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THERMOCHEMICAL DATA OF BARIUM PEROXIDE FROM THERMOGRAVIMETRIC MEASUREMENTS

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Decomposition temperatures of barium peroxide in equilibrium with the oxygen pressure in the gas phase have been determined by thermogravimetric measurements at temperatures from 670 to 843°. Enthalpies and entropies of the reaction $BaO_2 = BaO + 0.5O_2$ and of the formation of BaO_2 have been calculated.

Several reports are known regarding the equilibrium temperature of the reaction

$$BaO_2 = BaO + 0.5O_2$$

in a pure oxygen atmosphere. The results differ by as much as 100° from each other.

Table 1

Decomposition temperature of BaO_2 at $p(O_2) = 1$ atmosphere

Investigator	Decomposition temperature, °C
Le Chatelier [1]	800
Hildebrand [2]	840
Hedvall [3]	790
Centnerszwer and Blumenthal [4]	740

Hedvall tried to explain these differences by assuming the influence of small quantities of water which would form solid solutions of $BaO_2 + Ba(OH)_2$ and $BaO + Ba(OH)_2$ with limited reciprocal solubility. Hildebrand found the following equation for the dependence of the reaction on the temperature:

$$\log p(O_2) = -6850/T + 1.75 \log T + 2.8 \qquad (1)$$

According to the data of Centnerszwer and Blumenthal:

$$\log p(O_2) = -5800/T + 1.75 \log T + 2.8. \qquad (2)$$

Eqs. (1) and (2) yield an enthalpy of reaction of about −35.5 and −30.5 Kcal/mole respectively. These values are obviously too high.

Experimental

The measurements were made using a thermobalance described by Peters and Wiedemann [5] with the following properties: Reproducibility 2×10^{-5} g; sensitivity 10^{-5} g; accuracy of temperature measurements directly on the sample $\pm 0.2°$; sample temperature was measured using a platinum-platinum-rhodium thermocouple, calibrated at the gold-point. The sample was heated in a corundum crucible; the sample weight was between 1 and 2 g.

The balance was placed at atmospheric pressure in a gas line with a gas flow of 5 l/h of CO_2-free oxygen or oxygen-nitrogen mixtures, dried over phosphorus pentoxide. The composition of the gas mixtures was determined interferometrically with an accuracy of 0.2% abs.

The barium peroxide powder was purified as prescribed by Brauer [6], starting from $Ba(OH)_2 \cdot 8H_2O$. This was first recrystallized from water, dried and reduced in a corundum crucible at 800° in CO_2-free hydrogen to BaO; the latter was then oxidized at 500° to BaO_2. The material which had been in contact with the surface of the crucible was rejected.

Results

The data of Table 2 show the decomposition temperature of BaO_2 as a function of the equilibrium oxygen pressure in the gas phase.

Table 2

$p(O_2)$ atm.	$\log p(O_2)$	Temperature °C
1.000	0.000	843 ± 2
0.932	—0.035	831 ± 4
0.826	—0.087	820 ± 6
0.693	—0.156	800 ± 10
0.538	—0.269	770 ± 15
0.208	—0.680	670 ± 20

With decreasing oxygen pressure the slope of the decomposition curve $p(O_2)$ vs. T for BaO_2 becomes increasingly flatter while the uncertainty of measurements of the decomposition temperature becomes greater.

In the temperature range from 670 to 843° the assumption of genuine equilibrium and temperature independent caloric data seems justified since the plot of the values of $\log p(O_2)$ vs. $1/T$ °K (Table 2) yields a straight line (Fig. 1). The best slope was determined by a least squares analysis and gives for the equilibrium constant of the reaction $BaO_2 = BaO + 1/2O_2$:

$$\log p(O_2) = - 4170/T + 3.74.$$

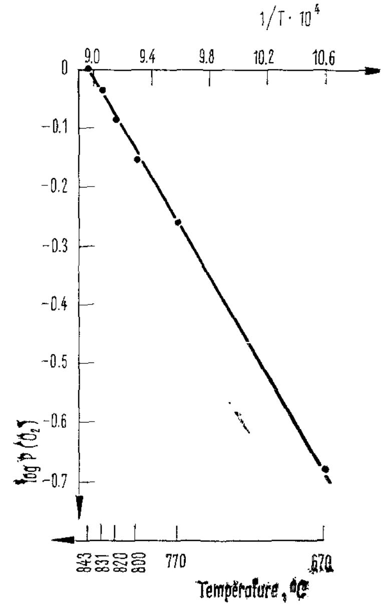

Fig. 1. Oxygen equilibrium pressure of $BaO_2 = BaO + 0.5O_2$ plotted against reciprocal temperature

The following values are all valid in the temperature range stated above:

enthalpy of reaction	$H = -19.1 \pm 0.5$ Kcal · mole^{-1};
entropy of reaction	$S = 17.1 \pm 0.4$ e.u.;
enthalpy of formation	$H(BaO_2) = -152.1 \pm 3$ Kcal · mole^{-1};
entropy of formation	$S(BaO_2) = 24.2 \pm 0.5$ e.u.;

Conversion into standard values was not possible because the required specific heat of BaO_2 was not available.

References

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Résumé — On a déterminé les températures de décomposition du peroxyde de baryum en équilibre avec la pression d'oxygène de la phase gazeuse, par mesures thermogravimétriques entre 670 et 843°. On a calculé les enthalpies et les entropies correspondant à la réaction $BaO_2 = BaO + 0.5\ O_2$ et à la formation de BaO_2.

Zusammenfassung — Zersetzungstemperaturen von mit dem Sauerstoffdruck in der Gasphase in Gleichgewicht stehendem Bariumperoxyd wurden thermogravimetrisch im Temperaturbereich von 670 bis zu 843° ermittelt. Enthalpie- und Entropiewerte der Reaktion $BaO_2 = BaO + 0.5\ O_2$ und der Bildung von BaO_2 wurden errechnet.

Резюме — Путем термогравиметрических измерений установлено, что разложение перекиси бария, в условиях равновесия с давлением кислорода в газовой фазе, происходит при температурах от 670° до 843°. Рассчитаны энтальпии и энтропии реакции $BaO_2 = BaO + 0.5\ O_2$ и образования BaO_2.