Kinetics and mechanism of thermal decomposition of silver oxide

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Abstract

The scheme of dissociative evaporation of Ag_2O in the form of free Ag atoms and O_2 molecules with simultaneous condensation of Ag vapor is used to interpret the kinetics of thermal decomposition of Ag_2O. A critical analysis of literature data and their comparison with theoretical calculations has shown that the main kinetic characteristics of Ag_2O decomposition, including the activation energy, absolute decomposition rate, and its dependence on the partial pressure of O_2 are in full agreement with the proposed mechanism of decomposition. Condensation of the low-volatile product (Ag vapor) in the reaction zone and partial transport of condensation energy to the reactant account for the features which are typical of solid-state reactions and manifest themselves in the appearance of periods of induction and acceleration in the course of the process. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The number of publications dealing with thermodynamics and kinetics of thermal decomposition of Ag_2O is by far the largest compared to the oxides of other metals. As far back as 1887, Le Chatelier [1] proved the reversibility of the reaction

$$2Ag_2O(s) = 4Ag(s) + O_2 \qquad (1)$$
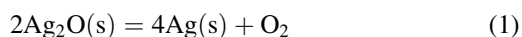
and established that the equilibrium pressure of O_2 at 573 K is as high as 15 atm. Studies of the thermodynamics of this reaction were continued by Lewis [2] in the 575–718 K interval, Keyes and Hara [3] (647–779 K), Benton and Drake [4] (446–464 K), and Otto [5] (447–554 K). By analyzing critically the above data, Otto [5] obtained for the enthalpy of this reaction at 298 K the value $\Delta_r H^0_{298} = 61.5 \, kJ \, mol^{-1}$.

The kinetics of decomposition of Ag_2O was studied first (in 1905) by Lewis [6], who drew attention to the existence of an induction period in the development of the reaction and to its autocatalytic character. These specific features of the reaction were later confirmed by Benton and Drake [7], Hood and Murphy [8], Averbuch and Chufarov [9], Garner and Reeves [10], Herley and Prout [11], Allen [12], Dubinin et al. [13] and Lagier et al. [14]. The temperatures varied in these studies from 447 to 673 K, and the activation energies, in the 118–180 $kJ \, mol^{-1}$ interval.

Despite the satisfactory agreement among the experimental results obtained by different authors, the true mechanism of Ag_2O decomposition still remains unclear. In particular, two important points have not obtained a convincing interpretation. First,

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one still cannot find an explanation for the tremendous difference between the *equilibrium* partial pressure of O_2 reaching about 30 atm at 603 K, on one hand, and the *equivalent* [15] partial pressure of O_2 (about 10^{-5} atm) corresponding to the decomposition rate of Ag_2O, on the other. Second, no reasonable interpretation of the nature of the induction period and the accelerating effect of metallic silver (and, judging from the data of Ref. [13], of other metals as well) on the process of Ag_2O decomposition has been put forward until now.

The objective of this work is in presenting an interpretation for the above and related aspects by applying a new approach to explanation of the thermal decomposition mechanism, which is based on a scheme involving dissociative evaporation of the reactant with simultaneous condensation of the low-volatile product. This approach has been employed earlier in the interpretation of the mechanism and kinetics of thermal decomposition of oxides [15], nitrates [16–18], carbonates [20], $Li_2SO_4 \cdot H_2O$ [21], $Mg(OH)_2$ [22], and of a number of other inorganic compounds [23].

2. Theoretical

The method to be employed below consists in comparing experimental data on the kinetic parameters with their theoretical values. The calculations are based on the classical evaporation model of Hertz–Langmuir, applied to the cases of dissociative evaporation of compounds. The scheme of theoretical calculation of the main kinetic parameters (the flux of the gaseous product J, the rate constant k, the product partial pressure P and the parameters of the Arrhenius equation, E_a and A) has been described in a number of previous publications [15–23]. Therefore, we are going to present below only some final relations necessary for the calculations in this work.

In the case of a binary compound S decomposed in vacuo into gaseous products A and B

$$S(s) \rightarrow aA(g) + bB(g) \tag{2}$$
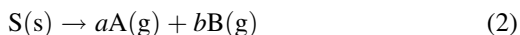
the flux of product A can be expressed through the equivalent partial pressure P_A (in atm) of this product corresponding to the hypothetical equilibrium of reaction (2) in the form

$$J_A = \frac{\gamma M P_A}{(2\pi M_A R T)^{1/2}}, \tag{3}$$

where M and M_A are the molar masses of the reactant and product A, γ the coefficient of conversion from atmospheres to pascals, and R the gas constant.

The flux of gaseous products J is connected with the rate constant k. For spherical particles, the fraction decomposed is described by the contracting volume model

$$\frac{d\alpha}{dt} = 3(1 - \alpha)^{2/3} k. \tag{4}$$

Taking into account some obvious relationships: $\alpha \equiv 1 - m/m_0$, $m = (4/3)\pi r^3 \rho$ and $J = -(dm/dt)(4\pi r^2)^{-1}$, where m, r and ρ are the mass, radius and density of reactant spherical particle(s), we obtain on rearrangement of Eq. (4) a simple expression

$$J = \rho r_0 k. \tag{5}$$

From Eqs. (3) and (5), we have

$$P_A = \frac{(2\pi M_A R T)^{1/2}}{\gamma M} \rho r_0 k. \tag{6}$$

This equation will be used for the calculation of the equivalent partial pressure of product A from the experimental value of k.

The theoretical value of the partial pressure of product A can be calculated from the equilibrium constant K_P for reaction (2). In the absence of reaction products in the reactor atmosphere, the situation corresponding to the *equimolar* evaporation mode, the partial pressure P_A can be expressed [15] as

$$P_A^e = a \left(\frac{K_P}{F}\right)^{1/v} \left(\frac{M_A}{M_B}\right)^{b/2v} = \frac{a}{F^{1/v}} \left(\frac{M_A}{M_B}\right)^{b/2v}$$
$$\times \exp \frac{\Delta_r S_T^0}{vR} \exp \left(-\frac{\Delta_r H_T^0}{vRT}\right), \tag{7}$$

where

$$F \equiv a^a \times b^b, \tag{8}$$
$$v = a + b \tag{9}$$

and

$$K_P = P_A^a \cdot P_B^b. \tag{10}$$

Here $\Delta_r H_T^0$ and $\Delta_r S_T^0$ are, respectively, the changes of the enthalpy and entropy in process (2).

If the partial pressure P'_B of one of the gaseous components greatly exceeds the equivalent pressure P_B of the same component released in the decomposition and if, in addition to that, the magnitude of P'_B remains constant in the process of decomposition, we call such evaporation mode *isobaric*. In this case,

$$P_A^i = \frac{K_P^{1/a}}{P_B'^{b/a}} = \frac{1}{P_B'^{b/a}} \exp \frac{\Delta_r S_T^0}{aR} \exp \left(-\frac{\Delta_r H_T^0}{aRT} \right).$$

(11)

As can be seen from Eqs. (7) and (11), the calculated activation energies for reaction (2) should be different for the equimolar and isobaric modes of decomposition, i.e.

$$E_a^e = \Delta_r H_T^0 / v \quad (12)$$

for the equimolar mode and

$$E_a^i = \Delta_r H_T^0 / a \quad (13)$$

for the isobaric one.

In order to take into account the partial transfer of the energy released in the condensation of low-volatile product A to the reactant, we introduced, as before [21,22], into calculations of the enthalpy of decomposition reaction (2) an additional term $\tau a \Delta_c H_T^0(A)$, where the coefficient τ corresponds to the fraction of the condensation energy transferred to the reactant. Thus, we can write

$$\Delta_r H_T^0 = a \Delta_f H_T^0(A) + b \Delta_f H_T^0(B) \\ - \Delta_f H_T^0(S) + \tau a \Delta_c H_T^0(A), \quad (14)$$

Table 1 lists the initial values of the thermodynamic functions [24] for all components of the assumed reaction

$$Ag_2O(s) \rightarrow 2Ag(g) + 0.5\,O_2 \quad (15)$$
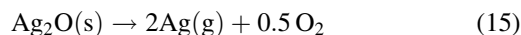
and Table 2, all the other parameters necessary for subsequent calculations.

Table 2
Parameters used in the calculations of decomposition rates

Parameter	Symbol	Value
Molar mass of Ag_2O	M	0.232 kg mol^{-1}
Molar mass of Ag	M_{Ag}	0.108 kg mol^{-1}
Molar mass of O_2	M_{O_2}	0.032 kg mol^{-1}
Density of Ag_2O	ρ	7140 kg m^{-3}
Enthalpy of reaction (15) at $\tau=0$	$\Delta_r H_{500}^0$	601.95 kJ mol^{-1}
Entropy of reaction (15)	$\Delta_r S_{500}^0$	319.35 J mol^{-1} K^{-1}
Condensation heat of 2Ag(g)	$\Delta_c H_{500}^0$	572.0 kJ mol^{-1}
Gas constant	R	8.3145 J mol^{-1} K^{-1}
Pressure conversion factor	γ	101325 Pa atm^{-1}

3. Results and discussion

At first, we shall use the above scheme to calculate the activation energies and silver-vapor partial pressure, which correspond to the assumed reaction (15), and compare them with the available experimental data. Then, we shall discuss the specific features of this reaction associated with the onset of the induction and acceleratory periods in the decomposition process.

3.1. Activation energies

Table 3 lists the conditions of measurement and the activation energies obtained in the studies we were able to locate. The least confidence is inspired by the work of Benton and Drake [7], where the measurements were carried out at a temperature lower by $150°C$ than those in the others. One measured the rate of pressure rise in the reactor. The amount of the evolved gas was estimated [7] as not over 5% of its total content in the sample. No identification of the gas was performed. Herley and Prout [11] and Dubinin et al. [13] believe that the lower decomposition temperature quoted in [7] is accounted for by the presence in the starting reactant of a considerable amount of

Table 1
Thermodynamic functions [24] used in the calculations

Species	State of aggregation	$\Delta_f H_{500}^0$ (kJ mol^{-1})	S_{500}^0 (J mol^{-1} K^{-1})
Ag_2O	s	-16.5	158.2
Ag	s	5.2	55.9
Ag	g	291.2	183.6
O_2	g	6.1	220.7

Table 3
Measurement conditions and activation energies for the thermal decomposition of Ag_2O

Technique[a]	Atmosphere	Temperature range (°C)	E_a (kJ mol^{-1})	Reference and year
M	O_2	327–353	133	[6] (1905)
M	Vacuum	174–198	149	[7] (1934)
M	Air	306–330	118	[8] (1949)
TG	O_2	300–400	121	[9] (1949)
M	Vacuum	305–339	180	[10] (1954)
M	Vacuum	330–380	121	[11] (1960)
M	Vacuum	280–320	151	[12] (1960)
TG	Vacuum	320–350	–	[13] (1967)
TG	Vacuum	330–390	120	[14] (1969)

[a] M and TG: manometric and thermogravimetric, respectively.

Ag_2CO_3, which forms in contact of Ag_2O with air. Silver carbonate decomposes, according to the measurements of Kadlec and Dubinin [25], within the temperature interval 167–194°C, which is in accord with the decomposition temperature of the sample quoted by Benton and Drake [7].

The value $E_a = (180 \pm 11)$ kJ mol^{-1} given in Table 3 for the study of Garner and Reeves [10] was calculated by us based on the data listed in Table 4. For reasons unclear to us, a different value, $E_a = 192$ kJ mol^{-1}, was obtained in Ref. [10] from the same data.

On the whole, the activation energies measured in different works are in a fairly good agreement with one another. The average value of E_a in vacuum is (143 ± 29) kJ mol^{-1}, and in an oxygen or air, (124 ± 8) kJ mol^{-1}. Theoretical values of E_a in vacuum (equimolar mode) and in an oxygen or air (isobaric mode) calculated from Eqs. (12)–(14) under the assumption that $\tau = 0.5$ are 126.4 and 158.0 kJ mol^{-1}. Considering the spread in experimental values of E_a, the agreement between theory and measurements in vacuum are quite satisfactory. In the case of the isobaric mode, the

Table 4
The results of experiments on decomposition of Ag_2O [10]

Temperature (K)	$k \cdot m^{1/3}$ (a.u.)
578.15	0.00877
580.55	0.0089
588.05	0.0148
588.15	0.0136
591.45	0.0165
592.45	0.0164
604.95	0.0468
611.65	0.0584

experimental data are found to lie, on the average, 34 kJ mol^{-1} below the theoretical values. The result obtained by Lewis [6] more than 90 years ago turns out to come closest to the theoretical value of 158 kJ mol^{-1}. It may be conjectured that the underestimation of E_a in Ref. [9] is caused by the self-cooling effect [22] at the high temperatures of the experiment, which reached 400°C. One should also take into account that determination of E_a in Refs. [8,9] was made from measurements of the decomposition rate at three temperatures only, and in Ref. [6], at four temperatures. Therefore, the reliability of these results is rather low.

3.2. Partial pressures

To estimate the equivalent partial pressure of Ag vapor corresponding to the decomposition rate of Ag_2O, we used the results obtained in Refs. [8,11] (Table 5). In both studies, the rate of O_2 evolution was determined manometrically. Hood and Murphy [8] carried out the decomposition in air, i.e. at $P_{O_2} = 0.21$ atm, and Herley and Prout [11], in vacuum. Both papers present the rate constants k for 603 K and the sample mass m. It was assumed in the calculations that because of the self-cooling decomposition takes place only on the outer surface of the sample, and that the temperature of the surface is equal to that of the furnace. In view of the results of Ref. [22], these assumptions appear reasonable enough. It was assumed also that the sample has spherical shape. The radius of the hypothetical "loose" spherical particle of Ag_2O was estimated from the obvious expression taking the apparent den-

Table 5
Experimental and theoretical partial pressures of Ag vapor in the process of decomposition of Ag_2O at 603 K

Atmosphere	m (mg)	r_0 (mm)	k (s^{-1})	P_{Ag} (atm)		Ref.
				Experiment	Theory	
Air, 1 atm	150	2.2	1.4×10^{-4} [a]	5.3×10^{-6}	6.7×10^{-6}	[8]
Vacuum	20	1.1	1.2×10^{-3} [b]	2.3×10^{-5}	7.9×10^{-5}	[11]

[a] From Fig. 5 [8] at $\alpha = 0.5$.
[b] From Fig. 4 [11].

sity of the powder ρ_p equal to 0.5ρ

$$r_0 = \left(\frac{3m}{4\pi\rho_p}\right)^{1/3}. \tag{16}$$

The experimental values of P_{Ag} were calculated using Eq. (6), and the theoretical ones, from Eqs. (7) and (11). The coefficient τ in the calculation of the theoretical values of P_{Ag} was assumed equal to 0.5 (see Section 3.3). As follows from the data listed in Table 5, the experimental and theoretical values of P_{Ag} agree fairly well, if we take into account the possible errors in the measurement of k and the approximations accepted in the calculation of the experimental values of P_{Ag}. (The threefold disagreement in the case of decomposition in vacuum is most probably due to the sample cooling in vacuum being substantially greater than that in air).

The rate of decomposition in air is by an order of magnitude less than that in vacuum, which is in accord with the difference between the equilibrium partial pressures in the isobaric and equimolar modes of Ag_2O decomposition by reaction (15). The latter conclusion is supported also by direct measurements of the decomposition rate of Ag_2O for different O_2 contents in the furnace [9]. In particular, the fivefold increase of P_{O_2} (from 10 to 50 Torr) resulted in a decrease of the decomposition rate from 1.76 to 1.33, with the extent of decomposition varying from 20% to 60%. According to Eq. (11), the difference should be $5^{1/4} \cong 1.5$.

Thus all the main kinetic characteristics of Ag_2O decomposition, including the activation energy, absolute decomposition rate, and dependence of decomposition rate on P_{O_2}, are in full agreement with the proposed mechanism of dissociative evaporation of Ag_2O in the form of free Ag atoms and O_2 molecules with simultaneous condensation of Ag vapor and

partial transfer of energy of condensation ($\tau = 0.5$) to the reactant. It should be pointed out that although there has been no direct observation of the presence of free Ag atoms in the primary products of Ag_2O decomposition, it manifests itself clearly in thermal decomposition in $AgNO_3$. We may recall that direct measurements of the relative content of the primary products released in decomposition of microgram amounts of $AgNO_3$ by the EGA-QMS method [17] showed the decomposition to proceed by the reaction

$$AgNO_3(l) \rightarrow Ag(g) + NO_2 + 0.5\,O_2. \tag{17}$$

Remarkably, decomposition of $AgNO_3$ and Ag_2O starts at practically the same temperature of about 570 K.

The above consideration accounts for the much lower equivalent partial pressure of O_2 compared to its equilibrium pressure at the same temperature. It is determined by the difference of the primary products for dissociative evaporation of Ag_2O by reaction (15) from the equilibrium composition.

3.3. Induction period and autocatalysis

Let us turn now to interpretation of the specific features in thermal decomposition of silver oxide, which manifested in the appearance of induction and acceleratory periods in the process and were observed practically by all researchers. The key steps in this process which may help in understanding the nature of these features are the condensation of the low-volatile product (silver vapor) at the reaction interface and partial transfer of the condensation energy to the reactant. The most plausible of all conceivable mechanisms appears to be thermal accommodation or, in other words, direct transfer of the energy at the reaction interface in collisions of the low-volatile molecules with the reactant and product

surface. For equal temperatures of the solid phases, one may expect equipartition of energy between the two phases, i.e. $\tau = 0.5$. Taking into account the lower temperature of the reactant surface, one may assume $\tau \geq 0.5$. In the present, initial stage of development of the theory, the coefficient τ plays the part of a fitting parameter, which permits one to fit the calculated activation energies and decomposition rates to experimental data. An analysis of the decomposition kinetics for a number of inorganic compounds in our previous works ($Li_2SO_4 \cdot H_2O$ [21], $Mg(OH)_2$ [22] and $MgSO_4$ [26]) and for Ag_2O in this paper shows that τ indeed assumes values within 0.5–0.6.

The necessary condition for energy transfer is the preliminary formation of the reaction interface. In the initial stage of decomposition, when the reactant surface is not yet covered by a film of the solid product, a considerably higher energy is required for decomposition. In the case of Ag_2O, for instance, the enthalpy of the reaction for τ equal to zero and 0.5 is 602 and 316 kJ mol^{-1}, respectively. To this difference in $\Delta_r H_{500}^0$ corresponds a difference between the reaction rates at 600 K by 25 orders of magnitude! The appearance on the Ag_2O surface of nuclei of a new phase (metallic silver) in condensation of supersaturated Ag vapor results, as they grow in number and size, to an increase of τ, and hence, of the reaction rate as well. This increase in the reaction rate continues until a solid film of the product has formed over all of the Ag_2O surface, when τ reaches a maximum (about 0.5).

This scheme of the process is in full agreement with experimental observations. Dubinin et al. [13] showed that the periods of induction and acceleration in Ag_2O decomposition disappear completely, and the reaction proceeds with the maximum rate from the very beginning, if Ag_2O powder particles are coated preliminarily by a layer of metallic silver. Deposition of metallic nickel on Ag_2O produced practically the same effect. This implies that the presence of the reactant surface of nuclei or of a film of a solid phase favors transfer of the condensation energy released by low-volatile products to the reactant, irrespective of the nature of this solid phase. Moreover, mechanical defects (scratches, cracks, breaks, etc.) on the surface are likewise conducive to nucleation of a new phase and formation of the product/reactant interface.

In the case of thermal decomposition of single crystals with an ideal, defect-free surface, nucleation is particularly strongly inhibited, so that the induction period may extend over an indefinitely long time. This point was repeatedly mentioned by many researchers studying dehydration of salts. To illustrate observations of record-long induction times, it appears appropriate to present here an excerpt from the classical work of Faraday [27]: "As a curious illustration of the influence of mechanical forces over chemical affinity, I will quote the refusal of certain substances to effloresce when their surfaces are perfect, which yield immediately upon the surface being broken. If crystals of carbonate of soda, or phosphate of soda, or sulphate of soda, having no part of their surfaces broken, be preserved from external violence, they will not effloresce. I have thus retained crystals of carbonate of soda perfectly transparent and unchanged from September 1827 to January 1833; and crystals of sulfate of soda from May 1832 to the present time, November 1833. If any part of the surface were scratched or broken, then efflorescence began at that part, and covered the whole. The crystals were merely placed in evaporating basins and covered with paper."

4. Conclusions

The use of the scheme of dissociative evaporation of the reactant with simultaneous condensation of the low-volatile product has permitted us not only to arrive for the first time at a quantitative interpretation of the kinetics of thermal decomposition of Ag_2O but to draw also some conclusions of a general nature bearing on the evolution of solid-state reactions. These are the following:

1. The mechanism of nucleation through condensation of supersaturated vapor of the low-volatile product becomes fairly obvious [28].
2. In the initial decomposition stage, in the absence of any nuclei on the reactant surface, which provide condensation of the vapor of the low-volatile product at the interface zone and energy transfer to the reactant, the decomposition proceeds much slower. The time taken to form the first nuclei on the surface of the reactant corresponds to the induction period.
3. The presence of defects or foreign impurities on the surface turns out to be equivalent to the appearance

of nuclei of a new phase. Because of this, the induction and acceleratory periods, in which the product film covers the whole surface of reactant and the reaction reaches steady state, become shorter or disappear at all.

4. One readily understands now the phenomenon of self-localization of the process, or, in other words, the confinement of the reaction surface to the zone adjoining the nucleus, defect or impurity inclusion. Due to condensation energy transfer to the reactant in this zone, the decomposition proceeds much faster.

5. The absence of product film on the surface of the solid reactant in the initial periods of decomposition accounts for the appearance of the low-volatile products (Ag, CdO, PbO, etc.) in the gaseous phase, as it was observed in the process of decomposition of microgram amounts of nitrates [16–18]. This phenomenon is most pronounced, if at the decomposition temperature the reactant is in the liquid phase and formation of such a film is unlikely. This was the case of $AgNO_3$ and $Cd(NO_3)_2$ decomposition [17].

6. Finally, the formation of a solid product through vapor condensation accounts for the perfect character of the crystalline lattice of the product.

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