the same velocity under unit potential gradient in solutions of all different concentrations. The validity of this assumption was denied by Jahn,[1] who explained his results by assuming increased speed with increased concentration. It is greatly to be hoped that further investigation will throw light upon the actual facts.

In later articles one of the authors will present a method of calculating relative degrees of ionization from conductivity and transference data without assuming that the ions move with the same velocity at different dilutions.[2] Methods will also be presented of calculating the free energy of dilution from freezing-point and vapor-pressure data.

The experimental work described in this article was done in the chemical laboratory of the University of Michigan.

CINCINNATI, OHIO, AND ANN ARBOR, MICH.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF THE UNIVERSITY OF PENNSYLVANIA.]

THE THERMAL DISSOCIATION OF BARIUM PEROXIDE.

BY JOEL H. HILDEBRAND.

Received January 15, 1912.

Introduction.

The equilibrium between barium oxide, peroxide and oxygen has a technical interest due to the use of barium peroxide in the preparation of hydrogen peroxide, and in the historic, though now almost abandoned, Brin process for oxygen. It must also share in the general interest given to all heterogenous equilibria by the discussion of the applicability to them of Nernst's heat theorem.[3] In addition to the researches of Boussingault and others on this equilibrium we have the measurements of Le Chatelier[4] of the dissociation pressures between 525° and 790°. In view of the discrepancies between later work and that of Le Chatelier, and the desirability of exact knowledge of this equilibrium, the following work was undertaken. Since its completion the writer has discovered a thesis by Wilhelm Becker, "Zur Frage der Erdalkaliperoxydbildung,"[5] to which reference will be made in the discussion of the results of this work.

Apparatus.

The accuracy of measurements of this sort depends greatly upon the accuracy with which the temperature can be maintained and measured.

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[1] See note, p. 245.

[2] The possibility of combining transference and conductivity measurements for calculating the degree of dissociation of electrolytes was suggested to the writer by Professor Lewis.

[3] Foote and Smith, THIS JOURNAL, **30**, 1344. Walden, *Ibid.*, 1350. Johnston, *Ibid.*, 1357.

[4] *Compt. rend.*, **115**, 655 (1892).

[5] *Prag.*, 1909. (Work done at Karlsruhe.)

Every effort was made, therefore, to measure the temperature with unusual care. For this purpose a Pt, Pt-Rh thermocouple was used, made by Heraeus and calibrated just before use by the Bureau of Standards. From the data given by the Bureau the constants in the familiar quadratic formula were calculated connecting temperature and e. m. f. The e. m. f. of the couple was determined by the aid of a Wolff potentiometer, a Leeds and Northrup "Type H" galvanometer, and a Weston cell, standardized by the Bureau of Standards. The constant potential was obtained from two large cells as described by Hulett.[1] The accuracy of this combination was tested further by determining the melting point of pure zinc. The e. m. f. at which the zinc solidified gave, by use of the formula for the couple, the true value, 419°. Any errors in the values for temperature given later can hardly be due to the method of measurement, but must be ascribed to the difficulty of maintaining high temperatures constant within one or two degrees. For the experiments in which precision was not required the temperature was determined by means of a Siemens-Halske galvanometer, the scale of which was corrected by use of the values obtained with the potentiometer. In all the precision work the cold junction was maintained at 0° by immersion in cracked ice.

The peroxide was heated in an electric furnace made by winding on a porcelain tube, 2.2 × 30 cm., two layers of "Nichrome" ribbon, $^1/_{16}$ inch wide and 0.0035 inch thick. The layers had resistances of 70 and 90 ohms, respectively. They were insulated from each other and protected from the tube by asbestos paper and a paste made of water glass and magnesia. The whole was packed with broken pipe covering into an earthenware pipe and the ends fastened with asbestos board and the water glass paste. The two coils could be connected either separately, in series, or in parallel, an arrangement permitting great variations in temperature without requiring a regulating rheostat of great capacity or the undue waste of current. A temperature of over 1000° was easily obtained with this furnace. To insure uniform temperature in the middle third of the tube, not only was the ribbon wound more closely at the ends than at the middle, but a copper tube 12 cm. long, and covered with water glass to prevent oxidation, was placed within the porcelain tube of the furnace. When the ends of this copper tube were plugged with asbestos the temperature was constant within one degree throughout the interior. The current heating the furnace was controlled by means of a rheostat and ammeter.

In order that the equilibrium pressures might be attained rapidly, the space to be filled by the evolved oxygen was made as small as possible, not only in the tube containing the peroxide, but in the manometer

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[1] *Phys. Rev.*, **27**, 33 (1908).

as well. The tubes used differed slightly in the different experiments so they will be described as the experiments are taken up in detail. The manometer was arranged so that mercury could either be poured in from a pipet at the top of the open arm or run out at the bottom through a stopcock, thereby making it possible to keep the mercury at approximately the same height in the arm leading to the tube containing the peroxide, in spite of changes of pressure in the latter. Moreover, immediately above the mercury the manometer tube narrowed to a capillary which led to the tube in the furnace and had a T-arm provided with a stopcock through which the apparatus was exhausted at the beginning of each experiment and oxygen could be removed later on. The open arm of the manometer was twice as long as the constant level arm, so that pressures could be measured between 0 and 2 atmospheres. The position of the mercury was measured on a scale clamped to the manometer, a sliding device being used to avoid parallax. Pressures could be read to within 0.2 mm., but the unavoidable temperature errors make such accuracy unnecessary.

A small but efficient home-made Antropoff pump[1] served for exhausting the apparatus and removing oxygen.

Material Used.

The barium peroxide used was prepared from "C. P." barium hydroxide. The latter was recrystallized and freed from carbonate, dissolved in cold water and treated with successive portions of hydrogen peroxide, precipitating hydrated barium peroxide. The first precipitate was rejected, the middle fraction being filtered, washed, pressed dry, and put at once into a desiccator over phosphorus pentoxide which was then evacuated. It was left thus for two weeks, during which time all but a trace of the water was removed, leaving the anhydrous peroxide. A portion of this material was tested with the spectroscope. No calcium or strontium could be detected.

Investigation of the Nature of the Phases.

Several preliminary measurements of pressure-temperature curves gave different values of pressure at the same temperature in the different experiments, showing the system to be divariant, which proved that, since there were two components, only two phases could be present, indicating that the barium oxide resulting from the decomposition of part of the peroxide did not, at least at first, appear as a new phase, but must form a solid solution with the excess of peroxide. This important fact is merely mentioned by Le Chatelier, no details being given. It seems to have escaped the notice, therefore, of even the most detailed text-books.

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[1] *Chem. Ztg.*, 34, 979 (1910).

In order to investigate the phase relations of the system, a study was made of the effect upon the pressure of removing successive portions of oxygen, the temperature being held constant. For this purpose a pipet-shaped vessel with a volume of about 20 cc. was made of Jena glass, the bulb filled with 0.708 g. of BaO_2, and a closed Jena tube slipped into the larger outlet of the "pipet." Into the larger tube of the "pipet" was inserted a slightly smaller one, closed at the inner end which was pushed into the middle of the charge and cemented to the "pipet" at the outer end with marine glue. This tube served as the protecting sheath into which the thermocouple was placed, the wires being insulated from each other by Jena tubing 1 mm. in diameter. The charged "pipet" was placed in the electric furnace and the smaller tube leading from the bulb was cemented to the manometer with marine glue. The ends of the electric furnace tube were plugged with asbestos as far in as the ends of the bulb of the "pipet."

The apparatus was exhausted to less than 1 mm. at 200°. The temperature was then raised to 750° and oxygen was removed in successive portions, collected in a eudiometer over mercury at the outlet of the pump, the volume, temperature, and pressure of the oxygen in the eudiometer, and the pressure of that in the "pipet" in the furnace being noted after each removal. The volume of oxygen removed was reduced to standard conditions, and the pressure corrected by frequent readings of the barometer, the proper temperature corrections being made in each case.

TABLE I.

I. $t = 750°$.		II. $t = 794°$.		III. $t = 710°$.		IV. $t = 710°$.		V. $t = 695°$.	
v.	*p.*	*v.*	*p.*	*v.*	*p.*	*v.*	*p.*	*v.*	*p.*
5.3	783	23.0	797	6.8	659	14.4	790	47.5	940
8.0	635	24.0	730	7.3	508	16.5	510	50.0	560
12.4	423	29.6	483	8.5	375	19.5	350	53.0	108
19.6	282	31.5	485	9.6	275	21.5	145	53.7	90
30.6	261	47.2	477	10.6	190	25.0	123	54.3	90
38.2	252	53.0	475	12.2	114	26.2	118	58.8	0
39.6	250	54.6	475	13.6	113	31.5	112		
47.4	250	58.0	430	16.2	110	34.0	112		
53.3	248	58.8	315	22.4	108	36.3	100		
59.2	250	60.1	197	28.1	102	37.7	104		
61.4	92	60.9	69			39.7	101		
63.3	35	62.1	0			42.4	104		
64.1	0					51.4	117		
						53.9	118		
						55.8	111		
						60.3	0		

The results are given in Table I and plotted in Curve I in Fig. 1. The higher pressures have no quantitative significance in this case because the volume of the "pipet," manometer, and connecting tubes was not known, hence it was impossible to calculate how much oxygen had been removed from the barium peroxide but still remained in the apparatus.

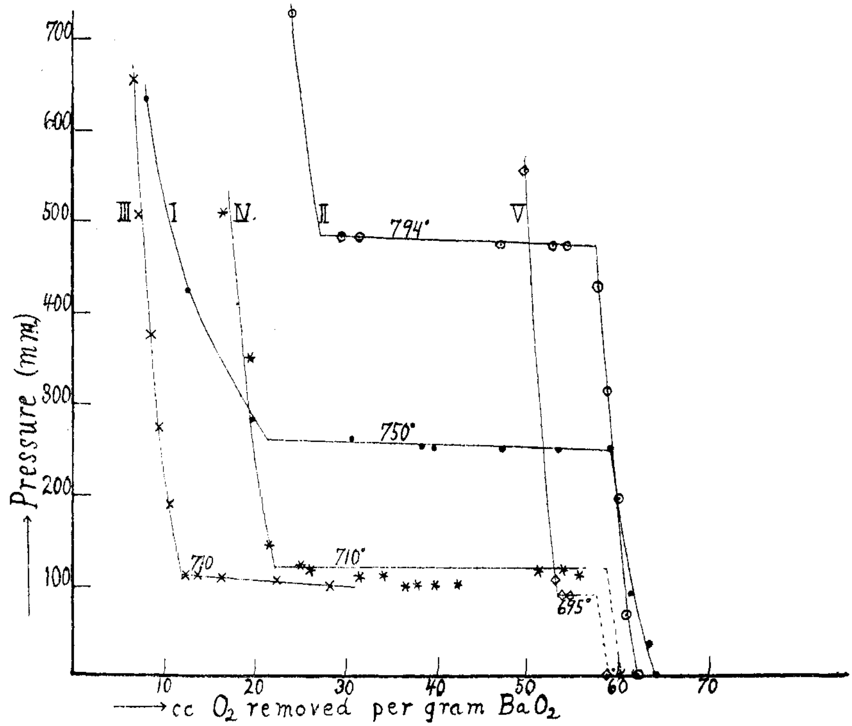

Fig. 1.

The results show quite clearly, however, that the system is divariant until about one-third of the peroxide has been decomposed, and then univariant till about 92% has been decomposed, and then divariant again. It is thus quite evident, in the light of the phase rule, that there can exist two solid solutions, one of barium oxide in peroxide, and another of peroxide in oxide, and that the usual pressure-temperature curve has a definite significance only in the region where these two solid solutions are saturated and coexistent. In the univariant system equilibrium is reached very rapidly; in the divariant system more slowly, since diffusion in the solid must take place till a new concentration is reached.

In order to ascertain more accurately the limits of the univariant system, containing tubes were made having as little volume as possible in excess of that occupied by the peroxide. The values given in Column II were obtained using a quartz tube as shown in Fig. 2. The end was blown into a bulb in an oxy-gas flame. The inner tube, protecting the couple, fitted snugly within the outer, connection being made between the latter and the manometer by means of the T-tube shown on the figure. The parts were cemented together by means of marine glue. A fine quartz tube insulated the wires of the thermocouple from each other (not shown in the figure). The bulb was packed tightly with 1.415 grams of barium peroxide in this experiment. When set up as described the free space in the tube was determined by collecting and measuring the air removed in the process of exhaustion. This was found to be 3.54 cc. The values given for "cc. of O_2 removed," in this and subsequent experiments, include the oxygen remaining in the apparatus, and thus represent the amount of oxygen removed, not from the apparatus, but from the peroxide. Since the charge contracts as it decomposes, and since the oxygen in the above free space of 3.54 cc. is not all at the same temperature, the correction is not very accurate, as a mean temperature had to be selected rather arbitrarily in reducing the volume to 0° and 76 cm. Of course, at lower pressures the amount in the tube is small, so that the correction is then small. Experiments III and IV, where the free space is still smaller, and the pressure when the system begins to be univariant is low, are thus more accurate than this one. The temperature in Experiment II was kept constant at 794°. A slight drop in pressure is noticed in the middle portion of the curve where the pressure should apparently be constant. The reason for this becomes clear in the next two cases.

Fig. 2.

In Experiment III, carried out at 710°, the charge was placed in a Jena tube, the lower temperature not requiring quartz. A thick-walled bulb was blown on the end of a tube and filled with 2.029 g. of peroxide. Into the tube between the bulb and the end connected with the manometer was slipped a closely fitting rod of Jena glass to reduce the free space as much as possible. The thermocouple was introduced into the other end of the furnace, so that the junction was beside the bulb containing the peroxide. The free space in the tube was reduced to 2.5 cc. by this arrangement. The system became divariant when about 12 cc. of oxygen had escaped from 1 g. of peroxide. The pressure decreased slightly and the evolution of oxygen ceased after 28 cc. per g. of peroxide had been withdrawn. This is in accordance with the fact that a slight amount of water must be present as a catalyst in order for the reaction to proceed. This behavior is reported by Le Chatelier and others, and is taken account of in the Brin process for oxygen, where the air used to regenerate the peroxide must not be completely dried, as the absorption will not then take place. This experiment having been performed two weeks later than the previous one, and the peroxide having remained in the desiccator in the interval, it contained less water, what there was being removed with the first portion of oxygen, leaving the charge too dry to react.

Experiment IV was carried out at the same temperature, 710°, the only difference being that a quartz tube was used instead of one of glass. The charge weighed 1.393 g., and the unoccupied volume was 2.5 cc. The results are shown in the table and curve. After the removal of 42.4 cc. of oxygen, the evolution ceased, as in the previous experiment. A few milligrams of water were admitted, whereupon the pressure rose slightly and the evolution of oxygen continued till 55.8 cc. were removed, after which, the water not having permeated the whole charge, the pressure fell and 60.3 cc. were obtained with difficulty.

In Experiment V the effect of a larger quantity of water is illustrated. The tube, of Jena glass, contained 1.019 g. of peroxide and 0.34 g. of water (of which much was driven out of the peroxide space before higher temperatures were reached). The free space was 1.2 cc. The temperature was 695°.

It is quite evident, from these results, that this equilibrium can be understood only by taking into account both the part played by the water present and the existence of solid solutions.

The presence of water introduces the equilibrium:

$$BaO + H_2O \rightleftarrows Ba(OH)_2.$$

It seems likely[1] that the barium peroxide decomposes first into oxygen and hydroxide, thus:

$$BaO_2 + H_2O \rightleftarrows Ba(OH)_2 + {}^1/_2O_2,$$

and that the oxide is formed from the latter, regenerating water. The complete equilibrium might therefore be written thus:

$$BaO_2 + H_2O \rightleftarrows Ba(OH)_2 + {}^1/_2O_2 \rightleftarrows BaO_2 + H_2O + {}^1/_2O_2.$$

In addition, the oxide and peroxide are soluble to a limited extent in each other. According to Johnston,[2] who measured the dissociation pressures of barium hydroxide at different temperatures the hydroxide and oxide seem to form no solid solutions with each other. It would seem unlikely, also, that the peroxide and hydroxide should form a solid solution, which is confirmed by the behavior of Curves III and IV, especially the latter. As the charge becomes dry the pressure falls about

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[1] See Dissertation of Becker, pp. 28–32.

[2] *Z. physik. Chem.*, **62**, 330 (1908).

20 cm., and then rises an equal amount upon the addition of a little water, and the consequent formation of hydroxide. Now Johnston gives the following values for the dissociation pressure of barium hydroxide:

t° C.	670	749	829	910	998
p (mm. of Hg)	17.4	55	149	355	760

Using the van't Hoff "reaction isochore" the pressure at 710° is calculated to be 28 mm., just a little more than the above drop as the material became dry, or as the hydroxide present was decomposed. The fall is not sudden as the amount of hydroxide present gradually becomes less and hence gradually less able to give off enough water vapor to exert the full equilibrium pressure. If equilibrium were attained the phase rule shows that when the following phases are present, gas (O_2 and H_2O), $Ba(OH)_2$, and two saturated solid solutions of barium oxide and peroxide, each on the other, the system is univariant, and therefore can exert only one pressure for every temperature. At the beginning and end of the curve, when only one solid solution is present, the system possesses an additional degree of freedom, so that concentration must be fixed in order to fix the pressure. The different values shown by the curves at which the system becomes univariant are evidently due to initial differences in the water or barium hydroxide contained in the charge. The original hydrated peroxide, though spread out in the desiccator in as thin layers as possible, would hardly dry uniformly, and even in the cold decompose slightly according to the second equation given above. The mutual solubilities of the oxide and peroxide may also increase with the temperature, as comparison of Curve II with the others would seem to indicate. However, the difference between the saturation points of II and IV, at different temperatures, is less than the difference between III and IV, at the same temperature, so that the results give no very definit information on this point. The increase would seem to be not very great, which would be in accordance with the practically constant heat of reaction calculated later.

These results accord with and further explain those of Becker, and give additional information concerning the control of this reaction.

Becker passed oxygen under slightly more than one atmosphere pressure over barium oxide heated to a definit temperature in an electric oven. Successive equal samples were acted upon by the oxygen of definit moisture content for equal times and the product analyzed, the results showing the per cent. of peroxide formed at various temperatures. Among other results obtained by him the following are typical:

Temperature	200	300	350	400	500	600	700	750	800	850	900
% BaO_2 using oxygen	3.7	17.3	71.1	96.4	100	100	96.9	61.9	18.2	3.4	0.9
% BaO_2 using air		18.2		70.4	69.2	52.8	30.9		5.9		

It is to be expected that the reaction will be incomplete at low temperatures on account of low velocity. The *gradual decrease* in the yield, however, for which Becker fails to account, can be explained only by the existence of a solid solution of peroxide in oxide, as otherwise the system would be univariant at the end, and as soon as the temperature had risen to a certain value the yield would fall at once to zero. A yield of 100 per cent. was obtained only at 600° and below, although the measurements of Le Chatelier would indicate this yield up to about 800° where, according to his measurements, given later, the dissociation pressure becomes one atmosphere. The curves here given, however, show that in order to obtain a yield of 100 per cent. not only must the pressure of the divariant system. be kept below that of the oxygen used, but also that of the univariant combination represented by the sloping first part of the curve. Air at one atmosphere pressure is insufficient to give a yield of 100 per cent. in reasonable time because of the low velocity at the corresponding temperature. The partial pressure of the water vapor present must also be just a little less than the dissociation pressure of barium hydroxide in order that the oxide may not be converted into hydroxide instead of peroxide. Some is necessary, however, in order that the reaction may take place. Where the concentration of the barium oxide varies the aqueous concentration varies accordingly. These results show why 100 per cent. BaO_2 is not on the market and show what conditions must be fulfilled in order to obtain it.

In using this reaction for preparing oxygen from the air the first method was to allow air to pass over barium oxide heated to a dull red heat, forming peroxide. The retort containing the material was then raised to a much higher temperature whereby oxygen was driven off. The process worked in this manner was slow and costly, the alternate heating and cooling of the retorts requiring much time and fuel. The process was greatly improved by alternating the pressure instead of the temperature in order to reverse the reaction. This effected a great saving of time and fuel, as the reversal could be quickly effected, thus making many cycles possible where before only a few were obtained. However, according to the Brin Oxygen Company the quantity of oxygen obtained in each operation was only one-tenth of the amount calculated from the weight of barium oxide used. The data here presented make this low yield intelligible. The temperature was held at about 700° and the air, purified from carbon dioxide, dust, and part of its moisture, was forced over the barium oxide at a pressure of about three atmospheres, corresponding to a partial pressure of oxygen of about 450 mm. of mercury. Reference to the curves already given will show that this pressure is quite insufficient, at 700°, to convert all the oxide into peroxide, even with a minimum amount of hydroxide present. With any considerable amount of hydroxide present the quantity of peroxide formed would be still less. The reverse operation would, according to the curves, be more nearly complete. Of course the yield would be still further reduced, in working the process on a large scale, by failure to obtain the true equilibrium.

The Pressure-Temperature Curve for the Univariant System.

Since the system is univariant for a considerable portion of the total range, provided that barium hydroxide is not present in too great quantity, a knowledge of the relation between temperature and pressure is of importance in this interval. This determination was made as part of the data secured from Experiment II, given above. The above experiment was interrupted after the removal of 47.2 cc. of oxygen and continued after the following data were secured, the interval requiring three hours. Equilibrium is attained quite rapidly in the univariant system, so that the time necessary for the experiment was consumed chiefly in waiting for the furnace to reach constant temperatures, and not in any lag of pressure. The temperature was measured as described above with the potentiometer, the e. m. f. being easily determined within 0.01 millivolt, which corresponded approximately to 1°. The results are given in Table II. The first column contains temperatures, the second the corresponding pressures in mm. of mercury at 0°. In the third column the heat of reaction is given calculated from one value to the next by means of the familiar formula of van't Hoff:

$$Q = \frac{4.571\ T_1T_2}{T_2 - T_1} \log p_2/p_1.$$

In the fourth column are given values of pressure calculated from the empirical equation,

$$\log p = -6850/T + 1.75 \log T + 3.807,$$

where p is expressed in mm. If p is expressed in atmospheres, the constant term becomes 0.926. The observed values, as is seen in the table, agree closely with those calculated from this equation.

Since it is probable that the partial pressure of the aqueous vapor present is not very different from that given in the dissociation of barium hydroxide alone,[1] the measurements of J. Johnston of that equilibrium, already given, enable one to calculate approximately the partial pressure of the oxygen in the equilibrium,

$$2BaO_2 = 2BaO + O_2,$$

bearing in mind always the fact that the oxide and peroxide in the above

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[1] In the present system the partial pressure of steam is probably slightly greater than from the hydroxide alone, as the resulting barium oxide has its concentration diminished by the dissolved peroxide.

equation are present in two saturated solutions of composition fairly constant. The fifth column in the table gives the values of aqueous pressure calculated by the van't Hoff equation to the temperatures of the present observations. The sixth column gives the partial pressure of oxygen found by subtracting the aqueous pressure just given from the smoothed values of total pressure given in column four. In the last column are given the heats of reaction calculated for the oxide equilibrium alone by using the partial pressures of oxygen. The mean value, 37420 cals., is in poor agreement with that given by Berthelot,[1] 24200 cals., even if proper allowance is made for the change of the reaction heat at constant pressure with the temperature, as it seems unlikely that the formation of solid solutions should give rise to such a large heat effect, and of the sign which would be indicated by the above difference. The formation of the solid solutions from the oxides is doubtless attended by an absorption of heat which is moreover not very great, since the solubilities appear to increase, and but slightly, with the temperature.

TABLE II.

Temperature.	Pressure (observed).	Heat of reaction (total).	Pressure (calculated).	Aqueous pressure.	Oxygen pressure.	Heat of reaction ($2BaO + O_2$).
540	2		2.8	.....	......	
618	18	.....	18.6	7.3	11.3	.....
655	41	36500	40.5	13.7	26.8	38300
697	91	34000	91.7	26.3	65.4	38000
737	193	36500	188	47	141	36900
794	479	34200	476	98	378	36900
835	871	34300	877	159	718	36800
853	1128	35400	1132	195	937	36800
868	1401	36700	1397	231	1166	37000
	Mean,	35370			Mean,	37420

The results given in Table II are plotted in Fig. 3, along with the measurements of Le Chatelier which are as follows:

t........	525	555	650	670	720	735	750	775	785	790
p.......	20	25	65	80	210	260	340	510	620	670

It will be seen that the pressures here given are lower than those of LeChatelier. His high pressures at 525° and 555° are surely incorrect.

Since the solid phases appear to be of nearly constant composition, it is interesting to note the order of agreement between these data and the equation given by Nernst[2] for the approximate calculation of heterogeneous equilibria,

$$\log p = -Q/4.571\ T + 1.75 \log T + C,$$

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[1] *Ann chim. phys.*, [5] 6, 209 (1875).

[2] "Thermodynamics and Chemistry," *Scribner's*, 1907.

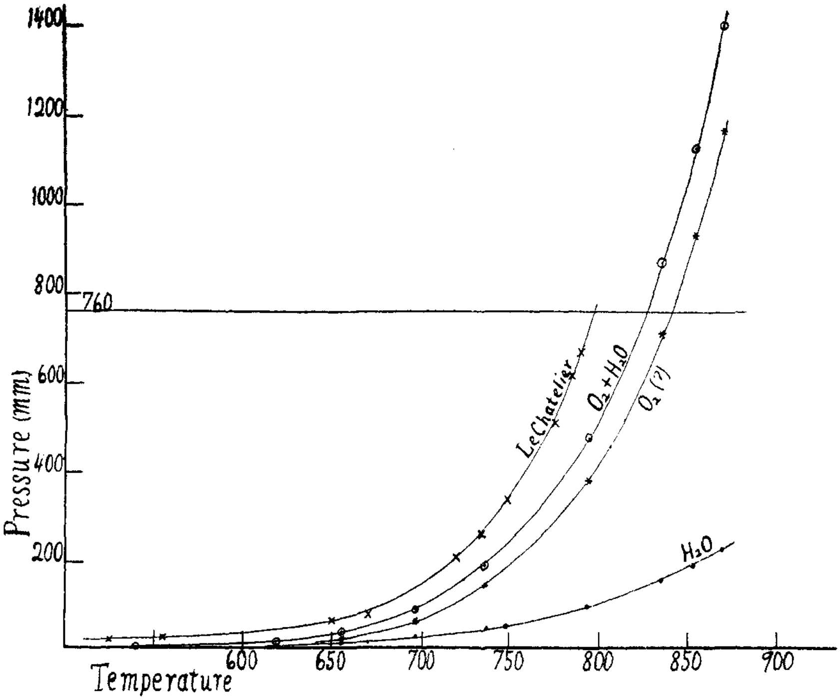

Fig. 3.

where C for oxygen is 2.8 when p is expressed in atmospheres. Q is the heat of reaction at constant pressure, and at temperatures not too far removed from absolute zero. Heats of reaction determined at ordinary temperatures will serve in approximate solutions, but the value calculated above, 37420 cals., will have to be recalculated to low temperatures before it can be substituted in the Nernst equation. This recalculation can be made by the relation involved in the Nernst equation, and which becomes apparent on comparing the value of $\frac{d \log p}{dT}$ obtained from that equation with the value obtained from the van't Hoff equation,

$$\frac{d \ln K}{dT} = \frac{Q_T}{RT^2},$$

the result giving the relation

$$Q_T = Q + 3.5T,$$

where Q_T is the heat of reaction at high temperatures, and Q that at low temperatures, or, more strictly, absolute zero. In the measurements from which Q_T has here been calculated, the mean temperature is about

1050 absolute, so that $Q = 33560$. The Nernst equation then becomes

$$\log p = \frac{-33560}{4.571\,T} + 1.75 \log T + 2.8$$

which gives the observed pressures very closely if the constant is 1.278 instead of 2.8. In view of the possible variation in the composition of the solid phases, the agreement may be regarded as all that could be expected. If the above partial pressures of steam are too low, as is very probable, the constants would be still closer to 2.8.

This investigation serves to emphasize one point which has been neglected in most work upon heterogeneous equilibria, namely, that it is necessary to determin the nature of the phases involved in a heterogeneous equilibrium before measurements of dissociation pressures are of final value. Dissociation pressures of divariant systems are of little use.

Summary.

1. In the thermal dissociation of barium peroxide it has been shown that solid solutions of the oxide and peroxide in each other are formed. The effect of this upon the pressure as oxygen is removed is indicated, and the limits shown between which the system is univariant. The effect of the moisture necessarily present is also shown.

2. The conditions necessary to obtain a quantitative yield of barium peroxide from oxide are explained.

3. The conditions are indicated which would be necessary for the complete reversal of the equilibrium.

4. The dissociation pressures have been measured in the interval where the system is univariant, *i. e.*, where saturated solutions of the oxides are present, and are given closely by the equation

$$\log p = -6850/T + 1.75 \log T + 3.807,$$

where p is expressed in mm. and T is absolute temperature.

5. The heat of the reaction at constant pressure and an average temperature of 775° is calculated to be 35370 cals.

6. Assuming that the partial pressure of steam present is the same as that given by barium hydroxide alone, as given by the measurements of J. Johnston, the partial pressure of the oxygen is calculated. From these values the heat of dissociation of the solid solutions is calculated to be 37420 cals.

7. According to the formula of Nernst, this heat of reaction becomes 33560 cals. at absolute zero, which agrees with the Nernst approximation formula for calculating decomposition pressures in heterogeneous equilibria except that the constant must be 1.278 instead of 2.8, as given by Nernst. The agreement is all that might be expected, considering the possible variation in the composition of the solid phases.