I do not mean to be unjust or harsh but when I think of the thousands of young men who year after year are subjected to deadening, uninspiring, humdrum teaching of science and are thus lost to the ranks of our workers, and of the possible brilliant, elect spirits among that number, I must cry out at the terrible waste. The field of knowledge is vast and growing vaster with the ever-widening horizon. The harvest is plentiful and the call for laborers is ever more insistent. It is necessary to impress this great truth that the true teacher must be a learner also, drawing constantly fresh inspiration from the fountain head.

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 8.]

CONCERNING SILVER OXIDE AND SILVER SUBOXIDE.

BY GILBERT NEWTON LEWIS.

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ON account of the uncertainty as to the correctness of the value at present accepted for the electrolytic potential of oxygen, I have attempted to calculate this extremely important quantity by an indirect method. One of the important data needed in this calculation is the decomposition pressure of silver oxide at 25°. The determination of this pressure is the subject of the present paper. Incidentally it will be necessary to consider the question of the existence of the silver suboxide, which has been described by certain chemists.

LeChatelier[1] was the first to show the reversibility of the reaction,

$$2Ag_2O = 4Ag + O_2.$$

By the decomposition of silver oxide in a closed tube at 300° he obtained a pressure of 10 atmospheres. On the other hand, by heating silver at the same temperature in oxygen at 15 atmospheres he observed the oxidation of the silver. He therefore placed the decomposition pressure of silver oxide between 10 and 15 atmospheres.

Knowing this pressure for one temperature, and the heat of decomposition, it should be possible to calculate with the aid of the van't Hoff equation, the pressure at another temperature. Such a calculation, however, must be made with great caution.

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[1] Z. physik. Chem. 1, 516 (1887).

It is especially important to make sure that at both temperatures we are dealing with precisely the same reaction.

Now Guntz[1] has undertaken to show that the pressure that he obtained by heating silver oxide in a closed tube at 358° was not the decomposition pressure of silver oxide but of silver suboxide. In other words he believed that the silver oxide decomposed first entirely into suboxide and oxygen according to the equation

$$4Ag_2O = 2Ag_4O + O_2,$$

and that the suboxide then partially decomposed until equilibrium was reached, according to the reaction,

$$2Ag_4O = 8Ag + O_2.$$

The existence of such a suboxide would not prevent the determination of the equilibrium pressure in the system Ag, Ag_2O, O_2, for this pressure could be readily calculated from the pressure of equilibrium in the system Ag_2O, Ag_4O, O_2 and that in the system Ag_4O, Ag, O_2.

I shall, however, show that in my experiments over a wide range of temperature silver suboxide never appeared, and that the experiments which led M. Guntz to believe in its existence must probably be interpreted otherwise.

I shall first describe measurements of the decomposition pressures obtained by heating silver oxide at several different temperatures, and then undertake to show that the pressures obtained are the true pressures of equilibrium in the system Ag_2O, Ag, O_2.

Two samples of silver oxide were used in these experiments. They will be referred to as A and B. A was prepared with the exclusion of carbon dioxide from hot dilute barium hydroxide and silver nitrate as described in my paper on the kinetics of the decomposition of silver oxide.[2] B was the preparation of Merck, labeled "highest purity." Both samples before being used were heated for several hours at 300°.

DECOMPOSITION PRESSURE OF SILVER OXIDE AT 325°.

The first experiment was made at 325°[3] in the thermostat of molten sodium and potassium nitrates which I have previously

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[1] C. R. 128, 996 (1899).

[2] Z. physik. Chem. 52, 310 (1905).

[3] All thermometers used were compared with Reichsanstalt standards. The corrected temperatures are given.

described.[1] The apparatus for measuring the pressure consisted of a stout brass tube, about 2 meters in length and 1 cm. in internal diameter, closed at the lower end, and at the upper connected with a metallic manometer. In the lower end of the brass tube was fitted a thin glass tube, 7 cm. high, containing the silver oxide (sample B). In order to diminish as far as possible the total air space in the apparatus the rest of the brass tube was filled as nearly as possible with a close fitting glass rod. After the apparatus had been exhausted through a stop-cock provided for that purpose, the lower end of the tube was introduced into the thermostat to a depth of about 30 cm.

The decomposition began in a few hours, and in five days the pressure reached a constant maximum as shown in Table I.

TABLE I.

Time in hours.	Pressure in atmospheres.
12	18.5
24	26.5
48	29.8
72	30.1
96	31.5
120	31.8
144	31.8

In order to approach the equilibrium from the other side the tube was then heated to a higher temperature for a few hours and returned to the thermostat. The pressure had risen to 34 atmospheres but gradually fell as shown in Table II.

TABLE II.

Time in hours.	Pressure in atmospheres.
0	34.0
24	33.4
48	32.5
72	32.3

It is apparent therefore that the pressure of equilibrium lies between 31.8 and 32.3 atmospheres. The manometer had been verified by comparison with a standard manometer, but may nevertheless have been in error by about half an atmosphere. We will take therefore in round numbers 32 atmospheres as the decomposition pressure at 325°.

During this whole experiment there was not the slightest leakage from the tube and the whole apparatus proved to be

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[1] Loc. cit.

eminently satisfactory. Unfortunately the work was interrupted at this point by my removal to another laboratory and the experiments had to be continued with new and simpler apparatus.

EXPERIMENTS AT 302°.

The next experiments were made in a bath of diphenylamine vapor. The first method tried was an indirect one. It consisted in heating the silver oxide in a closed glass tube, drawn out at one end to a capillary, cooling it suddenly by removal from the bath, opening the capillary under a gas burette and calculating from the volume of gas evolved and from the volume of the tube (exclusive of that occupied by the remaining mixture of silver and oxide) the pressure that had been exerted in the tube at the temperature of the bath.

Eight tubes containing different quantities of silver oxide were suspended in the vapor of boiling diphenylamine in a large iron receptacle, and kept there for six days. During this time it was found necessary to renew the diphenylamine several times on account of its gradual decomposition. The original substance (Kahlbaum's) boiled at 302°. In the course of the experiment several of the tubes were broken; in others the oxide was entirely decomposed, so that finally only one of the eight tubes could be used for determining the pressure. This was broken under water and 8.58 cc. (760 mm. 30°) of oxygen collected in the burette. The tube was weighed, then filled with ether, boiled to drive out all the air, refilled, and weighed. From these two weighings the volume of the tube was found to be 0.92 cc. The pressure at 302° must therefore have been $\frac{8.58+0.92}{0.92} \times \frac{273+302}{273+30}$, or 18.0 atmospheres. We shall show presently that this value is too small. The oxide used was sample A which decomposes far more slowly than B, and it is probable that equilibrium had not been reached when the tube was removed from the bath.

On account of the difficulty of determining when the reaction had come to equilibrium this indirect method was abandoned and the following adopted.

Two tubes, one having a bore of 1 mm., the other of 3 mm. were joined together and then drawn apart at the junction so as to form a fine capillary about 1½ meters long (BCD in Fig. 1). In the smaller tube, D, a short column of mercury was introduced and the open end sealed, thus making an ordinary closed manometer which could be calibrated in the usual way at the end of the experiment. The tube B was filled with silver oxide and sealed at the open end.

The large bath used in the previous experiment had also to be abandoned on account of its large consumption of diphenylamine, of which only a limited supply was available. A simpler bath made of a long-necked glass boiling flask was found to answer the purpose satisfactorily. The neck was about 2 cm. in diameter and was insulated on the outside by a jacket of asbestos. The temperature of the vapor in different parts of the neck was frequently tested. The variations over a considerable range rarely exceeded one-half a degree if contact with the walls was avoided. The tube B was therefore held in the neck by a simple framework which prevented its touching the walls.

In a previous paper I have shown that the decomposition of silver oxide is extremely slow until a large amount of silver has already formed, which acts as a catalyzer. Therefore in order to hasten the attainment of equilibrium the tube containing the silver oxide was heated at the beginning to a higher temperature than that of the bath until a part of the oxide was decomposed. It was then introduced into the bath and heated continuously, except that at the end of each twenty-four hours it was removed and the diphenylamine renewed. After being returned to the bath the pressure always assumed immediately its value previous to the removal of the tube, thus showing that during the rapid cooling and heating the reaction did not proceed to any appreciable extent.

During the experiment the temperature varied between 301.5° and 303°. We may take 302° as the average temperature. (One degree change of temperature causes a change of less than half an atmosphere in the decomposition pressure.)

The first experiment was made with sample B of oxide. After being enclosed in the tube it was heated gently with a Bunsen burner until small flecks of metallic silver appeared throughout the mass. It was then introduced into the bath, the manometer indicating a pressure of 6 atmospheres. At the end of two days the pressure had reached 16.7 atmospheres and was increasing very slowly. The tube was then removed from the bath and heated until a little more of the oxide was decomposed. When replaced in the bath the manometer registered 20.2 atmospheres and during the next twenty-four hours this pressure remained constant within one-tenth atmosphere. The tube was again removed and heated until on being replaced in the bath the pressure was 23.2 atmospheres. In the next twenty-four hours this fell to 21.6 atmospheres and in twenty-four hours more to 21.5 atmospheres.

This experiment shows that the decomposition pressure at 302° must be greater than 16.7 (contrary to the conclusions of LeChatelier), is probably not far from 20.2 and is certainly not greater than 21.5 atmospheres.

The experiment was then repeated with another tube containing the same kind of oxide. In this case a longer time was allowed for equilibrium to become established. Table III shows the pressure at the end of each twenty-four hours.

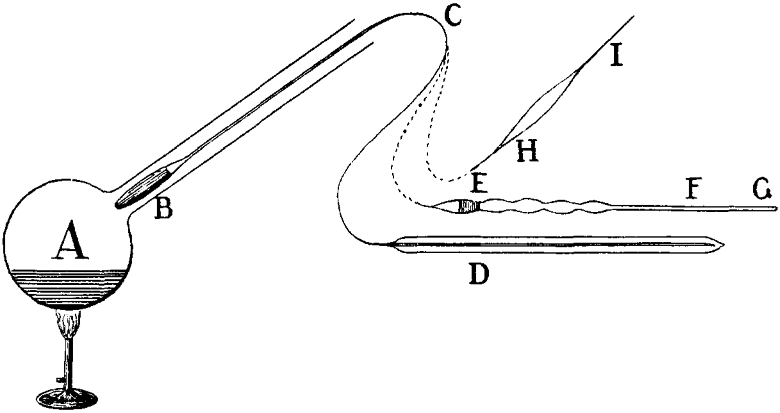
TABLE III.

Time in days.	Pressure in atmospheres.
1	11.1
2	15.1
3	17.3
4	18.8
5	19.5
6	19.7
7	19.7
8	19.7

It is evident from these two experiments that the true value for the pressure at 302° must lie between 19.7 and 21.5 atmospheres, and probably nearer the lower figure. Let us take 20.5 atmospheres as a value sufficiently exact for our purpose.

EXPERIMENTS AT 445°.

The next experiments were made at the temperature of boiling sulphur, the bath being constructed as in the last experiment. At this temperature also the first attempts were made with an indirect method. The simple method tried at 325° was not attempted here, as it seemed probable that the tube could not be cooled rapidly enough from this high temperature to prevent a displacement of equilibrium. Instead, the following method was tried. The construction of the apparatus is indicated in Fig. 1 (BCHI). A thick-walled glass tube, of not more than 2 mm.



internal diameter, was drawn out to form the long capillary C. The tube B, on one side of this capillary, was filled with silver oxide and sealed at the free end. The other tube was again drawn out to a capillary at I and sealed, leaving 3 or 4 cm. between H and I. During this construction a small piece of tar was placed loosely in the tube, where it narrowed to a capillary at H.

When the tube had been in the bath long enough for equilibrium to be established, a hot glass rod was brought for a moment in contact with the tube at H, thus melting the tar and causing it to run into the capillary. This heating was purely local and had no appreciable effect on the temperature of the gas in the tube HI.

After the tar had solidified the capillary was broken at C, leaving in the tube HI the same pressure that had existed in B. The capillary I could then be opened under water and the pressure calculated from the volume of gas evolved and the volume of the tube HI.

While this method was being used experiments were also made with a direct method, and a manometer was finally constructed which gave very satisfactory results.

The tube BCEFG was drawn from a single tube of the same sort used in the preceding method. At E it was drawn out into a series of small bulbs, as these proved to be stronger than a simple straight tube, and it finally terminated in a long capillary which had a nearly uniform bore (about 0.1 mm.) in the region

FG. The pressure was registered by a small mercury column, starting originally at E when at atmospheric pressure, and moving to a point F, about 10 cm. from the end of the capillary, when the pressure reached its maximum. On breaking the tube at C after the experiment the mercury invariably returned to its original position at E. The point G was then broken off within 0.1 or 0.2 mm. of the end and the volumes FG and EG determined by drawing in mercury successively to F and to E and weighing the mercury. The smaller quantity which weighed only a few milligrams was weighed on a fine assay balance. I believe that this manometer should give accurate results. The error caused by the capillarity of the mercury is not over 0.1 atmosphere, nor is it likely that the change in volume of the capillary tube under pressure would lead to any considerable error.

There were two difficulties in both the methods that I have described. At the high pressure of over 200 atmospheres which was here reached the glass tubes would explode on the slightest provocation. Fortunately, although explosions in the outer tubes were frequent, the tube B within the bath rarely gave way. This difference in behavior between two tubes of the same form, drawn from the same piece of glass is undoubtedly to be attributed to the annealing and toughening of the tube B resulting from the high temperature. The danger of explosion was reduced as far as possible by choosing flawless tubes and drawing them as carefully as possible. The fine capillaries never burst and probably could have withstood a much higher pressure than that to which they were subjected.

The other difficulty was that ordinarily enough silver oxide could not be packed into the tube B to give the pressure of equilibrium before being entirely decomposed. This difficulty was overcome by filling only one-half of the tube B with silver oxide, the other half with dry, powdered potassium permanganate, which decomposes instantaneously at the temperature of the bath and produces much more oxygen than the same volume of silver oxide. The two substances were separated by a small piece of asbestos.

Experiments in which the manometer was used showed that equilibrium was reached in from fifteen to forty minutes, according to the kind of oxide used. In one case an addition was made to the apparatus in an extra bulb at C, filled with potassium permanganate. After the manometer had come to rest as usual, the bulb C was gently heated causing a further increase of pressure. But this excess of pressure rapidly diminished through the re-oxidation of the silver in B and within less than ten minutes the manometer showed the original pressure, within a small fraction of an atmosphere, thus proving that we are dealing with a true equilibrium.

The first experiments with both methods gave disappointing results. Under similar circumstances the results obtained by the two methods were in full agreement (after allowing for the difference in compressibility[1] of the air and oxygen contained respectively in the tubes EG and HI), but the results obtained at different times ranged from 175 to 200 atmospheres. A more careful investigation of the temperature in the neck of the boiling flask pointed to the cause of the variations. A preliminary test had appeared to show the temperature to be the same in the neck and the body of the flask, but it was now found that the temperature in the former was subject to variations, depending upon a number of conditions, such as the angle at which the flask is held, the height of the heating flame, and other more or less adventitious circumstances. This difference between the sulphur and diphenylamine baths is probably not due so much to the higher temperature of the former as to the great viscosity of the liquid sulphur which condenses in the neck of the flask. The silver oxide had been put in the neck rather than the body of the flask in order to avoid possible changes in temperature due to spattering of superheated liquid. But this superheating was now proved to be small. A Reichsanstalt standard thermometer showed the temperature of the liquid to vary under varying conditions between 445° and 446°, that in the vapor immediately above, between 443.5° and 444.5°. Since the thermometer may have been in error by 1° or 2° (it was calibrated at 397° and at 505°) we will use for the temperature of the vapor in the body of the flask, where the tube B was placed in the following experiments, the commonly accepted value for the boiling-point of sulphur, namely 445°.

Four new experiments were now made, all by the second

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[1] Amagat : Ann. Chim. [5] 19, 345 (1880); [5] 22, 353 (1881).

method, with the manometer. For illustration I will give the details of the first of these experiments.

The mercury column which moved rapidly at first towards the end of the manometer gradually came to rest as equilibrium was reached. The positions of this column (distance from end of manometer) at intervals of about five minutes are given in Table IV. The experiment was begun at 10.25 o'clock.

TABLE IV.

Distance in mm.	Time.
65.0	10.32
53.9	10.35
49.0	10.40
45.9	10.45
45.5	10.50
45.2	10.55
45.2	11.00
45.2	11.05
45.3	11.10
45.2	11.15
45.2	11.25

The capillary at C was then broken and the manometer calibrated. 0.842 gram of mercury filled the whole manometer, 0.00413 gram filled it to the point, 45.2 mm. from the end, where the mercury column came to rest. If we assume Boyle's law, the pressure was therefore $\frac{0.842}{0.00413}$ or 204 atmospheres.

The results of this and three other similar experiments are given in Table V.

TABLE V.

No. of experiment.	Kind of oxide.	Pressure.
1	B	204
2	B	191
3	B	200
4	A	205

Experiment 2 differed from the others in that the silver oxide was almost entirely used up. The result is undoubtedly too low. Discarding this value therefore and taking the average of the other three the result is 203 atmospheres.

The preceding calculations have been based on the assumption that the air in the manometer obeys Boyle's law. According to the work of Amagat[1] the true pressure of air in the neighbor-

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[1] Loc. cit.

hood of 200 atmospheres is, at 0°, about 2½ per cent. higher than that calculated from the volume by Boyle's law. At 30°, the temperature of the manometer, this correction would be somewhat less, say 2 per cent. Making this correction, therefore, we get 207 atmospheres as the equilibrium pressure of silver oxide at 445°.

DOES SILVER SUBOXIDE EXIST?

M. Guntz[1] heated silver oxide to a temperature of 358° for fifty hours and obtained a pressure of 49 atmospheres. This he considered the pressure of equilibrium in the reaction

$$2Ag_4O = 8Ag + O_2$$

and cited as evidence for this view the following experiment: In a closed tube were placed known weights of silver and silver oxide and a quantity of potassium permanganate sufficient to yield enough oxygen to produce a pressure higher than 49 atmospheres at 358°. The whole was heated at this temperature for three days. The tube was then cooled rapidly and it was found that the silver had gained in weight and the silver oxide had lost in weight by amounts which indicated the formation of Ag_4O in both cases.

I shall show presently that in all my experiments carried on at temperatures from 300° to 445°, and with two different samples of silver oxide, the suboxide of silver was never formed. It seems difficult to reconcile my results with those of M. Guntz. Of course it is conceivable that the suboxide is capable of existence and that it appeared for some reason in one case and not in the other, just as occasionally some hydrate may be suddenly precipitated from an aqueous solution, although it may fail to appear many times under apparently similar circumstances. But I am inclined to believe that the experiments of M. Guntz can be explained without the necessity of assuming the existence of the suboxide. If the pressure in the tube that he used was greater than the decomposition pressure of silver oxide the gain in weight of the silver can be readily explained by its oxidation to silver oxide. The loss in weight of the silver oxide can only be explained by assuming that it contained water or carbon dioxide. I should consider this improbable if it were not for the fact that my own experiments have shown how difficult it is to prepare

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[1] Loc. cit.

and to keep silver oxide free from these impurities. It is perhaps not generally known that carbon dioxide, as well as water, is rapidly taken up by silver oxide from the atmosphere. One sample which I prepared in such a way that it was very free from impurity absorbed a large quantity of carbon dioxide while standing for a month in a loosely corked bottle. When carbon dioxide and water are once present they can be expelled only with great difficulty. Some of the former frequently remains after the silver oxide has been heated for an hour or two at 300°.

That silver suboxide was not present in any of the experiments that I have described will be evident from the following considerations. According to the phase rule silver, silver oxide, silver suboxide, and oxygen could not all exist together in equilibrium. In the absence of suboxide only one state of equilibrium is possible, that between Ag, Ag_2O, O_2. But in case the suboxide could form, two states of equilibrium would be possible, namely between Ag_2O, Ag_4O, O_2, and between Ag_4O, Ag, O_2. With a given quantity of silver oxide enclosed in a small volume the first equilibrium would exist, in a larger volume, the second.

In all the experiments previously described the final mixture in the tube has contained silver, as shown by the color, and by the metallic flakes produced upon grinding the whole in a mortar. In any given case, therefore, the remaining black powder must be a single phase, either all silver oxide or all silver suboxide. Let us assume that it is the latter and see to what consequences we are led. For example, let us assume that the pressure of 32 atmospheres which we obtained at 325° is the decomposition pressure of silver suboxide. Now suppose that we enclose so much silver oxide in a tube that if it should all decompose according to the reaction

$$4Ag_2O = 2Ag_4O + O_2,$$

a pressure of over 32 atmospheres would result. Then metallic silver could not form and the only possible equilibrium would be that between the oxide and suboxide.

This very experiment was tried. A glass tube was filled with silver oxide, sealed, and heated for a week at 325°. At the end of this time a considerable quantity of silver had formed, although, calculated from the volume of the tube and the amount of oxide, over 100 atmospheres would have been generated by the change from the oxide to the suboxide alone. A similar experiment was made at 345°. A small quantity of silver was placed in a tube and covered with a little glass wool. The rest of the tube was filled as full as possible with silver oxide. The tube was then sealed and left in the thermostat for five days, at the end of which time not only was the silver unoxidized but white spots of silver had appeared throughout the oxide.

These experiments show pretty conclusively the absence of silver suboxide. A still stronger proof is given by the experiments at 302°. In one of the experiments at this temperature which showed the pressure of equilibrium to be about 20 atmospheres, the volume of the tube and the manometer and the weight of silver oxide were determined. It was found that enough oxide had been used to produce a pressure of 35 to 40 atmospheres, if it had all changed merely to suboxide, yet a considerable quantity of silver was found in the final mixture.

Finally it was found possible to show by direct analysis that the black powder left in the tubes was not silver suboxide. It sometimes happened that at the end of the experiment the silver oxide was almost entirely decomposed in one part of the tube and apparently unchanged in another. This was due to the fact that the decomposition, being autocatalytic in character, progresses very rapidly at any point where it has once begun. In one experiment at 302° a considerable portion of the black substance left in the tube appeared to contain no silver. A sample of this weighing 0.0892 gram was heated in a tube connected with a gas burette. It yielded 4.71 cc. of oxygen (at 27°, 760 mm.). The above quantity of pure silver oxide should give theoretically 4.73 cc. This is an unexpectedly good agreement.

In the experiments at 445° there was no case in which the remaining oxide did not contain some silver, but two samples were chosen which appeared to be least decomposed. 0.205 gram of the first gave 7.24 cc. of oxygen (calculated for Ag_2O, 10.85 cc.; for Ag_4O, 5.42 cc.). 0.0851 gram of the second gave 4.35 cc. (calculated for Ag_2O, 4.52 cc.; for Ag_4O, 2.26 cc.). It is obvious that here also the black substance cannot be silver suboxide and is presumably silver oxide mixed with a certain amount of silver.

THE HEAT OF FORMATION OF SILVER OXIDE.

We have now obtained the pressure of equilibrium at different temperatures between silver, oxygen, and a certain black powder.

We have proved that this black powder is not silver suboxide but that at 302° and, presumably at the other temperatures as well, it has exactly the composition, Ag_2O. There still remains the possibility that this substance, although of the same composition as the silver oxide which exists at ordinary temperatures, may be an allotropic phase. In other words there may be a transition temperature, between room temperature and the temperatures of our experiments, at which a break in continuity in the properties of silver oxide occurs. This possibility must be eliminated before we can safely calculate the decomposition pressure of silver oxide at 25° from the pressures at the higher temperatures.

In order to decide whether we are dealing with the same phase of silver oxide at high and low temperatures, we will determine from the change in the decomposition pressure between 302° and 445° the heat of decomposition of the silver oxide occurring at these temperatures, and compare this value with the one obtained at ordinary temperatures by other methods.

The heat of decomposition may be found from the change of pressure with the temperature, by the aid of the equation of van't Hoff, which in this case has the form

$$\frac{dlnp}{dT} = \frac{Q}{RT^2} \qquad (1)$$

where p is the decomposition pressure, T the absolute temperature, R the gas constant, and Q the heat absorbed when 1 gram-molecule of oxygen is formed according to the equation

$$2Ag_2O = 4Ag + O_2.$$

This equation of van't Hoff is not strictly exact but is derived with the aid of two assumptions from the equation of Clausius,

$$\frac{dp}{dT} = \frac{Q}{T(v-V)} \qquad (2)$$

where v is the molecular volume of oxygen at the temperature T and at the pressure p, and V is the total change of volume of the solid system, that is, it is the volume of 2 gram-molecules of silver oxide less that of 4 gram-molecules of silver. Q is the heat absorbed during the decomposition. It may be replaced by the expression, $U + p\,(v-V)$, where U is the increase in internal energy accompanying the decomposition, and $p\,(v-V)$ is the work done. In the integration of the van't Hoff equation U is usually regarded as constant, but since we are dealing with a pretty wide range of temperature we shall obtain a more accurate result by regarding it as a linear function of the temperature according to the equation

$$U = U_0 - CT \qquad (3)$$

where C is the diminution in the heat capacity of the system during the decomposition of 2 gram-molecules of silver oxide. We may therefore write in place of equation 2,

$$\frac{dp}{dT} = \frac{U_0 - CT + p(v - V)}{T(v - V)} \qquad (4)$$

In order to obtain equation 1 from equation 2 or 4, it is necessary to make two assumptions: First, that the oxygen obeys the gas law, and second, that the volume V is negligible compared with v. Since the deviation of oxygen from the gas law is small at ordinary temperatures[1] and is undoubtedly much smaller at the temperature of our experiments, the first assumption will not lead to any appreciable error. The second assumption would also be justifiable, if it were not for the fact that in our experiments at 445° the pressure is so great and consequently the volume v so small that in comparison V cannot be neglected.

Regarding V not as a negligible but as a constant quantity, and assuming that $pv = RT$, I have succeeded in obtaining the integrated form of equation 4,

$$\ln\frac{p_1}{p_2} = -\frac{U_0}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) + \frac{V}{R}\left(\frac{p_1}{T_1} - \frac{p_2}{T_2}\right) + \frac{R - C}{R}\ln\frac{T_1}{T_2}\text{[2]} \qquad (5)$$

With the aid of this equation we are able to calculate from the decomposition pressures at any two temperatures the value of U_0. In order to do this we must know the values of V and C, but the terms in which these quantities occur are comparatively unimportant ones in the equation, and both these quantities can be disregarded altogether without very seriously influencing the result. Their approximate values will therefore suffice.

From the tables of Landolt and Börnstein we find for the densities of silver and silver oxide 10.5 and 7.5 respectively.

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[1] Amagat: Loc. cit.

[2] This equation may be readily verified by differentiating it. The resulting equation by suitable transposition and with the aid of the gas law can be readily shown to be identical with equation 4. Equation 5 may be obtained by an independent method from equations 6 and 7 of my paper entitled "Law of Physico-Chemical Change." Z. physik. Chem. 38, 205 (1901).

Calculating from these the molecular volumes we get approximately 20 cc. as the value of V.

The specific heat of silver oxide has not been determined but the value of C may be found from the principle of the constancy of the atomic heat in solids. The heat capacity of silver is doubtless approximately the same in the oxide and in the metal. C therefore is the difference between the heat capacity of oxygen in the gaseous and solid states. The heat capacity at constant volume of 32 grams of oxygen in the gaseous state is 5 (calories per degree). The heat capacity in the solid state is about 8,[1] whence C equals 3.

We will determine the value of U_0 in calories and therefore use for R the value 2.0, except in the next to the last term of equation 5, in which, if the pressure is expressed in atmospheres and the volume in cubic centimeters, R must be expressed in corresponding units and given the value 83.

We have three sets of experimental values (*a*) $T=445+273$, $p=207$; (*b*) $T=302+273$, $p=20.5$; (*c*) $T=325+273$, $p=32$. These may be used in equation 5 in pairs. Using values (*a*) and (*b*) we find for the first term of the equation, $ln\frac{p_1}{p_2}$, the value 2.31; for the third term, 0.06; for the fourth term, —0.11. Combining these we get for the second term the value 2.36, whence U_0 is 13600 small calories.

Using similarly values (*a*) and (*c*) we find for U_0 the same value, 13600.

From values (*b*) and (*c*) we find, $U_0=13300$. This value is to be given less credit on account of the nearness of the two temperatures used.

The remarkably good agreement between these values shows conclusively that we are dealing with the same reaction throughout the whole range of temperature from 302° to 445°. As the final result we will take $U_0=13600$ small calories or 136 K (Ostwald calories). From equation 3 the value of U at room temperatures is therefore 128 K. This is the increase of internal energy accompanying the decomposition of 2 gram-molecules of silver oxide. The heat of formation of silver oxide at room temperatures, exclusive of external work, is therefore one-half this value or 64 K.

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[1] See for example Ostwald's Lehrbuch.

HEAT OF FORMATION OF SILVER OXIDE, OTHERWISE DETERMINED.

For the heat of formation of silver oxide we find in the literature only two determinations which are at all trustworthy. Thomsen[1] allowed copper to act upon silver nitrate and from the heat of this reaction, the heat of formation of copper nitrate, and the heat of neutralization of silver oxide, calculated the heat of formation of the latter to be 59 K (*a*).

Berthelot[2] by a similar method obtained 70 K (*b*).[3]

In his experiments on the energetics of galvanic elements Jahn[4] obtained the following equation:

$$\mathrm{Pb + 2AgNO_3Aq = Pb(NO_3)_2Aq + 2Ag + 509K.}$$

Let us combine this equation with the following:

$$\mathrm{PbO + 2HNO_3Aq = Pb(NO_3)_2Aq + H_2O + 178K}\ \text{(Thomsen)},$$

$$\mathrm{Pb + O = PbO + 503K}\ \text{(Thomsen)},$$

$$\mathrm{Ag_2O + 2HNO_3Aq = H_2O + 2AgNO_3Aq + 104K},^{5}$$

whence,

$$\mathrm{2Ag + O = Ag_2O + 68K}\ (c).$$

A similar calculation can be made as follows: I have measured the electromotive force of the following cell (see following paper),

$$\mathrm{Hg, HgCl, KCl\,{}^{N}/_{10}, KNO_3{}^{N}/_{10}, AgNO_3{}^{N}/_{10}, Ag,}$$

and found it to be 0.393 volt at 30°. The temperature coefficient is -0.00121 volt per degree.

From these figures we find by the Helmholtz equation,

$$\mathrm{Hg + \overset{-}{Cl} + \overset{+}{Ag} = Ag + HgCl + 176K}$$

with this we will combine the following,

$$\mathrm{\tfrac{1}{2}Ag_2O + \overset{+}{H} = \overset{+}{Ag} + \tfrac{1}{2}H_2O + 52K,}$$

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[1] Not having Thomsen's book at hand, the values here attributed to him are taken from Ostwald's Lehrbuch.

[2] Ann. chim. 15, 186 (1878).

[3] All these values are for the "total" heats of reaction. I have chosen to use these values, which include the external work, since they are the ones commonly given in the literature. The reduction to the simple "internal" heat of reaction will be made later.

[4] Wied. Ann. **28**, 493 (1886).

[5] Thomsen gives 54 K, but Berthelot found 52 K by the neutralization of silver oxide with nitric acid, Ann. Chim. [5] **4**, 188 (1875), and also by its precipitation with alkalies, Ibid. [5] **4**, 503 (1875), and has recently verified this value by new experiments, C. R. **133**, 555 (1901).

$$HgCl + Cl = HgCl_2 + 219K.^1$$
$$Hg + 2Cl = HgCl_2 + 533K.^2$$
$$Cl + \tfrac{1}{2}H_2O = \overset{-}{Cl} + \overset{+}{H} + \tfrac{1}{2}O + 50K.^3$$

Hence,

$$2Ag + O = Ag_2O + 72K \ (d).$$

Recently Jouniaux[4] has determined the conditions of equilibrium at several temperatures between silver, hydrochloric acid gas, silver chloride and hydrogen, and has thus obtained the thermochemical equation,

$$Ag + HCl = AgCl + H + 71K.^5$$

Let us combine with this equation the following equations of Berthelot:

$$HCl + Aq = \overset{+}{H} + \overset{-}{Cl} + 174K,$$
$$\overset{+}{Ag} + \overset{-}{Cl} = AgCl + Aq + 157K,$$
$$\tfrac{1}{2}Ag_2O + \overset{+}{H} = \overset{+}{Ag} + \tfrac{1}{2}H_2O + 52K,$$
$$H + \tfrac{1}{2}O = \tfrac{1}{2}H_2O + 345K,$$

whence

$$2Ag + O = Ag_2O + 66K.$$

If instead of using the equations of Berthelot we use those of Thomsen[6] we get a different value, namely 60 K. The average of these is 63 K (*e*).

We have thus found five independent values of the heat of formation of silver oxide, varying from 59 K to 72 K. These values all include the external work. In order to obtain the mere change of internal energy, 3 K must be subtracted from each of the above numbers. We have then, (*a*). 56; (*b*) 67; (*c*) 65; (*d*) 69; (*e*) 60.

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[1] This value was obtained by Thomsen from the direct action of chlorine upon calomel. It is in all probability correct, as it has not been called into question in the critical work on mercury salts of Nernst, Z. physik. Chem. **2**, 23 (1888), and Varet, C. R. **120**, 620 and 921 (1893).

[2] This value was obtained independently by both Nernst and Varet.

[3] Thomsen's value is 50.5 K (Pogg. Ann. **148**, 177–1873), Berthelot's is 48 K (C. R. **109**, 546 and 590 (1889)). Thomsen's value is probably the more accurate.

[4] C. R. **132**, 1270 (1903).

[5] I have added 3 K to the value given by Jouniaux in order to obtain the "total" heat of reaction.

[6] Except the third (see a previous note).

Not one of these values alone can be regarded as reliable, on account of the uncertainty in the various data used, but they are all obtained from perfectly independent data, the only value entering into all being the heat of solution of silver oxide in acid, and this has been reliably determined. We may therefore regard the average of these figures with a good deal of confidence. This average is 63.4 K and is very close to the value (64 K) obtained in the preceding section. This very satisfactory agreement proves conclusively that the silver oxide which exists between 302° and 445° is, from a thermodynamic point of view, identical with that which exists at ordinary temperature.

DECOMPOSITION PRESSURE OF SILVER OXIDE AT 25°.

We are now able to calculate from equation 5 the equilibrium pressure between silver oxide, silver, and oxygen at 25°. For data we will take 20.5 atmospheres as the pressure at 302°; 64 K as the heat of formation of silver oxide at 25°; and for C the value 3, as before. The third term of the equation containing V, may be here neglected. We thus obtain $p_{25} = 5 \times 10^{-4}$.

When we consider the question of how much this value is affected by possible errors in the data used, we find that errors in p_{302} and in C have much less influence than an error in U_{25}. An error of 1 K in the latter would cause an error of about one unit in the significant figure of p_{25}. We may therefore regard this value as almost certainly correct within two units.

In the following paper I shall show that from this value of the decomposition pressure of silver oxide at 25° it is possible to calculate the electrolytic potential of oxygen, and that the value thus obtained differs very widely from the one at present accepted.

SUMMARY.

The equilibrium pressures in the system, silver oxide, silver, oxygen, at the temperatures 302°, 325°, and 445°, are respectively 20.5, 32, and 207 atmospheres.

It has been proved that silver suboxide was absent in all of the experiments and that probably it is incapable of existence, at least at these temperatures.

From the change of equilibrium pressure with the temperature the heat of formation of silver oxide is found to be 64 K (Ostwald calories).

The mean of five determinations of this quantity based on calorimetric data is between 63 K and 64 K.

The decomposition pressure of silver oxide at 25° is calculated to be 5×10^{-4} atmospheres.

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 9.]

THE POTENTIAL OF THE OXYGEN ELECTRODE.

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THERE are no more essential physico-chemical data than the changes of free energy accompanying those important chemical processes in which oxygen takes part. Many of these free energy changes could be calculated directly if the potential of the oxygen electrode, against a given concentration of hydroxyl ion, were accurately known. The purpose of the present paper is to determine the true value of this potential.

An oxygen electrode was first used by Grove in the cell which bears his name. The electromotive force of this cell, which is composed essentially of an oxygen and a hydrogen electrode dipping into an aqueous solution, has been measured by a number of experimentors.[1] The value most frequently met in the literature is 1.07–1.08 volts, as found by Smale,[2] who was the first to show that the electromotive force of such a cell is independent of the nature of the electrolyte used.

This value of 1.07–1.08 volts was generally accepted as the true electromotive force of the oxygen-hydrogen cell, or in other words, the true measure of the free energy of formation of water from its elements, but was later shown to be probably too low, by the work of Bose,[3] Wilsmore[4] and Czepinski,[5] who found that the electromotive force of an oxygen-hydrogen cell in normal sulphuric acid increases after several days' standing to 1.10–1.12 volts.

Assuming that between the substances present in the cell there is no reaction possible which can produce a greater change

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[1] See bibliography by Bose: Z. physik. Chem. 34, 730 (1900).

[2] Z. physik. Chem. 14, 577 (1894).

[3] Loc. cit.

[4] Z. physik. Chem. 35, 291 (1900).

[5] Z. anorg. Chem. 30, 1 (1902).