

THERMAL STABILITY OF THE SYSTEM BaO-BaO₂

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(Received October 15, 1990)

The thermal stability of barium peroxide obtained via the oxidation of BaO was studied. The investigations were carried out with a Q1500D MOM derivatograph. The flow rate of air or oxygen-argon mixtures was 25-30 l/h. It was found that the thermal properties of the BaO-BaO₂ system and of BaO₂ depend on the partial pressures of oxygen and water vapour during the process of oxidation of BaO. The most stable BaO₂ can be produced from high-purity BaO with a special crystal structure.

The thermal dissociation of barium peroxide was first studied by Le Shatelier in 1889 and later by Hildebrand [1] with a view to the general understanding of the equilibria in heterogeneous systems. They found that, at sufficiently high temperatures, in the system BaO₂-BaO-O₂ the chemical and phase content of the solid substance is determined by the oxygen pressure. The isothermal dependence between pressure and system content shows two regions of bivariant equilibrium, corresponding to the predominance of oxide or peroxide. There is also an interstitial region of monovariant equilibrium. Investigation of the isothermal dependence shows that limited solubility takes place in the system BaO-BaO₂. As a result, two types of equilibrium arise: a bivariant one, corresponding to the solution of BaO₂ into BaO and of BaO into BaO₂, and a monovariant one, in the region where two mutually saturated solid solutions exist.

Barium peroxide has the highest thermal stability among all known metal peroxides. When it is heated at atmospheric pressure [1, 2], intensive oxygen liberation begins at temperatures higher than 773 K. The method by which the barium peroxide is obtained is of great importance. Thus, in the heat treatment of peroxide [3] produced directly from barium nitrate in nitrogen and oxygen atmospheres, the active liberation of oxygen begins at tempera-

tures 50–100 deg higher than in the treatment of peroxide obtained from barium hydroxide and hydrogen peroxide.

It was shown by means of DTA methods [1] that the decomposition of barium peroxide is characterized by an endothermic effect at 1063 K in the heating curve. The melting point of barium peroxide at high pressures has not been determined. The mass obtained on heating softens at about 1073 K and loses its active oxygen entirely at 1173 K [2, 4]. According to other authors [5] barium peroxide melts at 723 K and loses its second oxygen atom at 1073 K. Massay *et al.* [6] deny the value of 723 K and state that the precise melting point is 1063 K. A melting point of 1108–1113 K was established [7] when specimens of technical barium peroxide were investigated by means of derivatography.

The dissociation kinetics of barium peroxide was studied in the temperature range 773–973 K at pressures of 0.1 Pa–27.1 kPa [1]. The dependence between the logarithm of the oxygen partial pressure and $1/T$ (T = dissociation temperature) is a straight line. The rate of decomposition increases as the oxygen pressure is decrease [8] and also in the presence of other oxides [9], such as chromic oxide, ferric oxide, etc. [10].

Volnov [1] followed the active oxygen loss from barium peroxide on heating in air and in atmospheres of argon, oxygen, carbon dioxide and water vapour ($P_{\text{H}_2\text{O}} = 3.2$ kPa). The peroxide has the highest thermal stability in the presence of oxygen. In an atmosphere of carbon dioxide or water vapour, it begins to decompose even at 473 K [11]. The high-vacuum decomposition of barium peroxide occurs in the diffusion region, in the temperature range 683–733 K [12]. Thus, it can be seen that the literature data concerning the thermal stability of barium peroxide are extremely dispersed.

The purpose of the present work was to report results of investigations of the thermal stability of barium peroxide obtained from different raw materials at different partial pressures of some of the gaseous components.

Experimental

Experimental procedure

The investigations were carried out on Paulik–Paulik–Erdey derivatographs of types Q–1500 and Q–1500D. The samples were heat-treated in the temperature range 293–1273 K, in atmospheres of air (flow rate 30 l/h), oxygen–air or oxygen–argon mixtures. Raw materials: 95% BaO (product of "Riedel de Haen"); BaO, the final product of decomposition of

99.5% Ba(NO₃)₂ (produced in REACHIM); mixtures of BaO (95%)-BaO₂ (85%, REACHIM).

Experimental data and results

The thermal stability of barium peroxide was studied immediately after it was obtained from 95% barium oxide and from barium oxide as the final product of heat treatment of barium nitrate in argon atmosphere. The experiments were carried out in oxygen-argon or oxygen-air mixtures (gas phase flow rate 30 l/h); weight of samples 250 mg; different rates of heating were used. As the data in Table 1 show, the process of oxidation of fresh BaO obtained from Ba(NO₃)₂ decomposition is completed at lower temperatures. The product is thermally stable at higher temperature. A lower final oxidation temperature will involve lower energetic expenses for peroxide production. The change in heating rate does not influence $T_{\text{final ox.}}$ of the fresh oxide. It varies between limits of 10 deg. The data concerning BaO ("Riedel de Haen") show that, when the average rate of heating is reduced from 10 to 5 deg/min, the oxidation is finished at a temperature 50 deg lower. The range of stability increases at the same time.

Table 1 Thermal stability of BaO₂, obtained from different barium oxides at $m = 250$ mg, gaseous atmosphere with 30 l/h gas flow rate and different rate of heating ($V_{\text{aver.}}$)

Raw materials				
BaO (Riedel de Haen)			BaO from Ba(NO ₃) ₂	
Atmosphere	83% O ₂ + 17% N ₂		83% O ₂ + 17% Ar	
$V_{\text{aver.}}$, deg/min	$T_{\text{fin.ox.}}$, K	$T_{\text{init.dec.}}$, K	$T_{\text{fin.ox.}}$, K	$T_{\text{init.dec.}}$, K
10	726	758	626	after 793
5	676	783	623	after 893
2.5	671	736	633	after 913

The next investigations were carried out with mixtures of oxide and peroxide, the oxide content varying from 10 to 100%. The mass of samples was 500 mg, the rate of heating was 5 deg/min, and the atmosphere was oxygen-argon or air with a 30 l/h flow rate. After the first oxidation to BaO₂, the second oxidation of the final product from all decompositions (fresh barium oxide) was performed under the same experimental conditions in order to establish the thermal stability of the barium peroxide obtained. The experimental data are presented in Table 2. A comparison of the results of the oxidations in air atmosphere reveals that the ranges of stability are wider for the first oxidation; however, the peroxide from the second oxidation is

thermally stable at higher temperatures. The second oxidation peroxide is stable at higher temperature in oxygen-argon atmosphere too, under these conditions, the ranges of stability are also wider. This is an indication that the freshly obtained barium oxide is more suitable as a raw material. When the data on the oxidations in air and in oxygen-argon atmosphere are compared, it can be seen that the peroxide stability increases as the oxygen partial pressure is elevated. This is in accordance with the thermodynamic equilibrium of the process. The presence of 40-80% BaO₂ in the mixture lowers the temperature at which the oxidation is completed.

Table 2 Thermal stability of BaO₂ in mixtures with BaO at double oxidation and decomposition. Gas flow rate 30 l/h, $V_{\text{aver.}} = 5$ deg/min and $m = 500$ mg

Atmosphere BaO content in the mixture, %	83% O ₂ + 17% Ar				Air			
	$T_{\text{fin.ox.}}$, K		$T_{\text{init.dec.}}$, K		$T_{\text{fin.ox.}}$, K		$T_{\text{init.dec.}}$, K	
III	First	Second	First	Second	First	Second	First	Second
10	718	803	786	828	696	778	753	813
20	661	763	731	793	660	628	756	863
30	641	883	681	903	648	836	713	883
40	633	863	862	953	636	851	700	888
50	677	770	730	884	673	893	766	923
60	645	735	727	853	653	855	713	875
70	653	733	740	773	636	861	713	897
80	643	758	734	903	616	738	721	793
90	651	815	705	893	690	833	798	883
100	693	823	763	917	731	833	823	883

To establish the influence of water vapour on the stability of the barium peroxide obtained, two consecutive oxidations and decompositions of the barium oxide (95%) were carried out in oxygen-argon mixtures with different contents of water vapour (controlled by driers). Investigations in air and in oxygen-air atmosphere without the use of driers were performed to serve as a basis for comparison. As may be seen from Table 3, the first oxidation of BaO in air atmosphere is completed at a temperature about 40 deg higher than in the atmosphere with higher oxygen partial pressure. In the two cases, the temperature range of stability is approximately equal: 80-90 deg, i.e. in air the product is stable at higher temperature. The results of the second oxidation show that, when a gaseous mixture with higher oxygen content is used, the peroxide obtained is stable in a wider range: 843-931 K (instead of 833-883 K in air atmosphere). Obviously, the thermal stability of

the peroxide is determined by the gaseous phase content and by the state and purity of the initial barium oxide, too.

Table 3 Thermal stability of BaO₂ obtained from 95% BaO in gaseous atmosphere with different water vapours content and 30 l/h gas flow rate

Gaseous atmosphere	Drier	Water content at 298 K, mg/l	T _{fin.ox.} , K		T _{init.dec.} , K	
			First	Second	First	Second
air	—	13.80	731	833	823	883
83% O ₂ +17% N ₂	—	2.35	693	843	773	931
83% O ₂ +17% N ₂	CaCl ₂	0.20	687	771	761	881
83% O ₂ +17% N ₂	P ₂ O ₅	2.5 · 10 ⁻⁵	663	751	984	933
83% O ₂ +17% N ₂	liquid N ₂	—	658	783	743	873
83% O ₂ +17% N ₂	saturation at 298 K	23.00	683	778	708	803

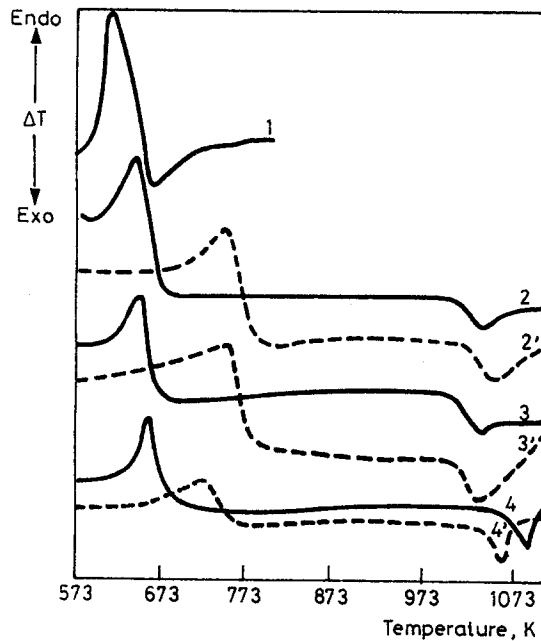


Fig. 1 DTA curves for obtained from:

- 1 BaO as a product of thermal decomposition of Ba(NO₃)₂
- 2 oxidation of BaO in the gas atmosphere 83% O₂+17% N₂ and P₂O₅-drier
- 3 oxidation mixture of 80% BaO+20% BaO₂ in the gas atmosphere 83% O₂+17% N₂
- 4 oxidation of pure BaO in the gas atmosphere 83% O₂+17% Ar
- 2', 3', 4' - curves of the BaO₂ obtained from the second cycle of oxidation

Diminishing the water vapour content to about 10^{-5} mg/l increases the thermal stability of the barium peroxide obtained, as follows from a comparison of the results of the first oxidation of the samples with driers. The absence of water vapour (drier: liquid N_2) reduces the stability. The results from the second oxidation are close to those from the first oxidation. The temperature ranges for the two oxidations are extremely narrow (25 deg) when the gaseous phase is entirely saturated with water vapour. The decomposition begins at temperatures lower by about 200 deg (for the first oxidation) or by about 100 deg (for the second oxidation) than the temperatures when the blowing gas is dried with P_2O_5 . Hence, a high water vapour partial pressure reduces the thermal stability of the barium peroxide obtained.

The processes of oxidation and decomposition are accompanied by pronounced thermal effects (Fig. 1). A shift in the extrema to higher temperatures is observed in the oxidation of the fresh barium oxide obtained after the first heat treatment. This is an indication of a lower reactivity of the solid phase obtained. This conclusion is confirmed by the changes in the form of the registered thermal effects, as well as by the pattern of the thermogravimetric curves.

Conclusions

The experiments permit the following conclusions:

- Barium peroxide characterized by a wide range of stability can be obtained in an atmosphere with a high oxygen partial pressure and with a water content of about 10^{-5} mg/l in the gaseous phase.
- The thermal stability of the barium peroxide is higher when the initial barium oxide has high purity and activity. The use of freshly obtained barium oxide is advisable when a peroxide stable at high temperatures is required.

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Zusammenfassung — Es wurde die thermische Stabilität von Bariumperoxid, erhalten durch die Oxidation von BaO, untersucht. Die Untersuchungen wurden mittels eines MOM-Derivatographen Q-1500D ausgeführt. Der Durchsatzstrom der Luft bzw. der Sauerstoff/Argon-Gemische betrug 25-30 l/h. Es zeigte sich, daß die thermischen Eigenschaften des Systemes BaO-BaO₂ bzw. von BaO₂ vom partiellen Druck des Sauerstoffes bzw. vom Wasserdampfdruck abhängen, der bei der Oxidation von BaO vorherrscht. Das stabilste BaO₂ konnte aus hochreinem BaO mit einer speziellen Kristallstruktur gewonnen werden.