Translated from *Uspekhi Khimii*, **43**, 782-792 (1975) U.D.C. 541.124 : 541.451

Thermal Decomposition of Solid Metal Oxides

G.V.Malinin and Yu.M.Tolmachev

Certain aspects of the kinetics and mechanism of the thermal dissociation of solid metal oxides are considered, and two types of decomposition differing in mechanism—radical and molecular—are discussed. The possibility of elucidating characteristic features of these types of dissociation is analysed. A list of 81 references is included.

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I. INTRODUCTION

The attention paid by research workers to the thermal dissociation of solid metal oxides is due primarily to the fact that such reactions, together with the dissociation of carbonates and sulphides, form, in Rostovtsev's descriptive expression[1], "a kind of cornerstone of the thermodynamic study of metallurgical processes". A fairly comprehensive literature has appeared on the thermodynamics of the thermolysis of metal oxides (see e.g. the monographs[1-4] and the references in them).

Far fewer kinetic studies have been made on the thermal decomposition of solid oxides. Yet investigation of the formal kinetics and detailed examination of the mechanism of these reactions is important for several reasons. Firstly, establishment of the fundamental kinetics of the thermolysis of solid metal oxides may be of practical value, since it is probable that such processes largely determine the chemistry of the thermal reduction with carbon of many readily dissociated oxides[5-9]. Secondly, the condensate dissociation (Kulikov's term[2]) of oxides belongs to the broad class of reactions

$$A(solid) = B(solid) + C(gas). \quad (1)$$

Investigation of the decomposition of oxides may be expected to clarify many features of such reactions, such as "nucleation", the autocatalytic effect, etc. Here it is noteworthy that, because the volume relations of the initial higher oxides do not greatly differ from those of the oxide products[10], pore formation, which usually complicates the investigation of topochemical reactions[11], has no marked effect. (An original technique permitting extremely delicate monitoring of the variation in the degree of dispersion of metal oxides during various redox reactions has recently been developed by Mardaleishvili et al.[12-14]) Thirdly, the kinetic behaviour of a substance reflects its intrinsic properties. Study of the kinetics of the decomposition of solid oxides and its mechanism will permit a deeper insight into the nature and structure of these compounds.

A most comprehensive survey of kinetic problems of the dissociation of metal oxides was made by Esin and Gel'd[4]. Garner[15] and Young[16] made detailed analyses of experimental results on the thermolysis of silver oxide.

II. FORMAL KINETIC INVESTIGATIONS OF THE THERMAL DECOMPOSITION OF METAL OXIDES

Until recently the kinetics and the mechanism of the thermal dissociation of oxides were investigated almost solely by the formal kinetic method, which consists essentially in finding the time dependence of the reaction velocity, and hence reaching conclusions on the reaction mechanism. Many formal kinetic equations, deduced from very different views on the mechanism of the processes, were suggested to describe the course of the heterogeneous decomposition of solids. Pavlyuchenko[17] reckoned that about forty such equations had been proposed. Kinetic investigation of the thermal decomposition of oxides and solids in general can be regarded as originating in 1905 with the work of Lewis on the thermolysis of silver oxide[18]. He gave a kinetic equation and attempted to explain the mechanism of the reaction.

Formal kinetic investigations have now been made on the decomposition of the oxides of silver[18-25], manganese[5,6,26], copper[8], terbium and praseodymium[27,28], chromium[29], lead[9,30-32], cobalt[7], and uranium[33-39]. Several of these papers, in particular those of Rostovtsev and his coworkers, as well as certain papers by Vlasov and Beketov, do not give formal kinetic equations for the reactions investigated, although they do contain graphs illustrating the dependence of reaction velocity on degree of conversion.

Investigations on the dissociation and the reduction of manganese and copper oxides, of great importance for the theory of metallurgy, were made under the direction of Chufarov[40-42]. Unfortunately, no quantitative data on the formal kinetics of the reactions were given, although indications appeared of their topochemical character. The effects of temperature and oxygen pressure on the rate of decomposition of the oxides were traced, and activation energies determined for the thermolysis of manganese dioxide, manganese sesquioxide, and copper(II) oxide.

Several conclusions can be reached from a general analysis of experimental data on the formal kinetics of the thermal decomposition of solid metal oxides.

If the range of homogeneity of the initial higher oxide is sufficiently wide, the decomposition curves obey the equations of diffusion kinetics within this region. For example, the thermolyses of $PrO_{1.72-y}$ and U_3O_{8-y} [29,38] are well described by the equation

$$\frac{X_0 - X}{X_0 - X_\infty} = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(-\frac{n^2\pi^2 Dt}{R^2}\right) , \qquad (2)$$

where R is the radius of a spherical oxide particle, t is the duration of the experiment, and X_0, X, and X_∞ are the quantities of oxygen in the oxide initially, at moment t, and after an infinite time respectively. The postulates made in deducing this equation—that the specimen consists of spherical particles of the same radius, that equilibrium corresponding to the final composition of the oxide is rapidly established at the solid–gas interface, and that the diffusion coefficient is independent of X—are obviously not too crude. This work[29,38] enables the relative ease with which oxygen atoms move through the oxide lattices to be assessed: the activation energy for the diffusion of oxygen in $PrO_{1.72-y}$ and in U_3O_{8-y} is respectively 42 and 45 kcal mole^{-1}.

In spite of the apparent complexity, treatment of experimental results by means of Eqn. (2) presents no great difficulty. The dependence of $\lg(X - X_\infty)$ on time when t is large should be linear with a slope of $-\pi^2 D/2.3R^2$. Having evaluated this quantity, we can easily plot the curve even at small values of t, and with R known, e.g. from measurements of specific surface, we can calculate the diffusion coefficient. It is therefore often inadvisable to use various simplified forms of the diffusion equation, e.g. the equation[43-45]

$$\alpha = kt^{1/2} , \qquad (3)$$

where α is the degree of conversion and k the specific rate constant.

When the ranges of homogeneity of initial and final oxides are narrow, the decomposition curves are described by extremely diverse equations of topochemical kinetics. The most usual[27,28,30,31] is the "contractile sphere" equation deduced by Roginskii and Shul'ts[46]. The experimental results satisfy the same kinetic equation for a fairly wide range of degrees of conversion, which, from our point of view, underlines the near invariability of the state of aggregation of the substances. Cracking of the fine oxide crystals is improbable, because the volume relations of initial and final oxides do not markedly differ. Nor should sintering greatly complicate the observed pattern, since kinetic examination of the decomposition of oxides is usually made in an inert atmosphere or in a vacuum at moderate temperatures.

Deviations from the curve at low degrees of conversion are due both to the complexity of nucleation processes[15,16,32] and to the possible occurrence of decomposition within the range of homogeneity of the initial higher oxide[26]. The slowing down of the reaction at high degrees of conversion probably has several causes, e.g. the formation of a dense layer of reaction products, through which oxygen must diffuse. Furthermore, dissociation may then occur within the range of homogeneity of the final oxide. An example of such behaviour is the decomposition of higher oxides of uranium to U_3O_{8+x}, the upper limit of which probably extends to the composition $UO_{2.76}$.[47]

Thus the kinetics of the thermolysis of oxides, while having much in common with other reactions of type (1), possesses its peculiarities resulting from the wide dissemination of non-stoichiometric compounds among the oxides.

III. CLASSIFICATION OF THE THERMAL DISSOCIATION OF METAL OXIDES

The mechanism of the dissociation of solid metal oxides is usually regarded as comprising the stages—"(i) formation of oxygen atoms adsorbed at the interface, (ii) their combination to molecules, (iii) desorption of oxygen molecules, and (iv) formation and growth of nuclei of a new phase"[4]—among which Lewis[18] assumed (ii) to be the slowest. Breakdown of the initial higher oxide is now regarded as meeting this criterion.

However, several experimental facts are inconsistent with this simple scheme[48]. Thus because the structure of the transition complex is closely similar to that of the reaction products of an endothermic reaction[49,50], for example, the activation energy of the thermal decomposition of oxides should, according to the above scheme, be similar in magnitude to the heat of reaction

$$M_nO_x \rightarrow M_nO_{x-1} + [O](\text{solid}) , \qquad (4)$$

where [O](solid) represents an oxygen atom adsorbed at the interface between initial and final oxides. The energy of interaction of such an atom with the matrix of the solid oxide is difficult to determine, but obviously the heat of reaction (4) should not greatly differ from the heat of reaction

$$M_nO_x \rightarrow M_nO_{x-1} + O(\text{gas}) , \qquad (5)$$

which can easily be calculated from tabulated enthalpies of formation. The heat of reaction (5) for oxides undergoing decomposition is usually considerably greater (by 40–50 kcal mole^{-1}) than the heat of reaction

$$2M_nO_x \rightarrow 2M_nO_{x-1} + O_2 . \qquad (6)$$

Experimental activation energies of the thermal condensate dissociation of oxides are usually closely similar to the heat of reaction (6), and in any case considerably smaller than the heat of reaction (5)[5-9,18-42].

The reason why this discrepancy was ignored for such a long time probably lies in the history of the development of kinetic investigations. Lewis's early work on the decomposition of silver oxide was followed by a fairly lengthy period (until the end of the 1940s) during which the kinetics of the dissociation of oxides remained almost uninvestigated. But very sound kinetic studies were made during this time on the decomposition of carbonates and hydrates[4,15,16], which showed that in the majority of cases the activation energy of these reactions was equal to the heat of reaction (1) with C representing the CO_2 or H_2O formed. This result is entirely consistent with the theory of the activated complex. By the start of the new period in the kinetic investigation of the thermal dissociation of oxides the view had already become deeply rooted that full identity existed between the decomposition of oxides and the thermolysis of carbonates and hydrates. Since molecular oxygen is an end-product of the former reaction, it was accepted as entirely natural, by analogy with the latter[26], that the activation energy should coincide with the heat of reaction (6).

There remains at least one further extremely interesting problem—the irreversibility of the thermal decomposition of certain oxides—which probably cannot be solved in terms of the existing model. This is of some practical importance, since the irreversibility observed with several higher oxides casts doubt on the significance of determinations of their dissociation pressures, e.g. of oxides of lead[51], manganese[52], and uranium[53].

In view of all the above considerations, further development of the theory of the thermal dissociation of solid metal oxides is obviously necessary on the basis of fresh experimental results.

A very useful method for elucidating the mechanism of a complicated process is to record the reaction intermediates; it has been widely employed in the kinetic investigation of homogeneous chemical reactions[54-56]. Atomic oxygen has recently been increasingly widely recorded as intermediate in several cases of the thermal decomposition of solids, including oxides[30-32,39,48,57-61]. Experiments have shown that the thermal dissociation of some oxides is accompanied by the evolution only of molecular oxygen, whereas both atomic and molecular varieties are evolved in the thermolysis of other oxides. Furthermore, the latter decompositions were found to be reversible, whereas those accompanied by the evolution only of molecular oxygen were irreversible[31,32,39,48,60,61]. (The possibility of the evolution of atomic oxygen in the thermal decomposition of certain solid metal oxides was probably first mentioned by Baikov and Tumarev in 1937.[62] It is interesting that their results are somewhat similar to those just mentioned. These workers found that oxides which were reduced irreversibly by carbon monoxide evolved almost pure carbon dioxide on reaction with carbon, whereas other oxides gave a nearly equilibrium mixture of the monoxide and the dioxide.)

It was proposed[48] that the differences in the behaviour of solid oxides should be used to classify their thermal decomposition into two types, according as both atomic and molecular oxygen or only the latter is evolved. It is noteworthy that the kinetic parameters (activation energy and pre-exponential factor) determined in oxygen (air) usually differ markedly for these two types of reaction. Available data indicate that the first type includes the thermal decompositions $Pb_3O_4 \rightarrow PbO$, $Co_3O_4 \rightarrow CoO$, α-$PbO_x \rightarrow \beta$-PbO_x, $U_3O_8 \rightarrow U_8O_{21}$, $UO_{2+x} \rightarrow UO_{2.00}$, and $CuO \rightarrow Cu_2O$; and the second type includes β-$PbO_2 \rightarrow \alpha$-PbO_x, $Ag_2O \rightarrow Ag$, α-$PbO_x \rightarrow Pb_3O_4$, α-$PbO_2 \rightarrow \alpha$-PbO_x, $UO_3 \rightarrow UO_{2.9}$, $UO_{2.9} \rightarrow U_3O_8$, ϵ-$UO_3 \rightarrow U_3O_8$, $CrO_2 \rightarrow Cr_2O_3$, β-$MnO_2 \rightarrow \alpha$-Mn_2O_3, and α-$Mn_2O_3 \rightarrow \beta$-$Mn_3O_4$. Harano's experiments[57,58] indicated that atomic oxygen was evolved in the thermal dissociation of HgO, ZnO, and PtO_2.

Since the percentage of atomic oxygen in the gas evolved in the thermal decomposition of oxides of the first type is quite high[32], these reactions can well be regarded as a simple method for generating atomic oxygen. The results discussed may have some applied value, since work is now being widely undertaken on the use of oxygen from metal oxides for oxidising fuels[63].

IV. MECHANISMS OF THE TWO TYPES OF DISSOCIATION OF OXIDES

Since the first type of thermal decomposition of oxides involves the evolution of both atomic and molecular oxygen, whereas the second type gives only molecular oxygen, it was suggested[30,48] that the reaction mechanism of the former is similar to that generally accepted, whereas the latter has a different mechanism. Molecular oxygen is evidently formed directly by breakdown of the initial higher oxide in the latter type. This provides a natural explanation of the similarity of the activation energy to the heat of reaction (6) observed with these reactions.

In order that oxygen [atoms] should leave the oxide lattice in pairs (as molecules) during thermal decomposition of the oxide, interaction should occur between oxygen atoms in the initial lattice. Ignoring the form of interaction (the nature of the chemical bond in oxides is a matter of controversy[64]), we can state that the mutual influence will be stronger the shorter the oxygen–oxygen distance, which is shortest in peroxides. In 1958 Pavlyuchenko and Rubinchik[65] concluded from the activation energies and the heats of reaction of certain peroxides that atomic oxygen was not formed in their thermal breakdown. This was confirmed by Harano's experiments[57] and by other results[60].

In contrast to peroxides, it is difficult in oxides to distinguish any pair of oxygen atoms whose interaction would differ significantly from that with other neighbours. However, it may be questioned how marked this difference should be. No criterion is available at the present time.

Several higher oxides contain comparatively short oxygen–oxygen bonds. In the Reviewers' opinion this indicates the possibility of interaction between such atoms. Thus in β-PbO_2 [66] every four pairs of oxygen atoms distant 3.03 Å apart and one pair with a distance of 3.38 Å are accompanied by a pair 2.67 Å apart. It may be suggested that such a pair is able to behave as a unit during the act of breakdown and form an oxygen molecule. The important factor is not so much the absolute value of the shortest oxygen–oxygen distance as its difference from the mean. The energy of the metal–oxygen bond is obviously also important.

A similar idea to the above has recently been put forward by Porai-Koshits and Atovmyan[67]: from the structure of certain compounds containing oxygen or sulphur they concluded that the shortening of the O...O and S...S distance along an edge common to adjoining MX_6 octahedra is a consequence of the mutual attraction of the non-metal atoms. (The presence of such octahedra, linked in various ways, can be monitored in most higher oxides.) This idea seems the more valid as the explanation of the shortened non-metal–non-metal distance once put forward by Pauling[68] is unconvincing in the light of modern data on the effective charges in oxides and sulphides[64]. The mechanism suggested for reactions of this second type is further supported by work[61] showing, from the topotaxy[69] of the reaction $CrO_2 \rightarrow Cr_2O_3$ and formulation of the principle of minimum rearrangement of the lattice (the maximum possible number of previous bonds are preserved in a reaction), that the CrO_2 lattice can be transformed into the lattice of chromic oxide by removing pairs of oxygen atoms. The pairs thus removed lay on a common edge of adjoining MX_6 octahedra (i.e. they were a comparatively short distance apart).

The mechanism suggested for reactions of the second type is consistent also with their irreversibility. Theoretical examination has shown[70] that, if molecular oxygen is formed immediately on breakdown of the initial higher oxide, it is desirable, for the reverse reaction to occur, that oxygen should reach the interface between initial and final oxides in the form of molecules. However, an oxygen molecule is comparatively large, and its insertion would produce appreciable distortions in the oxide lattice. Hitherto there has been no direct experimental evidence of the possibility of the dissolution of molecular oxygen in oxides[71]. Experimental studies of the introduction of large molecules into the lattices of less rigid substances, e.g. graphite, indicate the presence of large sorption hysteresis[72]. If the pressure is raised considerably above the equilibrium value during a reaction of the second

type, oxidation of the lower oxide is observed, but its rate is extremely low. Thus according to Otto[52] the equilibrium oxygen pressure in the β-MnO_2–α-Mn_2O_3–O_2 system at 475°C is 1.4 atm. By raising the pressure almost hundredfold, he was able to observe partial oxidation of the sesquioxide, but no such oxidation was observed during the first 200 h after the pressure had been raised. Equilibrium oxidation of the sesquioxide would have required a year. The less rigid the lattice of the lower oxide, the more readily should oxidation occur. This will probably explain why several higher oxides of metals, e.g. manganese and uranium, can be obtained by oxidising lower oxides if the latter have been obtained in a finely dispersed or an amorphous state. The thermal decomposition α-$Mn_2O_3 \rightarrow \beta$-$Mn_3O_4$ is very characteristic in this respect. The Reviewers' experiments have shown that only molecular oxygen is evolved. However, several investigators regard the thermal decomposition of manganese sesquioxide as reversible. Summarising the results of many workers, Rabkin et al. concluded[73]: "In some cases the conversion of Mn_2O_3 into Mn_3O_4 is a reversible process depending on temperature and time of heating, as well as on the degree of dispersion. However, prolonged heating at a high temperature leads to the formation of Mn_3O_4 showing no tendency to absorb oxygen."

The problem of the irreversibility of thermal decompositions of oxides of the second type can in general be regarded as solved. A series of crucial experiments should be undertaken. Furthermore, the appearance of many studies on the irreversibility of thermal decomposition of several hydrates and carbonates would have been extremely useful, since these systems can be investigated by improved analytical methods, such as infrared spectroscopy, nuclear magnetic resonance, and isotopic exchange.

As has been mentioned, the mechanism of the first type of thermal decomposition of oxides is probably closely similar to the generally accepted condensate dissociation of solid metal oxides. Since very few investigations have been made on the thermolysis of oxides in which the evolution of atomic oxygen has already been established, it is difficult to analyse the laws governing reactions of this type. Nevertheless, one question can usefully be raised. According to the simple scheme of the decomposition of metal oxides[4], the activation energy of such reactions should differ little from the heat of reaction (5) $\Delta H^{\circ}_{T}(O)$. Let us estimate the latter for a few oxides, for which reliable thermodynamic data are available[2,74]. Since heats of reaction usually vary little with temperature, the calculation was made for 298 K. Thus approximate values of 79, 84, and 94 kcal g-atom^{-1} O have been obtained for $\Delta H^{\circ}_{298}(O)$ for the reactions $Pb_3O_4 = 3PbO + O$, $Co_3O_4 = 3CoO + O$, and $2CuO = Cu_2O + O$ respectively. The activation energy of the thermal decomposition of red lead has been given[32] as $E_a = 45 \pm 15$ kcal mole^{-1}; Ashin and Rostovtsev[7] give $E_a = 70$ kcal mole^{-1} for the thermal dissociation of Co_3O_4, and $E_a = 57$ kcal mole^{-1} for the thermolysis of copper(II) oxide[8], the latter of which compares with the value 49 found by Tatievskaya and Chufarov[42]. (The recalculation of the activation energy for the last reaction based by Esin and Gel'd[4] on the results[42] is probably illegitimate.) Chufarov et al.[40,41] calculated the activation energy from the temperature dependence of reaction velocity at zero oxygen pressure in the system. The rate of decomposition of oxides in an atmosphere of the reactant gas can be written

$$v(T) = k(T)S\overline{(m - m_{\infty})}\left(1 - \frac{p}{P_{O_2}}\right), \qquad (7)$$

where $v(T)$ is the reaction velocity, $k(T)$ the rate constant, S the interfacial area, $(M - m_{\infty})$ the quantity of oxygen removed from unit interfacial area, p the oxygen pressure in the system, and P_{O_2} the equilibrium dissociation pressure at the experimental temperature. We see that $v \rightarrow v_{max}$ as $p \rightarrow 0$, and v_{max} is independent of the equilibrium oxygen pressure. Hence the temperature dependence of v_{max} is determined by that of k: i.e. in the formula

$$v_{max.} = A\exp\left(-\frac{E_a}{RT}\right) \qquad (8)$$

E_a coincides with the activation energy of the rate constant.

Thus the first type of thermal decomposition of oxides evidently exhibits the extremely rare relationship that the activation energy is smaller than the heat of reaction. A similar relation is found also in the thermolysis of mercury(II) oxide[75]. Observed activation energies are usually considerably smaller than heats of reaction also in the thermolysis of metal sulphides with the formation of sulphur atoms[76,77].

This can be explained on the hypothesis adopted by Benson for gas-phase dissociations[78], that products of the individual act of breakdown are formed in a frozen state. An approximate calculation shows that the heat of the non-isothermal reaction

$$Pb_3O_4 \rightarrow (3PbO + O)^* \qquad (9)$$

in which red lead is at 823 K, while PbO and O are 550 deg cooler, is smaller by 20 kcal than the heat of the isothermal reaction $Pb_3O_4 \rightarrow 3PbO + O$. Unfortunately, it is difficult to have a detailed picture for solid-phase reactions of the act of breakdown—to estimate the energy of interaction of oxygen atoms with the lattice, to determine the numbers of metal and oxygen atoms involved in a single act, etc.

An alternative explanation may be suggested for this aspect of the first type of dissociation of oxides, that a multistage mechanism is involved. The first stage—breakdown of the initial higher oxide—is strongly endothermic, but a large quantity of energy is evolved by the combination of oxygen atoms to form molecules. The latter energy (~ 5 eV, which is considerably greater than the energy of thermal phonons) may not be immediately disseminated as heat, but may be divided into two quanta each of 2–3 eV and transmitted resonantly to the interface, i.e. to the site of breakdown in the periodicity of the lattice. "Molecules" of the higher oxide situated at the interface are excited. The destruction of such excited states requires, of course, a considerably lower activation energy.

Further experimental work is required before final conclusions can be reached, but the mechanism of the thermal decomposition of metal oxides is in any case more complicated than had hitherto been thought.

Finally, we must bear in mind, when considering the sequence metal–oxides–oxygen, that oxides contain not only the main metal–oxygen bonds determining their nature but also certain other bonds. Metal–metal interaction must be taken into account in the lattices of several unsaturated oxides[79], and oxygen–oxygen interaction in those of higher oxides, the latter being especially pronounced in metal peroxides. Furthermore, some molecular character is present in metal oxides such as alumina and titania, evident in the fact that the metal does not interact in the same way with all the oxygen atoms surrounding it[80,81]. A feature of such oxides is that M_xO_y molecules pass into the gas phase when they are heated.

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Khlopin Radium Institute,
Leningrad