rise to vacancies in the anionic sublattice, as a result of which favourable conditions are created for the diffusion of carbon dioxide from the following layers of the crystal lattice. The rearrangement of the crystal lattice of the carbonate into that of the oxide and the formation of a three-dimensional nucleus of the new phase are in no way restricted. On the other hand, on the carbonate–oxide surface the desorption of carbon dioxide molecules is difficult. Their mobility is limited by forces associated with orientation correspondence. The diffusion of carbon dioxide through the calcium oxide lattice involves considerable difficulties. Gel'd et al.[54] showed that calcium carbonate and calcium oxide are virtually immiscible. The diffusion of carbon dioxide on the calcium carbonate–calcium oxide interface also appears unlikely, in the first place because such a surface may not actually exist and in the second place because the forces associated with orientation correspondence must give rise on this surface to a structure almost as compact as that in the bulk of the crystal.

Self-diffusion of carbon dioxide in the calcite lattice is impossible. This was demonstrated by Haul and Stein[55] by the radioactive tracer method. However, the development of the process due to the evolution of carbon dioxide from the bulk of the crystal or on the calcium carbonate–calcium oxide interface, which is associated with diffusion-dependent inhibition, could not give rise to the high rates of reaction which are observed in practice. Thus the complete dissociation of a small cube of polycrystalline calcite with an approx. 10 mm edge at 1140°C requires only 6–7 min.[43] These studies permit the conclusion that both the rapid development of the process and its acceleration are due in this case to the establishment of conditions of uninhibited (or almost uninhibited) evolution of carbon dioxide, i.e. the continuous regeneration of the "initial solid phase–gas" interface.

Under certain thermodynamic conditions and when the mobility of the particles is sufficiently high, a similar mechanism can also be postulated for the dissociation of oxides, sulphides, and other compounds. Of course, the

fundamental steps will be different. For example, in the dissociation of an oxide the fundamental chemical interaction consists in the removal of an electron (or electrons) from the oxygen to the metal. The subsequent stages involving the formation of O_2 and desorption of oxygen should take place more readily on the surface of the crystal, where favourable conditions for the initiation of the new phase do in fact arise. Consequently, the acceleration of the process can be accounted for no less successfully by the occurrence of the reaction on the crystal–gas interface, the "corrosion" of the crystal, and the development of this interface, and also by an increase in the number of defect sites [13,35].

It is noteworthy that in certain studies on the dissociation of carbonates the "degree of conversion–time" curve was not found to be S-shaped. This was observed in experiments with magnesium carbonate by Gordeeva et al. [47] and in experiments with lead carbonate by Kadlets and Dubinin [56]. In the "Proceedings of the Fifth International Symposium (Munich)" Wanmaker reported a similar conclusion concerning strontium carbonate [15].

In this connection it must be noted that these investigators worked with finely dispersed powdered salts. In Wanmaker's study [15] a relation between the rate of reaction and the dimensions of the particles was observed and the absence of an induction period was explained by the rapid generation of the nuclei of the new phase. One should also bear in mind that the increase in size of the particles, the recrystallisation of the initial preparation, can give rise to a considerable increase of the induction period and change the nature of the kinetic curve.

Thus the classical hypotheses concerning autocatalysis, which attribute exceptional importance to the A–B surface in this phenomenon, unduly reduce the role of the gas phase in the development process and also the role of the contact between the solid phase and the gas. Analysis of the literature data [11–27] shows that the phenomenon of autocatalysis is shown most clearly in interactions between solid and gas where the volume of the new solid phase is less than the volume of the substance consumed in its formation. The product must be fairly porous, so that diffusion-dependent inhibition can be excluded, if only in the initial phase, since the ascending branch of the autocatalytic curve corresponds to conditions determined by the reaction kinetics. The present author believes that the formal extension of the classical hypotheses concerning the mechanism of autocatalysis to the interaction of powders with a gas is therefore particularly inadmissible, and yet this is still encountered in modern literature.

We shall now consider the reduction of oxides to metallic iron, the process most frequently encountered in industry. In most practical cases a number of zones are observed in the reduction of crystalline oxides to the metals. Thus the reduction of fused magnetite, carried out by the present author together with Bystrova, leads to the appearance of metal and oxide zones which are clearly distinguishable even with the naked eye [52]. Under the microscope a transition zone, magnetite grains bordered by iron, is observed. The higher the degree of reduction the narrower is the transition zone and the clearer the boundary between the metal and the oxide. The occurrence of zones in the reduction of higher iron oxides has been observed in numerous studies (see, for example, Refs. 42, 57, 58).

When the oxide is finely ground, the process consists of several stages, the lowest oxide not being reduced until the reduction of the higher oxide is complete. Under certain thermodynamic conditions, the reduction of ferric oxide Fe_2O_3 is characterised by the presence of three stages in the reaction:

$$Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO \rightarrow Fe\ . \qquad (17)$$

The phenomenon of a number of stages is difficult to achieve and therefore it has been little investigated. It has been observed, for example, in the work of Rostovtsev et al. [59], who explain the presence of several stages by the synchronisation of the reaction in all the grains of the specimen or the sample, and the phenomenon of autocatalysis observed at the same time is accounted for by the classical mechanism, according to which a reaction an interface develops within each grain. Of course, on the basis of this mechanism it appears logical to assume the synchronisation of the reaction in all the grains of the ore. Otherwise the superposition of the maximum rate in one grain onto the minimum rate in another can lead to cancellation of effects. However, this interpretation of the process mechanism gives rise to the following objections.

1. In the first place the applicability of the classical mechanism of the reaction under the conditions of the experiments actually performed has not been demonstrated.

2. In an atmosphere of pure reducing agents, used in the experiments of Rostovtsev et al. [59], only one phase (the metal) can be stable. Therefore, under kinetic conditions (in the absence of diffusion-dependent inhibition), there could not be several stages.

3. In the synchronous reduction of grains in the absence of retardation of the supply of the reducing gas the duration of the process should be a small fraction of the duration actually observed. Furthermore, it would depend only on the size of the grains and not on the weight of the specimen.

In a conductimetric study of the oxidation and subsequent reduction of thin copper and iron wires it was shown that the time required for the complete reduction is smaller by a factor of tens and hundreds than the total oxidation time [60,61]. The reduction of oxidised iron and copper wires 0.20–0.50 mm in diameter in a stream of hydrogen at 500–900°C requires times ranging from 30 s to several minutes. In Rostovtsev's study the reduction of a finely ground hematite powder, the grain dimensions of which were smaller than the diameter of the oxidised wires in the work of the present author and Ermakov [61], took tens of minutes and sometimes actually exceeded 1 h.

Comparison of these kinetic characteristics throws doubt on the synchronous mechanism of the reaction in all the grains of the specimen. In this connection it appears that the classical explanation of the occurrence of maxima and minima on kinetic curves cannot be universal. One should also remember that in the discussion of the mechanism of autocatalysis in modern literature the concept of the A–B interface, its structural model, are not considered in a sufficiently concrete form. The surface of a pressed oxide powder accessible to reaction with the reducing gas may prove to be extremely large. Thus for spherical particles 0.01 mm in diameter, the total surface per cm^3 of such a powder is about 300 cm^2. [62]

If account is also taken of the presence of defects in the crystal structure of the powder grains and the possibility of the regeneration of this structure and the "oxide–gas" interface during the reduction process, as described above, it becomes clear that, under the conditions of Rostovtsev's experiments [59], the principal site where the reaction takes place may be not the "oxide–metal" interface but the "oxide–gas" interface. However, such a hypothesis requires the revision of the mechanism of autocatalysis and the mechanism responsible for the presence of several stages in Rostovtsev's experiments [59].

In the absence of diffusion-dependent inhibition in the crystal lattice of the solid phase, which is probably the case in the reduction of fine powders, it is essential to take into account in the kinetic analysis of the process the ratio of the rate of penetration of the reducing gas (V_1) through the external geometrical surface of the specimen into its deeper zones (towards the reaction surface) and the rate of the adsorption-chemical step (V_2). The rate V_1 depends on the difference between the concentrations of hydrogen in the centre of the gas stream and within the specimen, and is a maximum at the initial instant of reduction. The second rate (V_2) is associated with the area of the reaction surface and the degree of chemical supersaturation; at the beginning of the process it can be a minimum or even zero.

The penetration of the reducing gas into the specimen and the reverse diffusion of the product gas show to some extent the features of Knudsen molecular flow. Some hydrogen molecules encounter the reaction surface of the oxide comparatively rapidly, while others fail to react and pass into the bulk of the specimen.

According to Roginskii's theory, chemical supersaturation in the system is necessary for the process to occur at a finite rate. Under the conditions of the experiments analysed, it cannot be achieved instantaneously over the entire surface of the solid phase, i.e. throughout the bulk of the specimen. As the process develops, oxidising and inert gases are flushed out of the specimen by the hydrogen and the rate of consumption of the reducing gas increases both due to the increase of the degree of chemical supersaturation and also due to the involvement in the reaction of an increasing number of new sections of the oxide surface.

It appears that in this case it is more correct to attribute the rate of reduction corresponding to the ascending branch of the catalytic curve to the increase in the area of the "oxide–gas" interface and not of the "metal–oxide" interface. On the other hand, as the specimen is "saturated" by hydrogen, the rate of "diffusion" of this reducing gas decreases. Thus the values of V_1 and V_2 approach one another. Therefore the process is initially of the purely kinetic type but after a certain time it becomes of a mixed or even diffusion-dependent type.

In this connection, the phenomenon of several stages can be accounted for by the transition of the process from kinetic to diffusion-dependent conditions. In fact, if the rate of diffusion did not limit the rate of the further development of the process, chemical supersaturation could be fairly rapidly attained not only with respect to the first but also the second and third stages of the reduction. However, then we could not have several stages in the process. The ultimate result of the approach of the rate of the adsorption-chemical step to the rate of supply of the reducing gas is that the chemical reaction maintains in the specimen a gas composition which is close to the equilibrium composition for the given stage. If for some reason the rate of supply of the reducing gas increases, there is also an increase in the degree of chemical supersaturation in the system and hence in the rate of reaction.

The process could be self-regulated. However, the gradual disappearance of the initial oxide phase leads to a decrease in the area of the reaction surface and a lowering of the overall rate of the process, and the ultimate result is that the rate of penetration of the reducing gas again begins to prevail over the rate of its consumption in the given reaction stage: supersaturation with respect to the next stage is established.

In this way it is possible to explain the mechanism of autocatalysis and the phenomenon of several stages in the reduction of powdered oxides without resorting to the concept of the "metal–oxide" interface as the reaction surface, the doubtful hypothesis of the synchronisation of the reaction in all the specimen grains being eliminated. This mechanism is in good agreement with theory and experiment. A mathematical interpretation would be desirable for its further justification[63].

The above analysis of the conditions of autocatalysis and the stepwise reaction phenomenon in the reduction of higher oxides shows that an explanation, other than that given in the literature, of the minima and maxima on the kinetic curves for the relevant processes is possible. The formation of the A–B interface cannot by itself accelerate the process. It is also necessary to eliminate the inhibition of the transport of the reactants, i.e. to ensure that they come into contact. In many cases the successful occurrence of the process is probably associated with sufficiently high mobility of the fundamental species. In the low-temperature oxidation of metals the formation of very thin passive films several ångströms thick, which separate the reactants in space, leads to almost complete cessation of the process. If in this case autocatalysis does in fact take place, it is quite clear that the maximum rate is achieved on attaining a degree of reaction which is difficult to determine quantitatively even by the most refined experimental methods.

On the other hand, when the mobility of the species and the porosity of the product are sufficiently high and satisfactory contact is achieved between the reactants, the maximum rate can be attained at high degrees of reaction, which are readily determined experimentally. For example, in the reduction of cuprous and cupric oxides with carbon monoxide the highest rate was observed at high degrees of reaction, amounting to 20–70%, depending on the experimental conditions[64].

All that has been said does not exclude a certain role of the A–B interface and of the product B and its physical state in the kinetics of the reaction.

III. CATALYSIS BY A SOLID PRODUCT

In recent years the problem of catalysis by a solid product has been discussed frequently. Some authors believe that catalysis by a solid product is a specific feature of topochemical processes[25,32,65–70], while others deny that the product has any effect on the rate of reaction[30,31,56,71–74]. Each investigator bases his view on particular experimental data. In all the above investigations the area of the reaction surface could not be estimated. This is not only because of the difficulty of an accurate determination of the surface area of solids. It should be borne in mind that in powdered preparations the true surface area, which may be very high, in some cases cannot be entirely involved in the reaction at once and in crystalline specimens the area of the reaction surface changes during the process due to the "corrosion" of the crystals.

The present author believes that a categorical formulation of the question of the inevitable catalytic effect of the solid product on the topochemical reaction, in isolation from the experimental conditions and the physical state of the solid phases, is pointless. This follows if only from the vast experimental data which show that the appearance of the product can both accelerate the process (catalysis) and retard it (impedance). Therefore the assertion by Sakovich and Boldyrev[32] that the solid product formed in the reaction must *always* (author's italics) have a catalytic effect on the further process when there is an interface

between it and the initial material can be scarcely regarded as valid.

We shall now consider certain examples. In their study of the decomposition of silver oxide, Pavlyuchenko and Gurevich determined the rate of reaction from the change in the pressure of the oxygen evolved per unit time[31]. They observed that, when silver oxide was mixed with powdered silver obtained by the decomposition of the oxide, the rate of reaction did not change. However, complete removal of the product by careful treatment of the partially decomposed silver oxide with mercury did not retard but actually accelerated the process. Probably in this case catalysis by the product could not occur, being suppressed by the blocking effect of the silver produced. It is known that in some cases at high degrees of chemical supersaturation the reaction MO → M leads to the appearance of a very thin layer of metal which separates the initial phase from the gaseous medium and inhibits the process[50,75-77]. Earlier it was observed[70] that the mercury additive does not affect the rate of decomposition of AgO, the presence of copper has no effect on the decomposition of CuO[73], etc.

However, one cannot compare the effect of a product mixed mechanically with the initial preparation, and therefore making a very imperfect contact with the former, with the effect of a product formed as a result of the reaction, and as a rule corresponding to the parent phase as regards orientation and dimensions[78]. According to certain investigators, the catalytic effect of the product can occur only in those cases where there is sufficiently satisfactory contact between it and the initial substance. For catalysis, it is necessary to have a distinct interface between the solid phases. Boldyrev[25,79] frequently drew attention to this condition.

Boldyrev investigated together with Ermolaev the catalytic effect of solid products in the reduction of nickel and copper oxides with hydrogen[25]. The dimensions of the NiO and CuO particles were in the range 0.01–0.06 mm. It was found that, if NiO is subjected to partial preliminary reduction with hydrogen, the rate of its subsequent reduction under the same conditions is very much higher than the rate of reduction of the initial oxide. On treatment of the partially reduced NiO with a solution of mercuric nitrate, the rate-of-reduction curve was almost identical with the curve for the pure oxide. According to the authors, this proves the catalytic effect of the product.

Possibly this is so. However, can one regard such proof as unambiguous? Probably not. Above, the present author showed that the "corrosion" of crystals during the process and the reproduction of the initial solid phase–gas interface, the porosity, and also the defects in the crystal lattice can greatly accelerate the reaction. It is noteworthy that in the experiments of Boldyrev and Ermolaev the effect of these factors was not excluded. The "washing out" of the reaction centres and microcrystals by treatment of the partially reduced oxides with a mercuric nitrate solution can give rise to capillary forces so high that the defects are undoubtedly "healed", i.e. the initial preparation is "aged". This last condition must always be taken into account in the analysis of the kinetics of topochemical reactions[5]. Consequently the retardation of the process can be caused not only by the removal of the product (the catalyst) but also by other factors.

From the above standpoints, one can scarcely regard the catalytic effect of the product in experiments on the decomposition of pyrite as unambiguously proved[80]. Here there is a break in the kinetic curve, beyond which the rate of dissociation increases sharply. X-Ray diffraction studies confirm that, before the appearance of the break, a solid solution was formed, while beyond it crystals of the product were deposited. However, it remains obscure whether the acceleration of the process is due to the catalytic effect of the product or due to autocatalysis caused by an increase in the area of the reaction surface.

The essential feature of the mechanism of the accelerating effect of the product on the topochemical reaction is that the step involving the addition of a fundamental particle to an already existing small crystal of the new phase requires a smaller expenditure of energy (per gramme atom or per particle) than the formation of the three-dimensional nucleus of the new phase itself. In other words the activation energy for the two-dimensional growth of the new phase must be smaller than the analogous quantity for the three-dimensional growth of the solid product. Even a small difference between the two activation energies can give rise to an appreciable difference between the rate constants for the three-dimensional (k_V) and two-dimensional (k_S) growth of the new phase, since both k_i and E_i are related by the exponential expression

$$k_i = k_i^0 e^{-\frac{E_i}{RT}} . \qquad (18)$$

These postulates constitute the basis of the explanation of a number of features of the mechanism of topochemical reactions, for example in the work of Esin and Gel'd[37], Boldyrev[11], and others. Thus the following microscopic picture of the mechanism for the thermal decomposition of an oxide is suggested[21,81]. On the metal–oxide interface, electrons pass from the O^{2-} anion to the metal. As a result of the "relay" transition of electrons, an oxygen ion and not an oxygen atom will appear in the neighbourhood of the metal. An oxygen atom will appear on the outer surface of the oxide in the neighbourhood of the gas phase. The accumulation of such atoms should result in the formation of molecular oxygen and its desorption. A negatively charged crystal of a metal grows by attracting cations from the oxide lattice.

Apart from definite advantages, the mechanism has certain disadvantages. It is invoked in order to explain the catalytic effect of the product and therefore it is based on the presence of a distinct interface between the oxide and the metal. The growth of the metallic phase at this interface without the removal of oxygen anions should involve considerable steric hindrance. But the mechanism does not explain where and how the oxygen anions are removed.

The diffusion of oxygen, which is a slow process, could complicate the reaction. On the other hand, the occurrence of the process under kinetic conditions is evidence of unhindered removal of oxygen. This can be explained on the basis of the difference between the volumes of the new and old phases, leading to continuous regeneration of the pores, the oxide–gas interface, and the defects in the surface layer of the oxide. Probably this mechanism, taking into account the formation of pores and defects, may prove quite acceptable also for the reduction of oxides to metals by gaseous reducing agents.

Turning again to the relative values of the activation energies for the growth of the new phases in the bulk (E_V) and on the surface (E_S), it must be emphasised that in principle one cannot exclude also the possibility that

$$E_S > E_V \qquad (19)$$

In a slightly different form this confirms the principle of correspondence as regards orientation and dimensions, formulated on the basis of the systematic examination of the experimental data: "the phase reaction on the surface of a solid involves the formation of a new crystal lattice which corresponds, as regards orientation and dimensions,

to the crystal lattice of the initial surface if the energy (E) of deformation of the two-dimensional lattice of the new phase is smaller than the work (A) required for the formation of its three-dimensional nucleus... Otherwise, when $E > A$, the process takes place independently of the structure of the surface of the initial phase"[82]. Here it is appropriate to recall yet again Erofeev's data[17] on the formation of an amorphous product on the A–B interface. The above scheme probably does not exhaust the possible different versions of the mechanism of process catalysis by a solid product.

The accelerating effect of the gaseous product in some cases is striking. Thus the thermal decomposition of potassium azides takes place more rapidly in the presence of potassium vapour than in a vacuum[83]. The experimental data obtained by Tumarev and Pushkarev[84], who investigated the reduction of powdered cupric oxide (–0.050) [particle size 0.050 mm? (Ed. of Translation)] and a gaseous reducing agent (carbon monoxide) are of considerable interest. The product obtained was used as an activator. Three types of experiments were tried: (1) a 0.5 g layer of the activator was placed under a CuO sample (4 g), (2) 0.5 g was mixed with the sample, and (3) a 0.5 g layer was placed on top of the sample. In all cases the presence of the activator resulted in the reduction of cupric oxide at temperatures below 100°C, i.e. under conditions where the process did not develop in the absence of the product. The activator placed underneath the oxide sample proved to have the greatest effect, while the layer of activator on top of the sample to be reduced had no catalytic influence. The authors concluded that the catalysis is due to the activation of the reducing gas by the solid product. They postulate the desorption of the gas from the surface of the catalyst, which retains its activity during a period sufficient for transition to the reaction zone. It would be interesting to test how a change in the distance between the activator and the sample being reduced affects the interaction. Mass-spectrometric (or some other) analysis of the gas which has just passed through the layer of activator would be valuable.

The present author believes that in this case we are dealing with an unusual version of a chain reaction mechanism: an increase in the amount of the solid product results in an increase of the number of activated species in the gas phase which in turn accelerates the conversion of the initial solid phase into the product. Of course under these conditions the area of the reaction surface and its regeneration must be such that unhindered utilisation of an increasing amount of activated species from the gas phase is permitted. The attainment of a maximum rate and the subsequent retardation of the process must be treated here as a stage in which the capacity of the oxide surface to utilise all the active species from the gas has been exhausted.

Tumarev and Pushkarev's experiments confirm the present author's view, stated earlier, on the role of the gas phase, the porosity, and the oxide–gas interface in the mechanism of the reduction of oxides to the metals by gaseous reducing agents[35,61,63]. At the same time, Boldyrev's assertion[79] that the catalytic effects of the product can be shown only when the contact between the latter and the starting material is sufficiently good, probably cannot apply to all cases of acceleration of topochemical processes by the new solid phase.

When autocatalysis in the reduction of oxides to the metals is approached from the standpoint of electronic hypotheses, it is noteworthy that the formation of the metallic phase may be accompanied by a sharp increase in the number of free electron-acceptor energy levels. This in turn may facilitate and accelerate the reducing gas chemisorption stage, and may increase the amount of adsorbate on the surface of an oxide with mixed (electronic-ionic) conductivity[8,12,15]. Here the assertion[79] that contact between the solid phases is essential for catalysis to take place appears to be quite appropriate.

Analysis of the possible reasons for the acceleration of reactions (1) and (2) shows that they may be different, for example, in the dissociation of oxalates and carbonates, on the one hand, and the reduction of oxides, on the other. While in the first case the breakdown of the crystals, self-dispersion and regeneration of defects, can have a decisive effect on the course of self-acceleration, in the second case one must take into account the electronic factor in the chemisorption of the reducing gas. Thus analysis of the literature data leads to the following conclusions.

1. The classical mechanism of autocatalysis, which is based on the increase of the area of the interface in the course of the process is inadequate and cannot be universal.

2. Autocatalysis due to the increase in the area of the reaction surface and catalysis by a solid product are so mutually interconnected that in most experiments it is difficult to separate them and to investigate them in a pure form.

3. The gas phase, the development of porosity, and the regeneration of contacts between the initial solid phase and the gas play a major role in the development of autocatalysis.

4. Catalysis by the product can occur only when its inhibiting effect on the process is suppressed.

In connection with this last feature of the topochemical reactions analysed, the impedance phenomenon will be examined in greater detail.

IV. THE IMPEDANCE PHENOMENON

Numerous experimental data have now accumulated, showing how the physical state of the product influences the kinetics of the relevant topochemical reactions. It has been observed that in some cases the formation of the product lowers the rate of reaction. This is explained by the blocking of the initial solid phase, the separation of the reactants, and the occurrence of diffusion-dependent retardation. In other cases the product does not prevent appreciably contact between the reactants and cannot significantly retard or stop the process.

The available experimental data will now be quoted and initially those cases will be considered where the formation of a product separates the reactants and sharply reduces the rate of reaction.

1. All metals, except the noble metals, are thermodynamically unstable under the usual atmospheric conditions and should be oxidised. However, most of them, except for the alkali and alkaline earth metals, virtually do not oxidise. It has been shown that the reason for this stability is the formation of a thin protecting film of oxide, which separates the reactants and prevents further interaction of the metal with atmospheric oxygen[85].

2. High-temperature oxidation of metals yields in many cases a dense layer of scale, which lowers the rate of the process. The direct interaction between the oxidising gas and the metal is replaced by a slow diffusion-dependent process.

3. The blocking of the initial phase has proved to be particularly successful when the system is alloyed to

impart to it heat-resistant properties. Arkharov showed[86] that in this case high-temperature oxidation leads to the formation of a dense protective layer, consisting of spinel-type oxides with the smallest possible lattice constants.

4. Isothermal carbonation of calcium oxide crystals takes place with great difficulty, since the product (calcite) has a smaller density than the initial preparation and a continuous coating is formed. One may refer to the example quoted by Rostovtsev[87]: lime obtained by the heat treatment of calcite required exposure for three days to an atmosphere of carbon dioxide at 850°C in order to reabsorb two thirds of the carbon dioxide evolved.

5. In experiments on the reduction of polycrystalline specimens of fused magnetite with hydrogen the process was found to be retarded from its very beginning[52]. Despite its porosity, the coating produced presents a definite obstacle to the penetration of the reducing gas into the reaction zone. In this case Knudsen molecular diffusion of the gases (the reactant and the product) occurs. However, even such migration of gases can prove to be the rate-limiting step of the process.

6. In the reduction of natural magnetite single crystals Edstrom observed considerable inhibition of the process due to the formation of a compact layer of wustite as the product[42].

7. The reduction of oxides sometimes leads to the formation of the metal as a thin compact layer, although the appearance of a porous product would be expected from the relative volumes of M and MO. Thus in the reduction of cuprous oxide with carbon monoxide vigorous formation of metallic copper is observed from the very beginning of the process, so that, over a very short period, the initial solid phase becomes covered by a compact copper film, which protects the entire specimens from further action of carbon monoxide; the reduction of Cu_2O ceases[75].

A similar phenomenon was observed in the reduction of wustite with hydrogen[50,76]. Electron-optical studies showed that the iron film formed did not have any pores. In this case the reaction is very slow. According to the authors it was possible only by virture of the diffusion of oxygen through the thin metal film. Calculation of the activation energy for such diffusion gives 53 000 ± 4000 cal g-atom O.

8. The sintering or recrystallisation of spongy metal in the reduction can retard the reaction. This was observed, for example, in the experiments of Chufarov and Lokhvitskaya[22] in the reduction of magnetite with hydrogen and also in a comparative conductimetric study of the rates of oxidation of copper and the reduction of its oxides[60].

Here one should also bear in mind the possibility of a lowering of the catalytic effect of the product with increase in temperature. For example, the iron catalyst for the synthesis of ammonia is prepared by the fusion of iron oxides with K_2O, CaO, Al_2O_3, and SiO_2 additives with subsequent reduction of this mixture of oxides with hydrogen to the attainment of an active state[88]. As the reduction temperature is raised, the catalyst surface is deactivated.

At any rate the experimentally observed negative temperature coefficients of the rates of the topochemical reactions analysed probably cannot be attributed solely to the sintering and recrystallisation of the product.

9. It should also be noted that any autocatalytic process is completed with a continuous decrease of rate, which corresponds to the descending branch of the "rate–time" kinetic curve. The retardation of the process is not due only to the narrowing of the reaction front but also to an increase in the thickness of the outer layer of product[89]. In many cases one can observe how autocatalysis is replaced by impedance.

The above examples have been quoted to illustrate the role of impedance in the kinetics of reactions of types (1) and (2).

V. UNBLOCKING OF THE INITIAL SOLID PHASE

The weakening of the impedance or its suppression play an important role in the kinetics of the processes analysed. We shall now examine the experimental data which show that the loosening of the product and also the improvement of the contact between the reactants facilitate the process and accelerate it. Here the following data are relevant.

1. When the oxide film protecting the metal from the effect of the gas phase is scratched, the contact between the reactants is restored. This phenomenon is used to dissolve the metal and to isolate the protective film in a "pure" form, which constitutes one of the experimental proofs of the existence of protective films[29].

2. Periodic cracking of the scale under the influence of stresses arising in it during the high-temperature oxidation of metals is reflected in breaks on the kinetic curve. The breaks can be explained by the acceleration of the process due to the renewal of contact between the metal and the gas phase each time the scale cracks[90,91].

3. The oxidation of alkali and alkaline earth metals is accompanied by the formation of a loose layer of products. Even at room temperature under the usual atmospheric conditions the initial solid phase is completely converted into oxide after a relatively short time. Here one may refer to numerous experimental data: a typical example is the oxidation of barium at 17°C in "room" atmosphere[92].

4. In 1941 Arkharov established that the rate of oxidation of iron increases with the appearance of a wustite layer in the scale[93]. The appearance of structures with cationic vacancies (wustite or the porous modification of hematite) facilitates the diffusion of iron ions and accelerates the oxidation process. The heat resistance principle formulated by Arkharov is based on the prevention of the formation of the wustite phase and the creation of conditions for the formation of dense oxides of the spinel type[86].

5. Carbonate dissociation processes take place much more rapidly than the reverse reactions. The thermogram for the dissociation of calcium carbonate and the carbonation of calcium oxide, recorded by Potapenko for the same specimen[94], is very instructive in this respect. Heating and cooling of the preparation in a stream of carbon dioxide results in two temperature arrests, at about 918° and 888°C, the extent of the first being much greater than that of the second. Consequently at a given rate of supply or removal of heat, the amount of carbonate decomposed is greater than the amount formed. This is the result of the different rates of diffusion of carbon dioxide through the coating, which proves to be looser during dissociation (calcium oxide) than during carbonation (calcium carbonate).

6. In the reduction of oxides and ores to the metals the reaction product is frequently porous with an extremely large surface area. The methods of preparation of pyrophoric metals by reducing polycrystalline specimens at low temperatures are widely known. The reduction of iron ore usually results in the formation of "spongy" iron.

Bogdandy et al.[46], who investigated the mechanism of the reduction of porous iron ore, concluded that in most cases contact between wustite and the reducing gas is not impaired by a layer of metallic iron. On the basis of microscopic studies, Edstrom[42] explained the faster reduction of ferric oxide compared with other iron oxides by the earlier and more abundant formation of pores in the products.

7. A comparative conductimetric study[61,95] of the rates of oxidation and reduction of iron revealed marked loosening of the metal after the completion of the cycle incorporating the forward and reverse reactions. Because of this, the time consumed in the reduction of wire specimens until the recovery of the initial resistivity proved to be much lower than in the oxidation. Sometimes this difference is as much as 100%.

8. The crystallisation process in the dehydration of hydrates is accompanied by the formation of cracks (pores), usually perpendicular to the interface between the solid phases[96]. These pores facilitate the subsequent development of the process.

9. Some investigators have shown that the removal of the product blocking the initial solid phase and separating the reactants accelerates the process. For example, Pavlyuchenko and Gurevich observed that the removal of the product accelerates the decomposition of silver oxide[31].

Thus numerous experimental data suggest that in reactions between solid and gaseous substances the unblocking of the solid phase blocked by the condensed product may significantly facilitate the process. We now see the great importance of the physical state of the product in the kinetic analysis of reactions (1) and (2). Therefore a systematic arrangement of all these data, i.e. their generalisation in a single rule or principle is extremely desirable. This has been done only in the field of chemical corrosion of metals.

VI. THE PILLING–BEDWORTH RULE AND THE PRINCIPLE OF THE ACCELERATION OR RETARDATION OF REVERSIBLE TOPOCHEMICAL REACTIONS WITH PARTICIPATION OF GASEOUS AND SOLID REACTANTS

In 1923 Pilling and Bedworth[34] formulated a rule for the isothermal oxidation of metals, the significance of which is that the formation of a compact film of oxide on the metal inhibits the subsequent interaction of the latter with the gas, while the appearance of a loose (porous) product does not hinder the process. The type of product formed depends on the relative volumes of the metal oxidised and the oxide produced.

Mathematically the rule formulated by Pilling and Bedworth can be described by two formulae:

$$\frac{V_O}{V_M}=\frac{Md_M}{And_O}<1 \qquad (20)$$

and

$$\frac{V_O}{V_M}=\frac{Md_M}{And_O}>1\,, \qquad (21)$$

where V_O is the volume of the oxide formed in the interaction of one gramme-atom of the metal, V_M the gramme-atomic volume of the metal, A the atomic weight of the metal, M the molecular weight of the oxide, n the number of metal atoms in the oxide molecules, and d_M and d_O are the densities of the metal and the oxide respectively. Eqn. (20) is valid for the oxidation of alkali and alkaline earth metals. Here the formation of a loose film does not lead to the separation in space of the reactants M and O_2:

$$M+\tfrac{1}{2}O_2\rightarrow MO\,. \qquad (22)$$

According to other hypotheses[29], a very thin pseudomorphous film of oxide forms between the solid phases and cannot cause serious diffusion-dependent inhibition of the process. Therefore the law governing the growth of the oxide layer is linear.

Eqn. (21) holds in the oxidation of most of the technically important metals (aluminium, zinc, copper, nickel, manganese, iron, chromium, cobalt, tungsten, etc.). It leads to a parabolic or a logarithmic relation between the weight of the oxidised metal (or the thickness of the oxide film) and time [Eqns. (4) and (5)].

The Pilling–Bedworth rule is of limited applicability for the following reasons:

1. It takes into account only the ratio of the volumes of the solid phases, disregarding their structural features.

2. Apart from the true volume of the oxide, there exists also the apparent volume. The difference between the rates of diffusion of ions in the high-temperature oxidation of metals, for example, results in the apparent volume of the oxide becoming much larger than the volume calculated from the ratio of the densities of M and MO.

The experiments of Wagner[97] and Ol'shanskii[51] on the conversion of silver and copper into their sulphides showed that the process occurs via the preferential diffusion of the cations through the layer of the solid product. This leads to the appearance and coagulation of pores. In the limit cavities may form, which are, as it were, negative imprints of the oxidised specimen.

The formation of iron scale under industrial conditions is accompanied by the appearance in the inner layers of macropores which are visible even with the naked eye.

3. The occurrence of internal stresses in the oxide layer due to the different densities of the metal and the oxide, phase transitions, temperature oscillations (deviations from the specified temperature of the process), and other factors leads to the cracking of the scale, which may result in the degeneration of the parabolic relation to a linear relation, for example, as shown in Fig. 3.

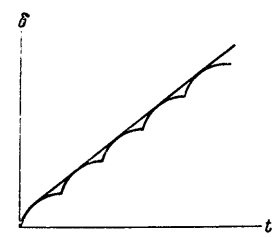


Figure 3. Transformation of a parabolic relation into one of a pseudolinear type.

4. It is possible to select such process conditions that, when Eqn. (21) holds, the product is loose (porous) and, conversely, when the inequality (20) holds, the product may become compact.

The development of the theory of the oxidation of metals suggests that the mechanisms of chemical and electrochemical corrosion have much in common, in addition to certain differences. Thus, according to the data of a number of investigators[51,98,99], chemical oxidation of a metal should be regarded as due to the operation of electrochemical cells in which the role of the metallic conductor and the electrolyte is fulfilled by the oxide phase which exhibits

mixed (electronic and ionic) conductivity. Electrochemical oxidation is also treated as the result of the operation of electrochemical corrosion cells[29].

However, in one case (in chemical oxidation) the reaction between iron and oxygen yields a compact oxide film. As a result, the reactants are separated in space, the process is retarded, and is possible only via the diffusion of elementary species. In another case (in electrochemical corrosion of iron) the product (rust) may be porous despite the fact that its volume is greater than that of the metal oxidised.

5. Finally, it is possible to set up such temperature conditions that the loose oxide begins to sinter, and, despite Eqn. (20), the process is retarded and the linear relation in kinetic plots is converted into one of a parabolic or logarithmic type; on the other hand, on loosening or sublimation of the compact oxide, it is possible to obtain a linear relation between the weight of the metal which has reacted and time.

The above considerations lead to the following conclusion. Under the conditions of isothermal oxidation of the metal, the protective film does not always have the density and the structure of the compact oxide of the same composition. Consequently, the main factors which influence the acceleration or inhibition of the process are not those defined by formulae (20) and (21) but the physical state of the product and the mechanism of the reaction. This conclusion is even more convincing if one goes beyond the limits of chemical corrosion into the wider field of topochemical reactions described by formulae (1) and (2). This is demonstrated by numerous experimental data, described in sections IV and V of the present review and in the literature[9,11,13,15].

Thus one may conclude that the modern state of the theory of topochemical processes analysed in the present article is not yet consistent with the experimental data which have accumulated. The Pilling–Bedworth rule and also Arkharov's heat-resistance principle have played a major role in the determination of the general trends in the acceleration or retardation of topochemical reactions; however, their applicability is restricted to the field of chemical corrosion of metals.

Dankov's principle of orientational and dimensional correspondence applies directly to the mechanism of the reactions considered. Its great theoretical and practical value is generally known. However, it does not determine directly the mode of acceleration or retardation of the relevant reactions.

One must of course bear in mind that no one rule or principle can pretend to be fully universal and cannot embrace all the wide variety of factors which influence the kinetics of topochemical reactions. How wide is the range of these factors, which include all the chemical and physical phenomena accompanying the development of the process, can be assessed if only from the thermal decomposition of solids[5]. At the same time the systematised experimental data on the blocking and unblocking of the initial solid phase in its interaction with the gaseous medium show how great is the role of impedance in the kinetics of topochemical processes. Analysis of the phenomenon of autocatalysis shows that the maximum rate can be attained at high degrees of reaction only when sufficient contact between the reactants is maintained throughout the entire period of self-acceleration and the chemical reaction takes place under kinetic conditions. It becomes clear that there exists in this field a more general kinetic principle, including as a special case the Pilling–Bedworth rule, of recognised value in the field of chemical corrosion of metals but which requires correction on going to the wider field of topochemical reactions.

Analysis of experimental data permits the formulation of the kinetic principle for topochemical reactions with participation of solid and gaseous reactants under isothermal conditions in the form of the following postulates:

1. When reactions of the type

$$A(solid) \rightleftarrows B(solid) + C(gas),$$

$$A(solid) + C(gas) \rightleftarrows B(solid) + D(gas)$$

are thermodynamically possible, the continuous formation of the product is possible only when the phases [i.e. the initial phase (A) and the gaseous phase] are in contact. An increase of the contact surface by dispersing phase A may accelerate the process, reduce its duration, and increase its extent.

2. The blocking of the initial solid phase by the product B (or A in the reverse reaction) leads to the separation in space of the reactants and the occurrence of hindrance to the process, which undergoes a transition from kinetic to diffusion-dependent conditions. Then both the rate of diffusion of elementary species through the crystal lattice of the compact product and the rate of Knudsen molecular flow may prove to be the rate-limiting component of the topochemical reactions considered.

3. When the solid phase is unblocked as a result of the cracking of the layer of product, by the formation in the latter of pores, or by its artificial loosening or even removal (for example by sublimation), the reaction may be significantly facilitated even under diffusion-dependent conditions, and under favourable circumstances (effective unblocking) may result in a return to kinetic conditions. Then, if during some period spontaneous growth of the reaction surface or an accelerating effect of the product is observed, the process may become autocatalytic.

In conclusion it must be emphasised that the above postulates are of the kinetic type and have nothing in common with the thermodynamic principle of the displacement of equilibrium (the Le Châtelier–Braun principle[100]), according to which the removal of the product should favour a higher degree of conversion regardless of the time consumed.

The necessity for a clear formulation of the principle governing the acceleration or retardation of topochemical reactions is dictated by the following considerations. In the first place the kinetic rules and principles available at the present time (the Pilling–Bedworth rule and the Arkharov principle) are restricted to the field of chemical corrosion. However, the experimental data which have accumulated show a considerable influence of the physical state of the product on the kinetics of a wider range of topochemical processes. Secondly the formulation of the principle should indicate the general pathways involved in the acceleration (and, where required, also retardation) of isothermal reactions of the given type. Thirdly one can encounter in the literature directly opposed views: some authors believe that the product inevitably accelerates the process, while others reject this. The above general principle shows that, depending on the process conditions and the physical state of the interacting solid phases, three cases are possible: (1) the product does not influence the rate of the process; (2) the product accelerates the reaction (catalysis); (3) the separation of the reactants by the product inhibits the process (impedance).

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