

### Summary

1. The density in grams per cubic centimeter of a gelatin solution of any concentration at any temperature is equal to the density of water at that temperature plus 0.00290 multiplied by the percentage concentration of the gelatin by weight.

2. The viscosities of gelatin solutions of various concentrations at 40° conform to Arrhenius' viscosity formula.

3. The viscosity-temperature curve of gelatin shows a sharp deflection at the transition point of the gelatin.

4. There are two maxima in the viscosity-hydrogen-ion concentration curve for gelatin solutions at 40°. These maxima are about equidistant from the neutral point of water and the effect of the iso-electric point  $P_H$  4.7 is not noticeable on the curve.

5. The transition point of gelatin Sol form A  $\rightleftharpoons$  Gel form B is at a temperature of 38.03°.

6. A change has been suggested in the method of estimating age of solution for viscosity determinations at temperatures below the transition point of the gelatin

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## THE PRESSURE OF OXYGEN IN EQUILIBRIUM WITH SILVER OXIDE

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### Introduction

The transfer of oxygen from the chemically combined or bound condition to the free condition is somewhat analogous to the passage of a substance from the solid phase to the gaseous phase. The combined oxygen in an oxide (or the combined carbon dioxide in a carbonate) may be conceived as occupying at any temperature and pressure a definite partial specific volume and regarded as the specific volume of the compound less the specific volume of the metal or other atomic residue. Thus for silver oxide the volume of a gram of oxygen, in the combined condition, obtained from the densities of silver oxide ( $Ag_2O$ ) and silver, would be 0.6472 cc. at ordinary temperatures, which in fact in this instance is about the estimated volume of 1 g. of oxygen in the free solid condition at  $-273^\circ$ .

In the case of silver oxide large pressures of oxygen are obtained at comparatively low temperatures and the gas law  $pv = RT$  is insufficient as an equation to calculate the equilibrium volumes of the oxygen. G. N.

Lewis,<sup>1</sup> who first studied the equilibrium conditions of this oxide, applied to his measurements a method of thermodynamic correlation based on the use of the Clausius equation ( $Q = T \frac{dQ}{dT} \Delta v$ ), and employed the equation  $v = \frac{RT}{p}$  which was sufficient for the range of pressures measured.

The term  $\Delta v$  represents the increase in volume of the products of the decomposition over the volume of the factors. For two mols of silver oxide  $\Delta v$  is the sum of the volumes of 1 mol of oxygen and 4 mols of silver diminished by the volume of 2 mols of silver oxide. The quantity amounts, therefore, to the difference in the volume of free oxygen diminished by the volume difference between silver oxide and free silver, all under the same equilibrium conditions of pressure and temperature. In support of the analogy of this type of equilibrium to that of a pure substance it may be pointed out that the volume of the free oxygen diminishes continuously with the rising pressure as does the saturation volume in the case of a pure liquid or solid. The volume difference between silver oxide and silver also increases regularly. The analogy will be really complete, however, if the heats of the transfer from combined to free state diminish and eventually vanish at the point where  $\Delta v$  is zero. It was a prime object of this work to examine as far as feasible this possibility. The density data available are incomplete for silver oxide, but the coefficients of expansion of the salts AgCl and AgBr are only about half again as large as that of silver, and if silver oxide is approximately similar the volume difference of salt and metal would increase very slowly with the temperature. Lacking data on the expansion of silver oxide the volume difference for silver oxide-silver will, in this paper, be taken as constant. The data to follow indicate that  $\Delta v$  may eventually vanish with rising temperature and pressure, but since  $Q$  finally increases with rising temperature  $\frac{dQ}{dT} \Delta v$  may become indeterminate.

The volumes of the free oxygen can be easily calculated by means of the equation of state<sup>2</sup> for oxygen when the equilibrium pressures and temperatures of oxygen over silver oxide are given. The constants of the oxygen equation of state were obtained from Amagat's data extending over a temperature range of 200° and pressure range of 1000 atmospheres. The data in connection with the equilibrium in the present investigation extend to a pressure of only about 400 atmospheres, but sufficient data are available not only to establish this important equilibrium, but to

<sup>1</sup> Lewis, *Z. physik. Chem.*, **55**, 449 (1906). The equilibrium values presented in this paper were sent some months ago to Professor Lewis to be used in certain calculations in connection with his free energy studies.

<sup>2</sup> *Proc. Nat. Acad. Sci.*, **3**, 323 (1917); *THIS JOURNAL*, **43**, 1452 (1921).

indicate that  $\Delta v$  probably does not vanish below the melting point of silver or perhaps that of silver oxide.

### Apparatus Details

The material in which the silver oxide was contained was of sterling silver reinforced by a steel jacket represented in Fig. 1.

The interior of the steel member G of diameter 12 mm. was covered uniformly with a layer of silver solder and then filled with molten sterling silver rubbed into soldering contact with the walls of the steel member. The silver case of the latter was bored out to a diameter of about 8 mm. The steel sheath C was filled with silver in a manner similar to G, bored, and left with a silver end which filled a section of the silver lining H of G. A chemically pure silver ring F served as a closing gasket forced to a tight closure by means of the steel ring E driven by the nut D. The lead tube A was prepared by drawing down a steel tube which inclosed a silver tube, and the composite tube so formed was silver soldered as indicated at B.

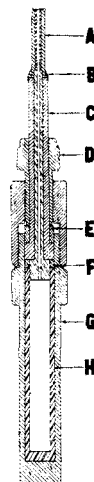


Fig. 1.

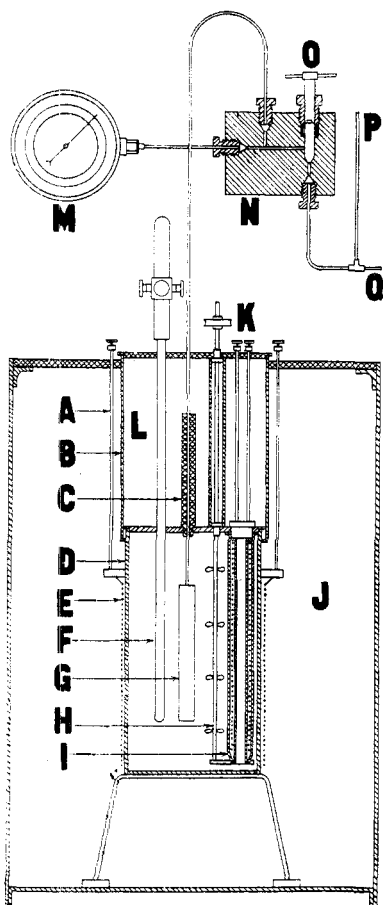


Fig. 2.

The constant temperature bath, Fig. 2, consisted of a sodium nitrate-potassium nitrate mixture contained in a steel vessel about which was wound a Nichrome resistance winding E. Two heats were provided by means of 3 terminal connections, one of which is designated by A. The tube G containing the material was passed through the steel cover of the bath which carried the stirrer and supplementary heater used for regulation. The space L was filled with insulating material, and the platinum resistance thermometer F served to measure the temperature. The connecting block N carried a stopcock O which served to close the bomb from a pump used to inject pure oxygen, since at the higher temperatures the volume of the apparatus was large enough to exhaust the oxygen contained in the quantity of silver oxide under observation. The oxygen pump was advantageous in changing at will the relative amounts of silver and silver oxide in the bomb and thus approaching the equilibrium pressure from higher and lower pressures.

Pressures were measured on the gage M indicating to 2 lbs. The gage was calibrated by means of one of the standard gages of the floating piston type in use in this Laboratory whose constant was obtained by direct comparison with a 9-meter column of mercury.

The silver oxide employed was prepared from c. p. silver nitrate solution obtained from c. p. silver. Crystals of  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  obtained by repeated crystallizations were used for the precipitating solution and the silver oxide was washed with distilled water free from carbon dioxide. Three days' washing was required to remove all traces of barium nitrate. The silver oxide was dried in a special bomb through which dry air, free from carbon dioxide, was circulated. The temperature of the drying was gradually raised to  $275^\circ$  during a period of 12 hours when the effluent gas from the bomb was found to be dry. The silver oxide gave on analysis a silver content of 93.09% as compared with 93.136% from the formula.

### Experimental Data

The measurements at temperatures lower than  $370^\circ$  confirm in every way the details given by Lewis regarding the slowness of the reaction at lower temperatures. In the present experiments about 20 hours was necessary to insure equilibrium at about  $300^\circ$  while above this temperature equilibrium was established very quickly. Altogether the pressures at 5 temperatures were measured, beginning at  $374^\circ$  and ending with  $500^\circ$ , and at each temperature 6 to 10 observations were made of the pressures as obtained from the formation and decomposition sides of the reaction. This control could be very conveniently obtained by means of the oxygen injection pump connected to the block N at P, Fig. 1. Oxygen could be allowed to escape through Q, which carried a steel stopcock not shown in the figure. Table I gives the new measurements and also the data of Lewis. The last column presents the pressures calculated for the measured temperatures by means of the equation written into the plot, Fig. 3. For comparison there has been drawn in this plot the dotted line representing the equation for the silver oxide equilibrium as computed by Pollitzer<sup>3</sup> on the basis of the Nernst theorem.

### Discussion of the Results

Fig. 3 and Table I present our data and those of Lewis in terms of the variables  $\log p$  and  $1/T$ . Within the limits of accuracy of the data it is evident that the points lie on a straight line whose equation is  $\log p = -\frac{2859}{T} + 6.2853$ . The free oxygen departs progressively from the simple gas laws, but the equation of state enables the volumes to be calculated at any temperature and pressure. The equation for  $\frac{dp}{dT}$  is obtained from the  $\log p$  equation given, or

$$\frac{dp}{dT} = \frac{2859 \times 2.3023}{T^2} p = \frac{6582}{T^2} p.$$

<sup>3</sup> "Die Berechnung Chemischer Affinitäten nach dem Nernstschen Wärmetheorem." Ferd. Enke, Stuttgart, 1912.

The heat of the reaction at any temperature is obtained from the Clausius equation by substituting therein the equation for  $\frac{dp}{dT}$ .

$$Q = 6382 \frac{p}{T} (v - 20.7)$$

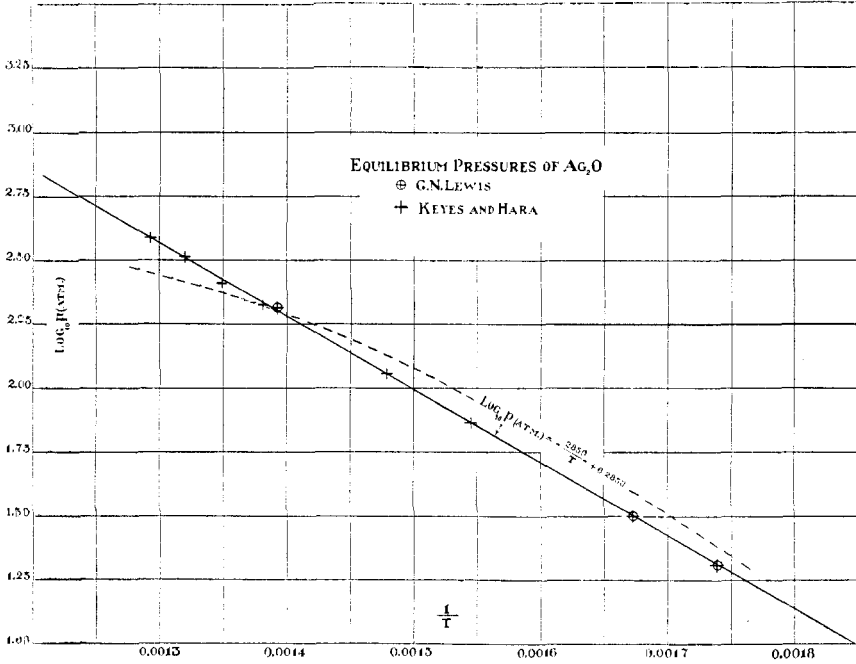


Fig. 3.

TABLE I  
EQUILIBRIUM PRESSURES IN ATMS. FOR THE REACTION  
 $2Ag_2O = 4Ag + O_2$

t	Pressure in Atm.		Mean Observed	T, abs.	$\frac{1}{T} \times 10^3$	Log p Obs.	P calc. by equation. <sup>a</sup>
	To left	To right					
374.0	.....	74.3	74.3	647.1	1.5454	1.8710	73.6
403.0	113	115.9	114.5	676.1	1.4791	2.0588	113.9
452.0	214.2	212.8	213.5	725.1	1.3791	2.3294	220.0
467.7	259.7	255.8	257.8	740.8	1.3499	2.4113	266.6
484.0	323.6	323.3	323.5	757.1	1.3208	2.5099	322.9
500.2	389.9	386.7	388.3	773.3	1.2932	2.5892	387.3
Equilibrium Pressures Measured by Lewis							
302.0	.....	.....	20.5	575.1	1.7388	1.3118	20.6
325.0	.....	.....	32.0	598.1	1.6720	1.5052	32.0
445.0	.....	.....	207.0	718.1	1.1393	1.3160	201.4

<sup>a</sup> Equation for equilibrium pressure,  $\log p_{atm} = -\frac{2859}{T} + 6.2853$ .

where  $v$  is the volume of a mol of oxygen in the free state under equilibrium pressure  $p$  at the absolute temperature  $T$ . The number 20.7 is the volume difference between 2 mols of silver oxide and 4 mols of silver using the densities given for ordinary temperatures 7.5 and 10.5. Evidently this number should increase with the temperature, since the coefficient of expansion of silver oxide undoubtedly exceeds that of silver. The increase would be comparatively slight and will be neglected. It should be noted that the above simple equation involves no approximations, but is based on the complete Clausius equation and upon experiment.

In Table II will be found the pressures and volumes of oxygen at the equilibrium temperatures given in Col. 1. The volumes calculated by means of the perfect gas laws are also listed and it will be observed that a very fair approximation to the true volume is obtained up to about 20 atmospheres, while at about 4000 atmospheres the actual volume is somewhat more than twice the volume calculated by means of the perfect gas equation. At the corresponding temperature it will be noted also that  $\Delta v$  is 24.71 cc. A graph of  $\Delta v$  indicates that  $\Delta v$  might vanish in the neighborhood of 1200°, although this might occur at a lower temperature on account of the larger expansivity of silver oxide as compared with silver. The silver would melt below 1200° and possibly the oxide also which would introduce complexities due to solutions.

TABLE II  
PRESSURES AND VOLUMES OF OXYGEN

Equil. temp. °C.	Equil. press. Atms.	$\frac{dp}{dT}$	Volume <sup>a</sup> cc. per mol. by exact equat.	Volume cc. per mol. by perfect gas laws	$\Delta v$	Total heat cal. per mol. of O <sub>2</sub>	Internal heat, $(Q - p\Delta v)$
25	1.75	0.05144	22208.0	22176.0	22187.3	13083	12142
300	19.8	0.397	2386.2	2374.4	2365.5	13042	11907
400	109.2	1.587	524.8	505.6	504.1	13046	11712
500	386.5	4.257	187.52	164.2	166.8	13313	11751
600	1026	8.856	95.81	69.76	75.1	14071	12204
700	2225	15.47	61.76	37.76	41.06	14973	12760
800	4179	23.90	45.41	21.12	24.70	15349	12848

<sup>a</sup> Equation of state for oxygen; pressure in atmospheres of 76 cm. of Hg; volume in cc. per g.

$$p = \frac{2.564}{v - \delta} T - \frac{1475}{(v + 0.09)^2}$$

$$\log \delta = 0.1420 - \frac{0.303}{v}$$

<sup>b</sup> Mean of Thomsen's and Berthelot's observed values combined with computations of Lewis, Ref. 1.

The last column gives the heat of the reaction diminished by the external work  $p \Delta v$  in calories. The specific heat of silver oxide has not been measured, but by Kopp's rule about 500 cal. would be added to the heat

at 200° giving 12642 cal. at ordinary temperatures, in excellent agreement with the mean of the observed values of Thomson and Berthelot and three others calculated by Lewis. It is of interest to observe that a minimum appears to exist at about 400–500° in the values of the internal heats, which indicates that the heat is tending to increasingly large values while  $\Delta v$  is diminishing continuously. The specific heat of silver oxide is required before further interpretation of the present equilibrium data is possible. The specific heats at low temperatures together with accurate values of the vapor pressure of liquid oxygen below one atmosphere will also provide material to test more adequately the application of the Nernst heat theorem to the type of equilibrium herein discussed.

### Summary

1. The equilibrium pressure of oxygen over silver and silver oxide has been measured, confirming the data of Lewis and extending them to higher pressures and temperatures.

2. The following equation (ordinarily derived by the use of the perfect gas law and by assuming the heat constant) is found empirically to represent the data exactly:

$$\log p = -2859/T + 6.2853,$$

where the pressure is in atmospheres, the temperature is degrees absolute, and common logarithms are used.

3. The Nernst heat-theorem equation, as given by Pollitzer to fit the data of Lewis, fails to represent the data.

4. Neglecting only the difference in the coefficient of expansion between silver oxide and silver, the following equation is derived from the Clausius equation for the external heat of the reaction, in calories per mol of oxygen,

$$Q = 6582 (v - 20.7) p/T,$$

where  $v$  calculated from the equation of state for oxygen is given in cc. per mol.

5. The value for the internal heat at 25°, calculated with the aid of Kopp's rule, is 12642 cal., in agreement with the mean of the measurements and computations (12640 cal.) considered by Lewis.

6. The internal heats, though they pass through a minimum at about 400–500°, increase again with rising temperature.

7. The analogy between this chemical reaction and a simple evaporation, therefore, breaks down since no sign is shown of a critical point, with the heat equal to zero, although  $\Delta v$  appears to be diminishing progressively.