

the latter used crystallized silver iodide it is evident that the divergence between the two is within the error of the measurement.

Summary.

A repetition of Braune and Koref's calorimetric measurement of the heat of formation of silver iodide using 1 *N* potassium cyanide instead of 3 *N* solution as solvent for silver iodide has been made. Their result, a value of 15,100 calories per mole of silver iodide, has been confirmed.

PRINCETON, NEW JERSEY.

[CONTRIBUTION FROM THE DEPARTMENT OF INORGANIC CHEMISTRY, COLUMBIA UNIVERSITY, No. 373.]

THE CATALYTIC INFLUENCE OF FOREIGN OXIDES ON THE DECOMPOSITION OF SILVER OXIDE, MERCURIC OXIDE AND BARIUM PEROXIDE.¹

BY JAMES KENDALL AND FRANCIS J. FUCHS.

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Introduction.

The results obtained by previous investigators on the decomposition of substances liberating oxygen are, for the most part, very indefinite and unsatisfactory. Particular reference may be made to the extensive work done on the decomposition of *potassium chlorate* under the catalytic influence of metallic oxides.² The decomposition temperatures recorded for *simple oxides* also vary widely.

| | ° C. | | ° C. | | ° C. |
|-------------------|---------|------------------|---------|------------------|----------|
| Ag ₂ O | 250-350 | BaO ₂ | 450-825 | CrO ₃ | 180-320 |
| HgO | 175-660 | MnO ₂ | 210-560 | CuO | 800-1200 |

The data for *mixtures of oxides* are, in general, still more divergent. It is often impossible to correlate the results of different observers, either because the relative amounts of the components are not specified at all or because mention is made in such a way as to leave it quite uncertain whether volume, weight or molecular composition units were employed.

The present investigation is an attempt to obtain systematic data on the dissociation equilibria of silver oxide, mercuric oxide and barium peroxide, as affected by the presence of other oxides. The choice of these three oxides as experimental material was made on account of their ease of preparation and their conveniently low decomposition temperatures. It was anticipated that the results would prove of interest not only with respect to the mechanism of the reactions actually studied, but

¹ Condensation of a thesis submitted by Francis J. Fuchs in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University, May 1920.

² See Sodeau, *J. Chem. Soc.*, **81**, 1067 (1902).

also in connection with the more general problems of heterogeneous catalysis³ and the action of promoters.⁴ The data for barium peroxide, finally, are of particular importance in view of the possibility of their application to the industrial revival of the Brin process.

The results of earlier work on the dissociation of the above oxides may first be summarized.

Previous Work.

Silver Oxide.—No direct determinations of oxygen dissociation pressures below 300° have been made, although many investigators⁵ claim that decomposition begins even below 200°. G. N. Lewis⁶ found equilibrium pressures of 20.5 atmospheres at 302°, 32 atmospheres at 325° and 207 atmospheres at 445°. Oxygen evolution proceeded very slowly at first, but the accumulation of finely divided silver in intimate admixture with the oxide accelerated its decomposition considerably. Finely divided platinum and manganese dioxide were also shown to catalyze the reaction. To explain these results, Lewis suggested that the decomposition of the oxide takes place in two stages: (1) $\text{Ag}_2\text{O} \rightarrow 2\text{Ag} + \text{O}$; (2) $2\text{O} \rightarrow \text{O}_2$. The slowness of the latter reaction controls the velocity of the decomposition and on finely divided surfaces the adsorbed gases may be expected to react much more rapidly.

Mercuric Oxide.—The oxygen dissociation pressures above 500° were first established by Pélabon⁷ and the curve has been extended below 500° by Taylor and Hulett.⁸ These latter investigators also examined the effect of finely divided platinum and certain metallic oxides upon the reaction, and found that while the rate of oxygen evolution was considerably increased, the equilibrium pressure was not significantly changed. The temperature at which the oxygen pressure equals 1 atmosphere is approximately 490° according to Pélabon, and 500° according to Taylor and Hulett. No difference in behavior between the yellow and the red modifications of mercuric oxide was obtained.

Barium Peroxide.—Hildebrand,⁹ in a careful investigation on the thermal dissociation of barium peroxide, showed that solid solutions between BaO and BaO_2 are formed, the oxygen pressure of the two saturated solutions reaching 1 atmosphere at approximately 825°. Le Chatelier¹⁰ obtained a lower value, 796°. The difference is probably due to the influence of traces of water upon the reaction.

Extensive work on the effect of other oxides on the decomposition of barium peroxide has recently been carried out by Hedvall.¹¹ Nearly all of the oxides tested re-

³ H. S. Taylor, *J. Ind. Eng. Chem.*, **13**, 75 (1921).

⁴ Pease and Taylor, *J. Phys. Chem.*, **24**, 241 (1920).

⁵ For example, Le Chatelier, *Bull. soc. chim.*, [2] **48**, 342 (1887).

⁶ G. N. Lewis, *Z. physik. Chem.*, **52**, 310 (1905); **55**, 449 (1906); *THIS JOURNAL*, **28**, 139 (1906).

⁷ Pélabon, *Compt. rend.*, **128**, 625 (1899). Earlier experimenters obtained very discordant results.

⁸ Taylor and Hulett, *J. Phys. Chem.*, **17**, 565 (1913).

⁹ Hildebrand, *THIS JOURNAL*, **34**, 246 (1912).

¹⁰ Le Chatelier, *Compt. rend.*, **115**, 659 (1892).

¹¹ Hedvall, *Z. anorg. Chem.*, **104**, 163 (1918); **108**, 119 (1919). These papers were not published until the present work was well under way. Some duplication of experiments consequently occurs, but in view of the different methods employed this is in a certain measure desirable, since it offers a good means of testing the reliability of the results obtained.

duced the decomposition temperature and increased the rate of oxygen evolution considerably. In some cases (for example, with cuprous oxide) high reaction velocities were found even at temperatures below 200°. With certain oxides the effect was considered to be purely catalytic, with others formation of a compound between barium oxide and the added oxide was indicated.

General Review.—In few of the above investigations do the results of different workers stand direct comparison, and it is obvious that the chief cause of the discrepancies is the variable physical condition of the materials used. No doubt exists that the reactivity of a solid phase is very considerably controlled by its previous history,¹² and it is futile to expect a strongly ignited oxide to show the same behavior as a sample freshly precipitated from aqueous solutions and dried at a low temperature.

In all of the present work, consequently, standard and reproducible methods of preparation have been adopted. The various oxides were obtained in a finely divided state by precipitation whenever possible, and dried first in a vacuum desiccator and then in a Freas oven regulated to 140°. All oxides were dried for at least two months before use. In the event of their not attaining constant weight within that period, it was necessary to remove the last traces of firmly retained moisture by ignition. This procedure was not adopted except as a last resort, since it is evident from the literature that extreme and prolonged ignition renders the oxides more or less inert. Some investigators have claimed that non-ignited samples do not give reliable results (possibly owing to adsorbed gases or traces of water), but the data here presented do not substantiate this view, as will be seen below.

Experimental.

It must be noted at the start that the aim of the present work is to secure a preliminary survey over a comparatively wide field rather than to obtain results of the highest accuracy for a few isolated systems.¹³ For each of the fixed oxides examined, and for each of the mixtures of these with other oxides, the decomposition temperature has been determined at a single pressure only, namely 1 atmosphere. Variations in the barometer were found not to affect the temperature beyond the limits of experimental error.

The compositions of all mixtures are expressed in molecular percentages. Mixture of the component oxides was accomplished by mechanical agi-

¹² See Rideal and Taylor, "Catalysis in Theory and Practice," Macmillan Co., 1919, p. 16.

¹³ It is planned to examine certain of the more interesting systems in greater detail in a subsequent investigation.

tation.¹⁴ That this was adequate to ensure intimate admixture was proved by comparing the results so obtained with those given by co-precipitated oxides in the case of the system silver oxide:mercuric oxide. The decomposition temperatures checked throughout within the limits of experimental error. That the temperatures determined are true equilibrium temperatures for an oxygen pressure of 1 atmosphere was established for each mixture by approaching the equilibrium point from both directions, *i. e.*, with rising and with falling temperature. Reproducible values, within experimental errors, were consistently obtained. In certain cases a slight difference apparently existent on first trial between the values recorded for rising and for falling temperatures was found on further examination to be due to the slowness with which equilibrium was attained. By decreasing the rate of temperature change, such differences could be proportionately diminished until they became, to all intents and purposes, negligible.

Description of Apparatus.—The apparatus used is shown in the accompanying diagram (Fig. 1.) The furnace was of the crucible type (Hoskins make), the interior heating chamber being cylindrical, 12.5 cm. in diameter and 12.5cm. deep. A special

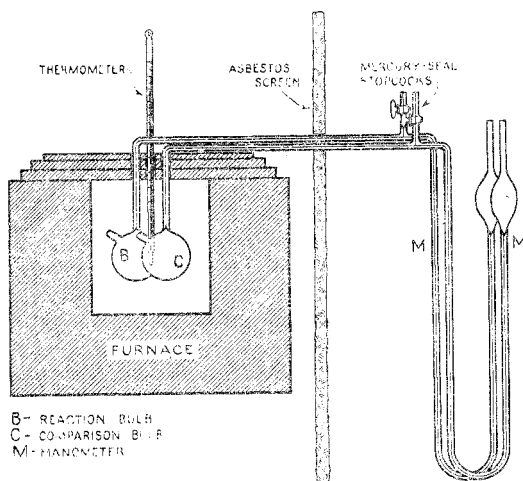


Fig. 1.

heating coil and rheostat capable of maintaining a constant temperature at any point up to 500° were employed. Temperatures were indicated on a nitrogen-filled thermometer¹⁵ of the Tycos type, reading to 500° and graduated for 75mm. immersion.

¹⁴ The separate oxides were first ground in a mortar to break up any caked masses. Every oxide employed was thus reduced to an approximate fineness of 100 to 200 mesh before use. The two oxides were then shaken up together in a closed test-tube until the mixture was apparently uniform. This was followed by a second light grinding in a mortar, after which the mixture was again thoroughly shaken.

¹⁵ The decomposition temperatures obtained were, in general, higher than was expected when the investigation was commenced. It is recognized that in many systems,

The bulb of the thermometer consequently occupied the central position in the heating chamber.¹⁶ The thermometer was calibrated while in position at the usual fixed points, and the standardization checked at intervals throughout the work.

The oxides under examination were enclosed in a thin-walled bulb of Jena glass, 25 mm. in diameter, joined to a capillary stem. The mixture was introduced into this reaction bulb through a short side tube, which was then sealed off. The extension of the capillary stem was bent, as indicated in the figure, to form a manometer, a mercury-seal stopcock for evacuating and charging with oxygen being also attached as shown. Benzyl benzoate (an inert, non-hygroscopic, non-volatile liquid of low density) was employed as manometer liquid, its movement on an attached millimeter scale being observed through a lens. An asbestos screen prevented radiation of heat from the furnace to the manometer.

A comparison bulb, with a blank charge of silica and a free volume as nearly as possible equal to that of the reaction bulb, was placed directly beside it in the heating chamber. This comparison bulb was attached to a second manometer, exactly similar to the first. Both bulbs were very carefully cleaned and dried before use.

Manipulation.—Before a determination was begun the two charged bulbs (already in position in the furnace) were filled with pure oxygen under atmospheric pressure through the stopcocks, and the benzyl benzoate in the two manometers adjusted to the same level. The temperature of the furnace was then raised very slowly and uniformly, and the change in level of the manometers noted. So long as nothing occurred in the reaction bulb, both liquid columns moved at uniform rates owing to the expansion of the enclosed oxygen. The ratio of these rates (very nearly unity, since the free volumes of the two bulbs were made as nearly equal as possible) was carefully established. As an arbitrary standard of unit volume change, a rise of 10 mm. in the comparison-bulb manometer (corresponding to a temperature change of approximately 2°) was fixed upon. As often as this unit volume change was indicated, the two stopcocks were opened to bring the systems back to atmospheric pressure, the temperature rising very gradually all the time.

Readings were continued in this way until the reaction-bulb manometer showed an abnormal volume change, indicating that evolution of oxygen had begun. The temperature was still allowed to rise slowly for about 50°, and the "rate of decomposition" arbitrarily measured by comparing the movements of the two columns. The current was then reduced where the curves are above 300° throughout, a thermocouple would have afforded a more convenient and accurate method of temperature measurement. In view of the inadvisability of changing the method when half-way through the work, however, the original set-up was retained.

¹⁶ The uniformity and constancy of temperature within the heating chamber were carefully tested. It was found that while a small temperature gradient existed at different heights, yet the temperature at different points near the center of the chamber remained constant and uniform, well within the experimental limits of accuracy, over extended periods of time. For very accurate determinations, a liquid bath would of course be preferable, but for the present work the air-bath here employed proved perfectly satisfactory.

sufficiently to cool the furnace gradually. Oxygen continued to be evolved for some time, as could be seen from the opposed volume changes in the two manometers, but as the temperature slowly fell a normal contraction was finally established in the reaction bulb. The temperature at which this first occurred was noted and compared with that at which oxygen evolution commenced. After the technique of the method had been mastered, these two temperatures in any single determination rarely varied by more than 2° to 5° . The experiment was repeated with new charges of oxides and with varying rates of heating and cooling until the equilibrium point had been satisfactorily fixed.

The results obtained for the various systems examined may now be presented. The first series, in which the decomposition of silver oxide is studied, is taken up somewhat in detail in order to make clear, certain points in the experimental procedure. The remaining systems are more briefly reported upon and subjected to a general discussion later.

The System $\text{Ag}_2\text{O} : \text{HgO}$.

Silver oxide was prepared by addition of a saturated solution of barium hydroxide to a warm solution of recrystallized silver nitrate in distilled water free from carbon dioxide. The precipitate was washed until free from barium hydroxide and nitrate, then carefully dried. Particular precautions were taken to prevent absorption of carbon dioxide at any stage of the preparation.

Mercuric oxide was obtained in a similar way by precipitation from hot solutions of mercuric chloride and barium hydroxide. The red precipitate was repeatedly digested with boiling water, filtered under suction and carefully dried.

| Ag ₂ O in mixture. %. | Equilibrium Temperature ($P_{\text{O}_2} = 1 \text{ atm.}$). | | | Relative rate of decomposition. 304° . |
|--|--|-----------------|--------------|--|
| | Rising. °C. | Falling. °C. | Mean. °C. | |
| 100 | 254 | 254 | 254 | 1.0 |
| 90 | 245 | 245 | 245 | 2.0 |
| 50 | 231 | 230 | 231 | 7.0 |
| 10 | 249 | 250 | 250 | 10.0 |
| 0 | 429 | 432 | 431 | ... |

The first column in the above table shows the molecular composition of the oxide mixtures used. The average decomposition temperatures for 1 atmosphere of oxygen, as obtained with rising and with falling temperature, follow. The mean of all results obtained is given in the fourth column. The last column indicates the catalytic influence of the added oxide (mercuric oxide) on the decomposition of the silver oxide at a fixed temperature, 304° (50° above the decomposition temperature of pure silver oxide). These relative decomposition rates were obtained by directly comparing the excess movements in the manometer levels for reaction bulbs containing the pure oxide and the different mixtures at this temperature, correcting for the various amounts of silver oxide present in each bulb.

The results obtained for pure silver oxide were in agreement with those of G. N. Lewis.⁶ When the oxide was first heated, oxygen evolution was extremely slow below 300° ; above this temperature it became increasingly more rapid. On subsequent heatings, decomposition was markedly

accelerated by the traces of finely divided silver already present.¹⁷ The results here given all refer to fresh samples of oxide. Although it was necessary to perform the work with great care in order to obtain concordant results, the samples used were evidently more reactive than Lewis's preparations. We are perfectly confident, from the regularity of the results, that the temperatures given above are true "oxygen equilibrium temperatures" and that the volume changes indicated in the manometer cannot be ascribed to evolution or absorption of minute traces of water or carbon dioxide present in the oxide. Direct tests showed that exceedingly small additions of water or carbon dioxide to the oxide mixtures produced very large and irregular volume changes, the vaporization of 0.0001 g. of water involving a depression of approximately 150 mm. on the manometer scale. In none of the measurements recorded in this article was any such effect observed.

Pure mercuric oxide also showed a very small decomposition rate, which is independent, however, of the period of heating. The decomposition temperature obtained for $p_{O_2} = 1$ atmosphere is much lower than that recorded by previous investigators, probably owing to the different methods of preparation employed.

The results for mixtures of the two oxides were more easily established. As will be seen from the figures in the final column, the decomposition temperature of silver oxide is lowered and the rate of oxygen evolution considerably increased in the presence of mercuric oxide. A series of measurements with "co-precipitated oxides" in the same proportions (obtained by adding barium hydroxide solution to a solution containing the requisite amounts of silver nitrate and mercuric chloride) gave substantially identical results, the actual mean temperatures obtained being 246°, 232° and 251° for the three mixtures tabulated above.

The System $Ag_2O : BaO_2$.

Barium peroxide was prepared from recrystallized barium chloride by addition of sodium peroxide, the two solutions being mixed at 0° under constant stirring. The precipitated octohydrate was filtered, washed thoroughly and dehydrated by heating first to 100°, then (after standing in a vacuum desiccator over phosphorus pentoxide for two weeks) to 350°, the heating being very carefully conducted in order to ensure a slow rise in temperature and prevent formation of barium hydroxide.

| Ag ₂ O in mixture. %. | Equilibrium Temperature ($p_{O_2} = 1$ atm.). | | | Relative rate of decomposition. 304°. |
|--|--|-----------------|--------------|--|
| | Rising. °C. | Falling. °C. | Mean. °C. | |
| 90 | 201 | 200 | 201 | > 4.0 |
| 50 | 200 | 198 | 199 | > 7.5 |
| 10 | 226 | 226 | 226 | > 15.0 |

As in the previous system, the decomposition temperature of silver oxide is lowered and the rate of decomposition markedly increased by the second oxide present. Here

¹⁷ For one sample, for example, the decomposition rates at 304° for three successive heatings were 1:3:6.

the oxygen evolution from mixtures of the two oxides at the fixed temperature 304° was so rapid as to carry the manometer liquid beyond the bend of the tube. The values given above are consequently merely minima.

The System $\text{Ag}_2\text{O} : \text{CuO}$.

Copper oxide was prepared by slow addition of 10% sodium hydroxide solution to a hot solution of carefully purified cupric sulfate. The precipitate, when completely transformed from bluish to deep black, was separated and repeatedly digested with boiling water until free from sulfate. It was then dried by heating first to 100° , then to 280° .

| Ag ₂ O in mixture. %. | Equilibrium Temperature ($p_{\text{O}_2} = 1 \text{ atm.}$). | | | Relative rate of decomposition. 304° . |
|-------------------------------------|--|-----------------|--------------|---|
| | Rising. °C. | Falling. °C. | Mean. °C. | |
| 90 | 249 | 249 | 249 | > 3.0 |
| 50 | 240 | 241 | 240 | > 8.0 |
| 10 | 249 | 250 | 250 | > 50.0 |

In this system the temperature of decomposition of the silver oxide (254°) is not significantly affected; the rate of oxygen evolution, however, is enormously increased.

To test the effect of the previous history of the added oxide on the temperature and rate of the decomposition, the experiments for the equimolecular mixture were repeated with cupric oxide which had previously been ignited to a red heat several times.¹⁸ The relative inactivity of such a specimen was shown by the fact that the equilibrium temperature was changed to 252° , the rate of oxygen evolution also falling off considerably.¹⁹

The System $\text{Ag}_2\text{O} : \text{MnO}_2$.

Manganese dioxide was prepared by adding potassium chlorate in small quantities to a boiling, slightly acid solution of recrystallized manganese nitrate. The precipitate was separated off, washed repeatedly and dried first at 100° and then at 300° in an atmosphere of oxygen.

| Ag ₂ O in mixture. %. | Equilibrium Temperature ($p_{\text{O}_2} = 1 \text{ atm.}$). | | | Relative rate of decomposition. 304° . |
|-------------------------------------|--|-----------------|--------------|---|
| | Rising. °C. | Falling. °C. | Mean. °C. | |
| 90 | 220 | 220 | 220 | > 4.0 |
| 50 | 229 | 231 | 230 | > 4.0 |
| 10 | 271 | 272 | 271 | 10.0 |
| 0 | 418 | 420 | 419 | ... |

For the 90% and 50% mixtures, the usual phenomena (lowering of decomposition temperature and increase in rate of decomposition) are again encountered. For the 10% mixture, however, although the rate of oxygen evolution at 304° is apparently greater than that of pure silver oxide, the actual equilibrium temperature is raised.

Pure manganese dioxide is found to have a definite decomposition temperature of 419° ; the rate of decomposition at that point is slow, but becomes much more rapid above 480° . Previous experimenters have obtained very discordant values for this oxide. Moissan²⁰ gives 230° ; Wright and Luff,²¹ 390° ; Gorgen,²² 400° ; Hempel,²³ 470° .

¹⁸ The dissociation temperature of CuO was found by Foote and Smith, *THIS JOURNAL*, **30**, 1344 (1908), to be about 1025° .

¹⁹ Compare Lemoine, *Compt. rend.*, **162**, 702 (1916).

²⁰ Moissan, *Ann. chim. phys.*, **21**, 232 (1880).

²¹ Wright and Luff, *Ber.*, **11**, 2144 (1878).

²² Gorgen, *Compt. rend.*, **110**, 134 (1890).

²³ Hempel, *Z. Elektrochem.*, **18**, 729 (1912).

to 500°; while Meyer and Rötgers²⁴ state that no dissociation is observable below 530° in air or below 565° in pure oxygen. These discrepancies are undoubtedly due to differences in the physical condition and in the completeness of the dehydration of the oxide.

The System $\text{Ag}_2\text{O} : \text{Fe}_2\text{O}_3$.

Ferric oxide was prepared by addition of excess of ammonium hydroxide to a clear solution of recrystallized ferric chloride. The precipitate was digested with boiling water several times until free from chloride, dried by heating to 100° and finally dehydrated by ignition in a porcelain crucible.

| Ag ₂ O in mixture. %. | Equilibrium Temperature ($p_{\text{O}_2} = 1 \text{ atm.}$). | | | Relative rate of decomposition. 304°. |
|--|--|------------------|---------------|--|
| | Rising. ° C. | Falling. ° C. | Mean. ° C. | |
| 90 | 222 | 224 | 223 | > 2.5 |
| 50 | 247 | 248 | 248 | > 5.0 |
| 10 | 270 | 268 | 269 | > 10.0 |

The results are very similar to those obtained with manganese dioxide in the preceding table.

The System $\text{Ag}_2\text{O} : \text{CeO}_2$.

Cerium dioxide was prepared by addition of ammonium hydroxide to a solution of purified ceric nitrate. The precipitate was thoroughly washed, dried at 100°, then very slowly raised to a red heat to complete the dehydration.

| Ag ₂ O in mixture. %. | Equilibrium Temperature ($p_{\text{O}_2} = 1 \text{ atm.}$). | | | Relative rate of decomposition. 304°. |
|--|--|------------------|---------------|--|
| | Rising. ° C. | Falling. ° C. | Mean. ° C. | |
| 90 | 248 | 250 | 249 | 1.0 |
| 50 | 269 | 273 | 271 | 1.5 |
| 10 | 280 | 280 | 280 | 4.5 |

In this series the catalytic influence of the added oxide upon the decomposition of the silver oxide is still less pronounced than in the cases of manganese dioxide and ferric oxide. The 90% mixture gives a decomposition temperature only slightly below that of pure silver oxide, while the decomposition temperatures for the remaining mixtures are considerably higher. The rate of oxygen evolution for the various mixtures at 304° is less than in any of the previous series.

The System $\text{Ag}_2\text{O} : \text{SiO}_2$.

Silicon dioxide was obtained by addition of hydrochloric acid to a solution of sodium silicate. The gelatinous precipitate was washed, ignited to a powder, washed repeatedly till free from salts, dried and re-ignited.

| Ag ₂ O in mixture. %. | Equilibrium Temperature ($p_{\text{O}_2} = 1 \text{ atm.}$). | | | Relative rate of decomposition. 304°. |
|--|--|------------------|---------------|--|
| | Rising. ° C. | Falling. ° C. | Mean. ° C. | |
| 90 | 250 | 251 | 250 | 1.5 |
| 50 | 261 | 263 | 262 | 2.0 |
| 10 | 285 | 284 | 284 | 5.0 |

The results are substantially identical with those given by cerium dioxide mixtures.

The System $\text{Ag}_2\text{O} : \text{CrO}_3$.

Chromic anhydride was prepared by careful addition of conc. sulfuric acid to a well-stirred solution of recrystallized sodium dichromate. The precipitated chromium trioxide was separated by filtering through glass wool, washed with conc. nitric acid

²⁴ Meyer and Rötgers, *Z. anorg. Chem.*, **57**, 104 (1908). See however, Askenasy and Klonowski, *Z. Elektrochem.*, **16**, 107 (1910).

until free from sulfate, dried as completely as possible on a porous tile and finally heated to constant weight at 120°.

The decomposition temperatures for pure chromium trioxide given in the literature vary widely. Arctowski,²⁵ for example, claims that rapid decomposition occurs just above the melting point (180–190°), while Honda²⁶ has more recently reported a *minimum* temperature of 320°, the resultant lower oxide having the composition Cr₆O₁₅. The present experiments indicated melting of the oxide at 180° and an equilibrium temperature for $p_{O_2} = 1$ atmosphere at 190°. Owing to the volume change involved in the change of state the manometer readings were difficult to interpret unless the temperature was varied extremely slowly. The above values are to be regarded as only approximate.

With mixtures of chromium trioxide and silver oxide containing 90% and 50% silver oxide no concordant results could be obtained. After the melting of the chromium trioxide around 180° rapid oxygen evolution was noted at about 200° with rising temperature, but with falling temperature decomposition ceased at much higher points, 225° and 245° respectively. The mixture containing 10% of silver oxide, however, gave a definite equilibrium temperature of 161°, *i. e.*, below the melting-point of chromium trioxide.

Mercuric Oxide Systems.

| Added oxide. | HgO in mixture. %. | Equilibrium Rising. ° C. | Temperature Falling. ° C. | ($p_{O_2} = 1$ atm.) Mean. ° C. | Relative rate of decomposition, 471°. |
|--------------------------------|-----------------------|-----------------------------|------------------------------|--|---------------------------------------|
| | 100 | 429 | 432 | 431 | 1.0 |
| CuO | 90 | 398 | 400 | 399 | > 1.0 |
| | 50 | 380 | 382 | 381 | > 2.0 |
| | 10 | 419 | 419 | 419 | > 10.0 |
| BaO ₂ | 90 | 279 | 281 | 280 | > 1.0 |
| | 50 | 278 | 276 | 277 | > 1.5 |
| | 10 | 282 | 284 | 283 | > 7.0 |
| MnO ₂ | 90 | 369 | 371 | 370 | > 1.0 |
| | 50 | 225 | 224 | 225 | > 1.5 |
| | 10 | 354(?) | 380(?) | 367(?) | > 10.0 |
| Fe ₂ O ₃ | 90 | 399 | 399 | 399 | > 1.5 |
| | 50 | 410 | 411 | 410 | > 5.0 |
| | 10 | 425 | 423 | 424 | > 20.0 |
| CeO ₂ | 90 | 414 | 414 | 414 | > 2.0 |
| | 50 | 430 | 431 | 431 | > 2.0 |
| | 10 | 439 | 439 | 439 | > 5.0 |

As in the case of silver oxide systems, copper oxide and barium peroxide both lower the decomposition temperature and increase the rate of oxygen evolution.²⁷ Copper oxide, as before, has the greater effect upon the rate of the reaction, barium peroxide the greater effect on the equilibrium temperature.

Ferric oxide and cerium dioxide again exhibit much less pronounced influence, the decomposition temperature being only slightly changed. Manganese dioxide here induces a far greater temperature decrease. The results for the 10% mixture, however, are rather uncertain.

²⁵ Arctowski, *Z. anorg. chem.*, **9**, 29 (1895).

²⁶ Honda, *Science Repts. Tohoku Imp. Univ.*, **4**, 897 (1915).

²⁷ A reference temperature of 471° (40° above the decomposition point of pure HgO) has been chosen for comparing rates of reaction in the above table.

Attempts were also made to examine the effect of chromic anhydride and silicon dioxide on the decomposition of mercuric oxide. With chromic anhydride, phenomena similar to those described in the silver oxide series were observed. The 90% and 50% mixtures showed rapid evolution with rising temperature immediately after fusion of the chromium trioxide, *i. e.*, below 200°. With falling temperature, decomposition ceased at much higher temperatures. The 10% mixture gave a definite equilibrium temperature of 171°.

With silicon dioxide no satisfactory results could be obtained. The 90% mixture evolves oxygen at a temperature slightly below the normal, while with the remaining mixtures, the decomposition temperature is considerably raised. No consistency could be attained, however, between results with rising and with falling temperatures.

Barium Peroxide Systems.

| Added oxide. | BaO ₂ in mixture. % | Equilibrium Temperature. ($p_{O_2} = 1 \text{ atm.}$) | | Mean. °C. |
|--------------------------------|-----------------------------------|---|-----------------|--------------|
| | | Rising. °C. | Falling. °C. | |
| CuO | 90 | 317 | 320 | 318 |
| | 50 | 322 | 322 | 322 |
| | 10 | 328 | 329 | 329 |
| MnO ₂ | 90 | 342 | 342 | 342 |
| | 50 | 322 | 326 | 324 |
| | 10 | 330(?) | 337(?) | 333(?) |
| Fe ₂ O ₃ | 90 | 321 | 324 | 323 |
| | 50 | 345 | 344 | 345 |
| | 10 | 357(?) | 360(?) | 358(?) |

The equilibrium temperature for pure barium peroxide (approx. 825°) being far beyond the limits of the present work, no column of relative rates of decomposition can be included in the above table. For all of the mixtures listed, however, the rate of oxygen evolution even below 400° was already quite rapid, so that the catalytic effect of the added oxides upon the reaction is in all cases very considerable.

The presence of copper oxide, manganese dioxide or ferric oxide lowers the decomposition temperature of barium peroxide by nearly 500°. With the 10% mixtures of the last two oxides, the results obtained were not altogether satisfactory, the figures given above being the mean of several rather divergent determinations.

With cerium dioxide mixtures, no indications of oxygen evolution were given at 520°, the limit of temperature measurement.

In the presence of silicon dioxide, decomposition of the barium peroxide was found to begin at much lower temperatures. With rising temperature, values of 247°, 295° and 309° were obtained for mixtures containing 90%, 50% and 10% of barium dioxide respectively. With falling temperature, however, these figures could not be duplicated.

Discussion of Results.

Silver Oxide Systems.—From the tables given above, it is evident that the decomposition temperature of silver oxide for $p_{O_2} = 1$ atmosphere is very markedly affected by the presence of other oxides. In all cases the first addition of a foreign oxide lowers the decomposition temperature. With larger amounts a minimum value is reached, while an excess of added oxide may actually raise the decomposition temperature above the normal. Invariably, however, the rate of oxygen evolution is increased.

If we are to retain the view that a catalyst, however much it may hasten

the attainment of equilibrium, cannot alter the equilibrium point of a reaction, then it is certain that the influence of the foreign oxides throughout this series is not purely catalytic, since the equilibrium point is undoubtedly changed. The increase in the rate of oxygen evolution may it is true, be ascribed entirely to adsorption effects, as indicated by Lewis,⁸ but the wide variations in the decomposition temperature cannot be satisfactorily explained on the basis of adsorption alone. All of the results, indeed, point to the conclusion that the added oxide enters directly into the reaction.

The simplest and most plausible assumption that can be made is the formation of transient intermediate compounds between the two oxides.²⁸ Such compounds could be regarded as *salts* produced by the combination of a basic and an acidic component, and the relative instability of the salt would determine the change in the decomposition temperature. Silver oxide being characteristically basic, we might expect other basic oxides to give very unstable complexes with it. In point of fact, the decomposition temperature is lowered most considerably by barium dioxide and mercuric oxide. The complexes of silver oxide and more acidic oxides, on the other hand, might be predicted to be more stable. In line with this, we find excess of ferric, manganese, ceric and silicic oxides raising the decomposition temperature.

In the system $\text{Ag}_2\text{O}:\text{CrO}_3$, the formation of a salt (Ag_2CrO_4) between the two components may be definitely established. The salt is produced in the reaction bulb just above the melting point of chromium trioxide with considerable evolution of heat and partial decomposition. With falling temperature, oxygen evolution ceases at much higher temperatures, indicating that the complex is more stable than chromium trioxide. It is still, however, slightly less stable than silver oxide.

Mercuric Oxide Systems.—The results for this series are substantially similar to those given by the corresponding silver oxide systems, and the same explanation may be adduced. Barium dioxide lowers the decomposition temperature very considerably, cupric oxide has less effect, ferric and ceric oxides have very little influence upon the equilibrium point. The results for chromium trioxide mixtures point to the formation of a relatively stable compound, mercuric chromate, HgCrO_4 . In the same way the discordant results for silicon dioxide mixtures with rising and falling temperatures may be explained by the production of mercury metasilicate, HgSiO_3 .

It is important to note that the results here obtained are in direct opposition to those of G. B. Taylor and Hulett.⁸ The only explanation that

²⁸ Compare Lewis, "A System of Physical Chemistry," Longmans, Green and Co., 1918, vol. 1, p. 456. The formation of solid solutions might affect the results in isolated systems, but could scarcely be adduced as a general phenomenon.

can be suggested at present is that the oxides employed by these investigators were rendered inactive by previous prolonged ignition.

Barium Peroxide Systems.—The three oxides listed (cupric oxide, manganese dioxide and ferric oxide) all lower the decomposition temperature nearly 500° . If, as appears probable from the results of Hedvall and Zweigbergk,²⁹ barium dioxide evolves oxygen simultaneously with silver oxide and mercuric oxide in its mixtures with these two oxides, then in their presence its decomposition temperature is still further decreased. Cerium dioxide is much less active. The results for silicon dioxide mixtures are, as before, best explained by the formation of a stable silicate.

Hedvall and Zweigbergk have already obtained evidence in favor of the assumption that, in the majority of systems containing barium dioxide and a foreign oxide, salt formation is the predominant factor in controlling the decomposition. The present results are in general agreement with their data. Quantitative agreement is hardly to be expected in view of the different methods of treatment of the oxides employed. There is, besides, no evidence that the values given by Hedvall and Zweigbergk (as obtained by the determination of breaks in the heating curve) represent true equilibria. In all probability the decomposition temperatures recorded are, in general, too high.

General Review.—A mixture of two substances, each of which evolves oxygen when heated alone, almost always decomposes much more readily than either of its separate components. In certain cases each substance simultaneously promotes the decomposition of the other. Silver oxide and hydrogen dioxide, for example, mutually decompose one another at ordinary temperatures.³⁰ In other instances only one of the components loses oxygen. Thus the decomposition temperature of potassium chlorate is very considerably lowered by the presence of foreign oxides, the case of manganese dioxide being the most familiar. The mechanism of this reaction has been the subject of much speculation. From the work of Sodeau³¹ it has been definitely established that the manganese dioxide must enter directly into the decomposition cycle, since a crystalline sample is transformed into a finely-divided powder in the course of the reaction.

Much of the work on the catalytic effect of foreign oxides on the de-

²⁹ Hedvall and Zweigbergk, *Z. anorg. Chem.*, **108**, 119 (1919). A convenient summary of the results obtained by these workers may be found in *Ann. Repts. Chem. Soc.*, **17**, 40 (1920).

³⁰ Various theories have been advanced to explain this reaction, Liveing's hypothesis of local energy transfer being particularly interesting. (See Rideal and Taylor, "Catalysis in Theory and Practice," Macmillan Co., 1919, p. 42. The action of other oxides on H_2O_2 has recently been investigated by Loemine (*Compt. rend.*, **162**, 702 (1916)).

³¹ Sodeau, *J. Chem. Soc.* **77**, 137, 717 (1900); **79**, 247, 939 (1901); **81**, 1066 (1902).

composition of potassium chlorate is open to question (contradiction between the results of different investigators being frequent) yet a survey of the more reliable data shows that those oxides which have been found to be most active in the present work are also most active in promoting the decomposition of potassium chlorate and hydrogen dioxide. Our knowledge of the whole subject of heterogeneous catalysis is still so elementary that it is dangerous to attempt to draw any final conclusions as to the part which the added oxides play in these processes. For the several series of systems here studied, however, the hypothesis of the formation of intermediate complexes would appear to provide a logical explanation of the experimental facts. In any quantitative study of the rate of decomposition in any particular mixture, of course, adsorption effects would also need to be taken into consideration.

In a subsequent article the practical application of the results obtained for barium dioxide systems to the Brin oxygen process will be discussed, and the effect of the simultaneous addition of more than one foreign oxide upon the temperature and rate of the decomposition investigated. In certain other reactions (*e. g.*, the oxidation of carbon monoxide to the dioxide in the purification of hydrogen³²) it has been discovered that an enormous increase in the catalytic activity of a single oxide may be induced by the presence of a very small amount of a second oxide which alone may be relatively inert. In the removal of carbon monoxide as a toxic gas from air, similarly, it has been found³³ that mixtures of oxides (*e. g.*, MnO_2 , CuO , Co_2O_3 , Ag_2O) are much more efficient than any single component. If this "promoter action" is similarly pronounced in the decompositions here studied (and preliminary experiments indicate that this is the case) then the fascinating possibility arises of resurrecting the Brin process industrially by carrying out the whole cycle of operations at ordinary temperatures. Whether this is feasible in practice remains, of course, to be tested.

Summary.

The effect of foreign oxides upon the temperature and rate of decomposition of silver oxide, mercuric oxide and barium peroxide under an oxygen pressure of one atmosphere has been experimentally investigated.

In almost all of the systems examined, the added oxide induces a considerable change in the decomposition temperature. Most commonly there is a marked lowering in this point, thus (to cite an extreme case) an equimolecular mixture of barium dioxide and cupric oxide has an oxygen equilibrium pressure of 1 atmosphere at 322° , approximately 500° below the decomposition temperature of pure barium dioxide. In a few systems a

³² Rideal and Taylor, *op. cit.*, p. 29 *et seq.*

³³ Lamb, Bray and Frazer, *J. Ind. Eng. Chem.*, **12**, 213 (1920).

comparatively small rise in the decomposition temperature is indicated. In all instances, however, the rate of oxygen evolution is significantly increased.

It must be emphasized that the decomposition temperatures recorded refer to true equilibrium conditions, concordant values being obtained with rising and with falling temperature. Disagreement with the results of previous investigators is, in certain systems, very evident. Much of the earlier work in this field is, however, not directly comparable, owing (in large measure) to differences in the physical condition of the materials employed. As far as possible, standard and reproducible methods of preparation have here been adopted.

The results obtained have been tentatively ascribed to the formation of unstable intermediate compounds between the two oxides present. The increased rates of decomposition may be referred to adsorption effects, but the large temperature changes point strongly to the actual participation of the added oxides in the reaction. Direct evidence was given in certain mixtures of the production of relatively stable complexes.

A later article will continue the study of systems of the types here examined, with particular reference to the Brin oxygen process and the important question of "promoters."

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, SYRACUSE UNIVERSITY.]

THE PREPARATION AND STUDY OF THE RARER ALKALI BROMATES. RUBIDIUM BROMATE.

BY HAROLD D. BUELL AND C. R. McCROSKEY.

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Some time ago the preparation and some of the properties of cesium bromate were discussed in *THIS JOURNAL*.¹ In the present paper the work has been extended to the rubidium bromate, which like the cesium salt, has had no mention in chemical literature. Some further data on cesium bromate have been added in this paper.

Preparation of Rubidium Bromate.

A sample of rubidium chloride, of doubtful purity, was converted into the alum² and this was recrystallized several times. The solution of the pure alum was digested with an excess of barium carbonate on the hot plate for several hours, and after filtering, treated with barium hydroxide and then with carbon dioxide. After again filtering, the solution gave no tests for traces of aluminum, barium, potassium, cesium or sulfate.

¹ McCroskey and Buell, *THIS JOURNAL*, **42**, 1786 (1920).

² Browning, "Introduction to the Rarer Elements," John Wiley and Sons Co., 1919, p. 15.