At low gelatin concentrations the values of (R_1-r) and (R_2-r) are rather close together, thus giving us a good idea of the thickness of the gelatin layer on the gold particles. This comparatively close agreement between the (R_1-r) and the (R_2-r) values also shows that in dilute sols practically all of the gelatin is adsorbed upon the gold particles. At higher concentrations the minimum and maximum values of the thickness of the layer differ widely showing that in this case only part of the gelatin is adsorbed.

Summary

1. A centrifugal apparatus for the study of the changes taking place in fine-grained sols during centrifuging has been described. The name "ultra-centrifuge" has been proposed for this instrument.

2. The theory of the methods for determining size and distribution of size of particle from observations—direct or photographic—of the sol during centrifuging has been further developed.

3. Results of measurements of size and distribution of size of particle for gold sols of average radius 2.3, 3.6, 7.1, 11.6$\mu\mu$ have been given. The determinations made by means of the ultra-centrifuge give radius values which are from 11 to 38% higher than those arrived at by means of Zsigmondy's nuclear method.

4. The nature of the protective action of gelatin upon fine-grained gold sols has been studied by means of the ultra-centrifuge. Minimum and maximum values for the thickness of the gelatin layer adsorbed around the gold particles have been calculated.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF McGILL UNIVERSITY]

THE PROPERTIES OF PURE HYDROGEN PEROXIDE. V. VAPOR PRESSURE

BY O. MAASS AND P. G. HIEBERT

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The determination of the vapor-pressure curve of pure hydrogen peroxide is important because the data makes possible the calculation of the latent heat of evaporation, Trouton's constant, etc., physical constants which are of particular interest when compared with the corresponding ones for water. The experimental difficulties which have to be overcome in the measurement of the vapor pressure of hydrogen peroxide are many. At high temperatures hydrogen peroxide decomposes when in contact with glass. A mercury manometer cannot be used directly because of the immediate decomposition which takes place when peroxide comes in contact with the mercury surface, the latter being attacked and covered with a scum which makes accurate pressure readings impossible.

Furthermore, on account of the low vapor pressure of hydrogen peroxide at room temperatures, condensation occurs in all parts of the apparatus not artificially heated.

An apparatus was devised which makes use of an oxygen screen between the peroxide vapor and the mercury manometer, the oxygen being supplied by the hydrogen peroxide vapor itself. The vapor-pressure curve was determined over the range 10° to 90°. The effect of the slight decomposition due to the glass at the higher temperatures was eliminated in a manner to be described.

A diagram of the apparatus used is shown in Fig. 1.

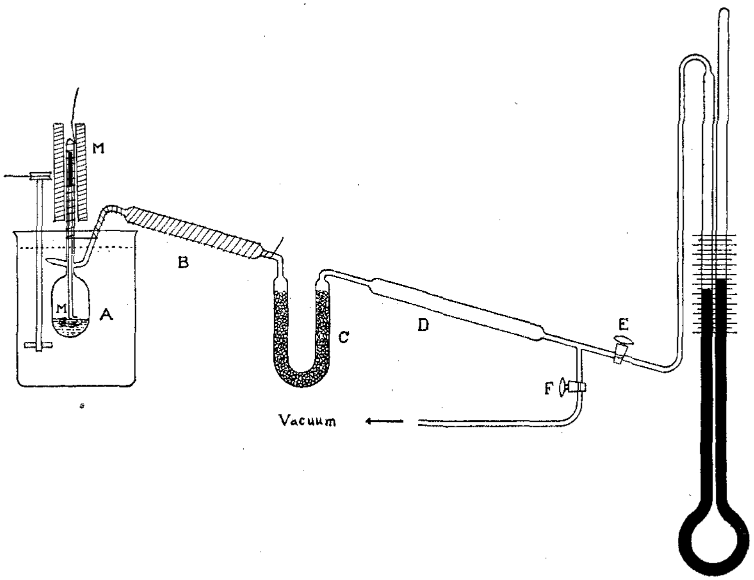

Fig. 1.

The flask, A, of about 150cc. capacity, was sealed by means of a side tube to a tube, B, containing granular manganese dioxide. This in turn was sealed to two drying tubes, C and D, containing calcium chloride and phosphorus pentoxide, respectively. From these a tube led to a manometer and a T-tube to a large sulfuric acid vacuum pump,[1] both tubes being provided with taps, E and F, as shown in the diagram. The flask, A, was fitted with an extra side tube for introducing the peroxide and with a magnetic stirrer, MM, as shown.

The flask, A, was placed in the thermostat which could be regulated to 0.1° at any desired temperature within the range to be examined. The long neck of the flask (which was necessary for the stirrer), the small diameter tube connecting to B, and B itself were wound with Nichrome wire enclosed between layers of asbestos, so that when a current of 2 to 3 amperes was sent through, the temperature of this portion of the apparatus was maintained at approximately 200°. The side arm which was sealed off after the introduction of the peroxide was well below the surface of the water in the thermostat.

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[1] Maass, THIS JOURNAL, **42,** 2570 (1920).

A preliminary experiment in which a receiving flask and condenser were substituted for the drying tubes showed that when a current was passed through the Nichrome wire and hydrogen peroxide was distilled into the flask under a vacuum, no trace of hydrogen peroxide passed through the manganese dioxide tube. The manometer was equipped with a calibrated glass scale, the limit of error being 0.1 mm., and the system was tested for defects. It was found that the vacuum pump maintained a constant pressure of 0.1 mm., when the apparatus was empty.

About 20 g. of pure hydrogen peroxide, prepared in the manner described elsewhere[2] and containing by analysis 99.98% of H_2O_2, was introduced into the flask A through the side tube by means of a capillary pipet extending to the neck of the flask. After the tube was sealed the thermostat was filled with ice water and the system exhausted. The current was then turned on and maintained constant until the temperature of B and the connecting tubes was constant. The thermostat was then heated to the desired temperature, and it was found that when the tap, F, leading to the vacuum pump was closed, pressure equilibrium throughout the system was established within a few seconds when the peroxide was vigorously stirred. The stirrer was so arranged that it would break through the surface of the liquid peroxide with every stroke.

Between every two readings at the different temperatures the system was exhausted, the hydrogen peroxide boiling vigorously. When the tap F was closed the vapor pressure of the peroxide in the flask forced some of the peroxide vapor into the manganese dioxide tube where it was decomposed to oxygen and water. The oxygen was dried by the calcium chloride and the phosphorus pentoxide, and thus only dry oxygen was permitted to come in contact with the surface of the mercury. This oxygen being in pressure equilibrium with the hydrogen peroxide vapor gave the pressure reading directly.

The following factors had to be taken into account. Sufficient time had to be allowed for true pressure equilibrium to be established; otherwise the pressure recorded would be too low. On the other hand, as time went on, oxygen would diffuse back from B and the decomposition of the peroxide in any portion of the flask, A, would cause too high a pressure to be recorded. Hence, each vapor pressure was determined as follows. Tap F was opened to an evacuated chamber of 30-liters capacity in series with the pump. The peroxide in A boiled vigorously, sweeping out any oxygen in this portion of the apparatus. Tap F was then closed and the pressure in the manometer read at 15-second intervals, these readings being plotted on a curve which showed that the pressure rose rapidly to a constant value at the lower temperatures and at the higher temperatures, that is above 50°, showed a constant slight increase as time went on. In the latter case the straight line showing this constant slight increase was extended back to zero time when tap F was

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[2] Maass and Hatcher, This Journal, **42**, 2548 (1920).

closed, and this pressure taken as the true vapor pressure. Throughout each measurement the peroxide was stirred vigorously. At each temperature two such determinations were made and found to check within 0.1 mm.

After the vapor pressure had been determined to as high a temperature as was considered safe, the flask was cooled and determinations were again made at lower temperatures as a check upon those previously determined before the higher temperatures had been reached. The change in vapor pressure due to the decomposition of the peroxide was found to be negligible. The peroxide was then cooled in ice, the apparatus was cut apart and the peroxide analyzed. It was found that no greater drop in concentration than 0.4% occurred throughout the whole series of experiments.

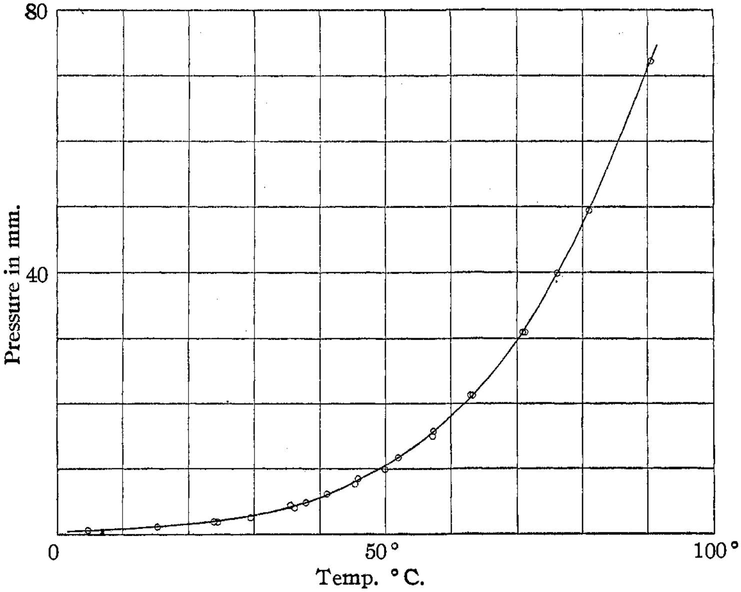

Fig. 2.

The vapor pressures of hydrogen peroxide as obtained from two samples of peroxide by the method described above are given in Table I, and are represented graphically in Fig. 2. It will be seen that the two sets of values are in close agreement and that although the determinations were made with two different samples of peroxide the values obtained fall upon the same curve.

In Table II, Col. 1, are given a number of values of the vapor pressures of hydrogen peroxide taken from the vapor-pressure curve drawn on a large scale, at temperatures from 10° to 90°. In the second column are

TABLE I

VAPOR PRESSURE OF HYDROGEN PEROXIDE

First sample		Second sample	
Temperature °C.	Vapor pressure mm. of Hg 0°C.	Temperature °C.	Vapor pressure mm. of Hg 0°C.
23.85	1.8	4.65	.55
29.45	2.6	15.20	1.1
36.10	4.1	24.45	1.9
41.15	6.2	35.50	4.4
45.80	8.6	45.40	7.8
51.95	11.8	57.40	15.8
57.30	15.0	63.25	21.3
63.05	21.3	71.25	31.0
70.85	31.0	76.10	40.0
81.05	49.5	...	..
90.35	72.3	..	..

given the logarithms of these vapor pressures, in the third column the temperatures corresponding to the vapor pressures and in the fourth column the reciprocals of these temperatures on the absolute scale. In Fig. 3, Curve 1, the logarithms of the vapor pressures are plotted against the reciprocals of the absolute temperatures.

TABLE II

DATA FOR VAPOR-PRESSURE EQUATION

Vap. pres. (P)	$\log_{10} P$	Temp.	$1/T \times 10^3$
1.1	0.0414	15	3.471
1.5	.1761	20	3.412
2.1	.3424	25	3.355
2.75	.4393	30	3.299
4.0	.6021	35	3.246
5.7	.7559	40	3.194
7.8	.8921	45	3.144
10.4	1.0170	50	3.095
13.8	1.1399	55	3.048
18.1	1.2577	60	3.002
23.3	1.3674	65	2.958
29.65	1.4720	70	2.915
37.6	1.5752	75	2.873
47.4	1.6758	80	2.832
59.1	1.7716	85	2.792
71.5	1.8543	90	2.754

It is seen that the relationship is represented by a straight line. The equation for this line is found to be

$$\log_{10} P = -\frac{0.05223 \times 48530}{T} + 8.853 \qquad (1)$$

where P is the vapor pressure and T the absolute temperature.

On account of the great similarity between hydrogen peroxide and water from the point of view of association[2] water was taken as a reference liquid and the Ramsay and Young rule applied. Table III, Col. 1, gives the pressures and Cols. 2 and 3 show the temperatures on the absolute scale of hydrogen peroxide and water, respectively, corresponding to these pressures.

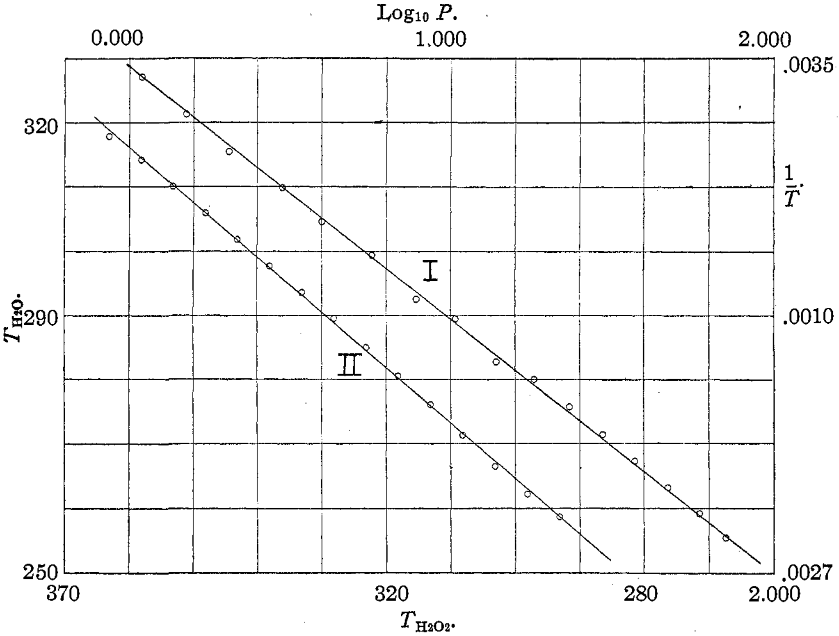

Fig. 3.

Table III

Hydrogen Peroxide and Water Temperatures at Equal Pressures

Pressure	$T_{H_2O_2}$	T_{H_2O}	Pressure	$T_{H_2O_2}$	T_{H_2O}
1.5	293.1	258.7	18.1	333.1	293.6
2.0	298.1	262.2	23.3	338.1	297.8
2.75	303.1	266.3	29.65	343.1	301.9
4.0	308.1	271.3	37.6	348.1	306.05
5.7	313.1	276.15	47.4	353.1	310.25
7.8	318.1	280.65	59.1	358.1	314.3
10.4	323.1	285.0	71.5	363.1	318.0
13.8	328.1	289.3	...	...	....

As will be seen from Curve II, Fig. 3, where these temperatures are plotted, a straight line is obtained giving $\frac{T_{H_2O_2}}{T_{H_2O}} = 1.138$. From this the boiling point of pure hydrogen peroxide is evaluated as 151.4°, which is probably more accurate than that given by the vapor-pressure equation which gives a value 151.1° as the boiling point.

From Equation 1 it follows that the molecular latent heat of evaporation is 11,610 calories, and it follows that Trouton's constant is 27.3, showing that hydrogen peroxide is associated, the similarity to water whose constant is 26.2 being again very marked.

Assuming that the boiling point of hydrogen peroxide is on the same corresponding scale as that of water, the critical temperature of the former is found to be 458.8°.

Two vapor pressures for hydrogen peroxide have been recorded in the past; one[3] at 69° and the other[4] at 85°. The first of these is 3% higher and the second is 9% higher than the values found by the authors. G. N. Lewis[5] used the value of Wolffenstein and that of Brühl for the calculation of the free-energy change in the vaporization of hydrogen peroxide, and incidentally estimated the heat of vaporization. He stated that the data gave too high a value for Trouton's Constant and predicted that the latent heat of evaporation would be lowered by a thousand calories when further data were available. This prediction has been proved to be correct. Using Equation 1 for the calculation of the vapor pressure at 25°, the free energy in the vaporization is found to be only 1% less than that calculated by Lewis.

The information obtained in this investigation together with the data previously determined enables one to estimate the slope of the univariant systems passing through the triple point and these compared with the corresponding ones for water, in atmospheres per degree, are given below.

	dP/dT Liquid-vapor	dP/dT Solid-vapor	dP/dT Solid-liquid
H_2O_2	0.000033	0.000040	+152
H_2O	.00044	.00048	−132

The solid-liquid systems for hydrogen peroxide and water slope in opposite directions. Hydrogen peroxide differs in this respect from water and undergoes, like the vast majority of substances, a decrease in volume on solidification. The values obtained for Trouton's constant together with the other physical constants which are affected by molecular association in the liquid state, show that hydrogen peroxide and water in the liquid condition are associated to the same extent. Yet the density curve of liquid hydrogen peroxide shows no maximum corresponding to that of water. If, therefore, triple hydrogen peroxide molecules corresponding to trihydrol exist, these must have a smaller volume than the unassociated peroxide molecules with which they are in equilibrium. It will be of great interest to subject hydrogen peroxide crystals to X-ray analysis since the information obtained from such experiments taken in conjunction with the facts pointed out above might throw light upon the behavior of water.

[3] Wolffenstein, *Ber.*, **27**, 3307 (1894).

[4] Brühl, *Ber.*, **28**, 2847 (1895).

[5] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., **1923**, p. 495.

Acknowledgment is hereby made of a Fellowship granted during the time of this research by the Honorary Advisory Council for Scientific and Industrial Research of Canada.

Summary

The vapor-pressure curve of hydrogen peroxide has been determined with a considerable degree of accuracy and the relation between pressure and temperature may be represented by the equation,

$$\log P = -\frac{0.05223 \times 48530}{T} + 8.843$$

The following physical constants have been calculated for hydrogen peroxide; boiling point, 152.1°; latent heat of evaporation, 341.5 cal.; Trouton's constant, 27.3; and critical temperature, 459°.

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[CONTRIBUTION FROM THE LABORATORY OF COLLOID CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

MEASUREMENTS OF THE MOBILITY OF EGG ALBUMIN AT DIFFERENT ACIDITIES[1]

BY NORMAN D. SCOTT AND THE SVEDBERG

RECEIVED JULY 22, 1924 PUBLISHED DECEMBER 13, 1924

In an earlier article,[2] Svedberg and Jette showed that the well-known U-tube method can be applied to the study of the cataphoresis of protein if one determines the position of the protein layer by photographing its fluorescence when illuminated with ultraviolet light.

In this preliminary paper, no quantitative measurements were reported. The apparatus had not been calibrated to determine the effective potential gradient and the pictures were not distinct enough to make possible accurate measurements of boundary positions. A detailed report by Mr. Jette of the faults and difficulties of the former apparatus helped greatly in constructing a new apparatus with which fairly accurate quantitative measurements were possible. The method has now been used to measure the mobility of egg albumin at different acidities with two different buffer mixtures.

The Apparatus

A brief description of the apparatus is given on pp. 185–187 of Svedberg's "Colloid Chemistry," with drawings which show the cataphoresis tube and the general arrangement for illumination and photography.

Pyrex glass was used in making the cataphoresis tube because of its slight fluorescence. It was made in one piece including the connecting siphon tubes which served

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[1] A portion of a thesis submitted by Norman D. Scott in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Wisconsin.

[2] Svedberg and Jette, THIS JOURNAL, **45**, 954 (1923).