in this stage of the reaction nearly all of the activated molecules decompose, since collisions, which could cause deactivation, have now become infrequent. The decomposition of acetaldehyde is an example of a reaction in the process of transition from the high pressure bimolecular stage to the unimolecular stage; the decomposition of azomethane indicates the transition from unimolecular to low pressure bimolecular.

There are several possible types of bimolecular reactions and in some cases it may be found possible to decide, by methods which have been indicated, to which of them any particular reaction belongs; of course, in general, all of the types proceed together, but one of them may account for all but a negligible fraction of the total reaction.

The formula for the velocity of unimolecular reactions proposed by Dushman is not in agreement with experimental data; indeed, the rates of these reactions have a much greater range of variation than is permitted by this formula.

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[CONTRIBUTION FROM THE PHYSICAL CHEMICAL LABORATORY OF MCGILL UNIVERSITY]

SULFUR DIOXIDE AND ITS AQUEOUS SOLUTIONS.
I. ANALYTICAL METHODS, VAPOR DENSITY AND VAPOR PRESSURE OF SULFUR DIOXIDE. VAPOR PRESSURE AND CONCENTRATIONS OF THE SOLUTIONS

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The following is the first of two papers dealing with some of the physical properties of various phases of the two component system sulfur dioxide-water. The investigation had its beginning in an attempt to measure the conductivities of concentrated aqueous solutions of sulfur dioxide.

It was soon found, however, that other properties of sulfur dioxide had to be investigated before the conductivity could be measured. From some of the results obtained, these preliminary investigations proved to be of at least as great an interest as the main one and consequently the present paper is devoted solely to these. This work may be conveniently divided into the following topics: Purification of Sulfur Dioxide, Analysis of Sulfurous Acid, Vapor Density Determinations, Vapor Pressures of Pure Sulfur Dioxide and its Aqueous Solutions, Concentrations in the Two Liquid Phase System, Sulfur Dioxide–Water.

A second paper, dealing with the conductivities and containing a theoretical discussion of the equilibria involved, will follow.

Purification of Sulfur Dioxide

It was found that particularly pure liquid sulfur dioxide could be obtained commercially. In order to test the gas for sulfur trioxide, it was passed into an acid solution of barium chloride, in which air-free water had been used, and from which the air was excluded. No precipitate was formed. The only impurity found in the sulfur dioxide was a small trace of water. The gas from the cylinder was therefore passed over phosphorus pentoxide tubes and condensed in tubes by a carbon dioxide-ether mixture. The liquid was then distilled a number of times *in vacuo*, the initial and final fractions being rejected. Cardoso[1] mentioned a yellowish liquid left as residue after some of his distillations. There was no sign of any such residue in the distillations carried out with the condensed product. The distillation was carried out in an all-glass apparatus. The pressure was controlled by means of a manometer. A tap leading from the purification apparatus was glass sealed alternately to the various pieces of apparatus (described in the following sections) where the experiments with the sulfur dioxide were to be carried out.

As a proof of the purity of the final fraction of sulfur dioxide, its vapor pressures were measured in the neighborhood of the boiling point and were found to agree exactly with the values obtained by Henning and Stock.[2] The vapor pressure determinations of these investigators were made with the greatest precision over the range -60 to $-10°$, and constituted one of the few physical constants of pure sulfur dioxide which was accurately known when this work was started.

Analysis of Sulfurous Acid

The estimation of sulfurous acid is described in most textbooks on quantitative analysis as being carried out very easily by means of a reaction with iodine which depends on the reducing power of sulfurous acid. It was soon found that in practice the titration of sulfurous acid by iodine was not so simple as the textbooks led one to believe. No constant results were obtained and two consecutive titrations of samples of the same sulfurous acid solution gave values differing by as much as 20%.

A search of the literature soon disclosed that others had met with similar results and various remedies had been suggested.[3] After considerable time had been spent in following some of the methods referred to above, a modification of them was worked out which gives accurate and reproducible results. This is true to such an extent that sulfur dioxide itself was used to calibrate the iodine solution.

A glass bulb B (Fig. 1) of 2–3 cc. capacity ending in a capillary tube bent in the manner shown was attached to a glass tube connected through tap A to the sulfur

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[1] Cardoso, *J. chim. phys.*, **23**, 829 (1926).

[2] Henning and Stock, *Z. Physik*, **4**, 226 (1921).

[3] (a) Bunsen, *Ann. chim. phys.*, [3] **41**, 339 (1854); (b) Fordos and Gelis, *Compt. rend.*, **20**, 771 (1845); (c) Finkner, "Quant. Analyse," **1871**; (d) Volhard, *Ann. Chem. Pharm.*, **242**, 94 (1873); (e) Macauley, *J. Chem. Soc.*, **121**, 553 (1922); (f) Raschig, *Z. anorg. Chem.*, **17**, 577 (1904); (g) Hudson, *J. Chem. Soc.*, **127**, 1332 (1925).

dioxide purification apparatus and through tap D to a vacuum pump. After evacuation about 1 cc. of liquid sulfur dioxide was condensed in the bulb and the capillary sealed off with a hand blowpipe at the point marked C. The bulb was allowed to warm up to room temperature and then weighed. The bulb was then again cooled down by a carbon dioxide–ether mixture and the capillary broken off near the sealed end. By having a thin capillary but one whose walls were thick relative to its diameter and, furthermore, by using a new file to scratch the glass, no splintering occurred, so that the two broken parts represented the total weight of glass. The bulb is then allowed to warm up after the capillary is immersed in 50 cc. of a 2 *N* sodium hydroxide solution F, as shown in Fig. 1. The liquid sulfur dioxide which boils off is completely absorbed in the sodium hydroxide solution which then rises in the capillary as soon as all the liquid sulfur dioxide has evaporated. The moment this happens and before the liquid rises beyond a few centimeters the capillary is sealed off at E above the rising liquid. This bit of capillary is cleaned, dried out and, together with the sealed off bulb and piece of capillary first broken off, is carefully weighed. The difference in weight between this and the first mentioned weighing gives the weight of sulfur dioxide absorbed by the sodium hydroxide solution to an accuracy of 0.1 mg.

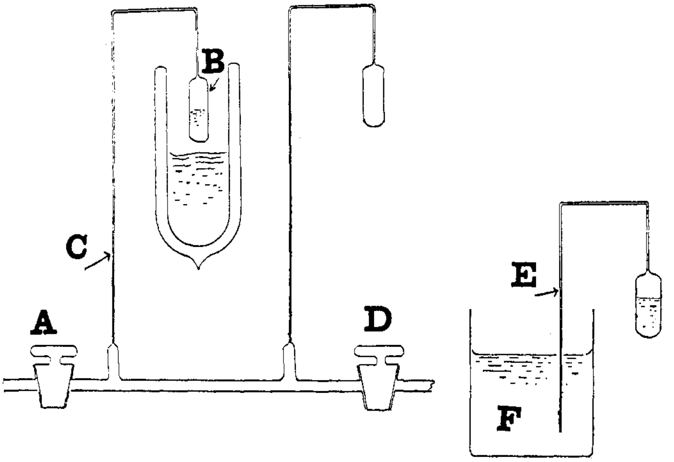

Fig. 1.

The essential feature governing the accuracy of the subsequent analysis was the solution of 0.1 g. of sugar in the 50 cc. of sodium hydroxide solution before the sulfur dioxide was absorbed. The 50 cc. was then made up to 250 cc. in a graduated flask, care being taken to wash all of the solution into the latter. This solution was then placed in a buret and 25 cc. of an iodine solution to be standardized was measured out from a pipet into an Erlenmeyer flask. This was diluted with an equal volume of water and 2 cc. of concentrated hydrochloric acid was added. The iodine solution was vigorously swished around in the Erlenmeyer flask and the sulfite solution was run in until the iodine color disappeared, a very sharp and final end-point being obtained. The above procedure can be used for any sulfurous acid solution by making the solution strongly alkaline, adding a small amount of sugar and then following the above directions.

The reasons for some of the steps in the procedure are explained by the following considerations. Only a strong alkalinity insures that no loss of sulfur dioxide takes place due to evaporation. Sulfite solutions oxidize in an inconsistent and most exasperating manner. Evidently the rate of oxidation is greatly increased by catalysts present in the form of small traces of impurities. In Ostwald's "Inorganic Chemistry,"[4] it is mentioned that the oxidation of sulfite is inhibited by the presence of a small amount of sugar, which Ostwald calls an anti catalyst. Of course, the probable action of the sugar is that it inhibits the action of the catalysts. The iodine solution is made strongly acid just before titration to neutralize the alkalinity of the sulfite solution.

As has already been indicated, at first no consistent results whatever could be obtained in the titrations even when the solutions were first treated with sodium bicarbonate. The method outlined above in the absence of sugar gave inconsistent results. This, as well as the importance of sugar for both uniformity and consistent results, is shown by Table I.

TABLE I

COMPARATIVE RESULTS IN SULFUROUS ACID ANALYSIS

Series	SO_2 dissolved in 250 cc., g.	Time after solution complete, min.	Sulfite soln. required per cc. of iodine soln., cc.	SO_2 per cc. of iodine soln., g.
A	0.9470	30	0.735	0.002760 by first titration
		50	.760	.00604 by last
		240	.900	
		2160	1.610	
B	1.022	30	.665	.002718
		50	.660	.002718
		240	.665	.002718
		2180	.665	.002718
C	1.095	30	.620	.002716
		50	.614	.002716
		2180	.620	.002716

The results A were obtained with a sulfite solution to which no sugar had been added. B and C illustrate the constancy of the sulfite solution in the presence of sugar and also the accuracy with which titrations can be repeated. It may be of interest to record the results obtained from an experiment in which this effect of sugar on oxidation was tested. Sulfur dioxide was passed into an acid solution of barium chloride, made up from water through which air had been passed. The solution was divided into two parts, one of which contained a trace of sugar. It was found that the oxidation of the sulfur dioxide, as indicated by the formation of the white precipitate of barium sulfate, proceeded very much more slowly in the beaker which contained the sugar.

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[4] Ostwald, "Grundlinien der Anorganische Chemie," 4th ed., Verlag T. Steinkopff, Dresden und Leipzig, 1919, p. 323.

Vapor Densities of Sulfur Dioxide

Reliable values for the vapor densities of sulfur dioxide were known only at 0°.[5] The work described in the following sections required an accurate knowledge of the vapor densities at other temperatures and therefore measurements were carried out over the range −6 to 32°.

The method employed was similar to that described by Maass and Russell.[6] The values for M, the apparent molecular weight, as obtained by this method are given in Table II.

Table II

Variation of M with Temperature

T, °C.	p, cm.	M
34.05	75.33	65.20
22.9	75.93	65.27
10.35	75.50	65.42
1.4	75.54	65.60
0.8	75.59	65.61
− 6.55	75.53	65.76

From the graph the value for M at 0° is found to be 65.62 which gives the weight of one liter under standard conditions as $65.62/(0.08209 \times 273.1) = 2.927$ g. This agrees exactly with the figure obtained by previous investigators. As was mentioned above the zero degree value was the only one which had hitherto been determined accurately.

It may be of interest to show that the apparent molecular weight is the most convenient way of tabulating p, V, T data for a gas from the point of view of calculating the weight of any quantity of gas taken out of a given volume. Use is made of the fact that up to pressures of several atmospheres, the apparent molecular weight at a definite temperature varies in a linear way with the pressure[7] so that in the case of sulfur dioxide, whose theoretical molecular weight is 64.06, the apparent molecular weight at any pressure, p, is $[64.06 + (M-64.06)p]/76$. Hence the weight of gas contained in a volume, V, at pressure, p, and temperature T,°A., is

$$\{[64.06 + (M-64.06)\,p]/76\}\ Vp/RT\ 76$$

It follows (without going through the algebraic steps) that the amount of sulfur dioxide taken out between pressures p_1 and p_2 is given by

$$\frac{p_1 - p_2}{76}\left\{64.06 + \frac{M - 64.06}{76}(p_1 + p_2)\right\}\frac{V}{RT}$$

which is a more exact and general equation than that deduced by Maass

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[5] (a) Baumé, *J. chim. phys.*, **6**, 1 (1908); (b) Jaquerod and Pintze, *Minn. Geneve*, **35**, 589 (1908); (c) Guye, *Chem.-Ztg.*, **36**, 402 (1912); (d) Scherrer, *Sitz. Akad. Wien*, **123**, IIA, 931 (1914).

[6] Maass and Russell, This Journal, **40**, 1847 (1918).

[7] Maass and Mennie, *Proc. Roy. Soc.* (*London*), **110A**, 198 (1926).

and Boomer.[8] The above formula was used in all subsequent work, the values of M being read off from a graph.

Vapor Pressures of Pure Sulfur Dioxide and of its Aqueous Solutions

In the following section, measurements of the vapor pressures of pure sulfur dioxide and its aqueous solutions are described. The tables containing the results are grouped together at the end of the description of the experimental details. The results of other investigators follow so that comparisons may be made.

The apparatus which was devised for the measurement of vapor pressures is shown in Fig. 2. Tap A led to the sulfur dioxide purification apparatus and tap E to a vacuum pump. B was a flask separated from a small bulb L by a Morrison pressure tap C.[9] Another pressure tap D led to the bulb F containing the solution, stirred by a glass stirrer H in which an iron nail was sealed. This stirrer was operated by a solenoid I in series with an automatic current breaker.[10]

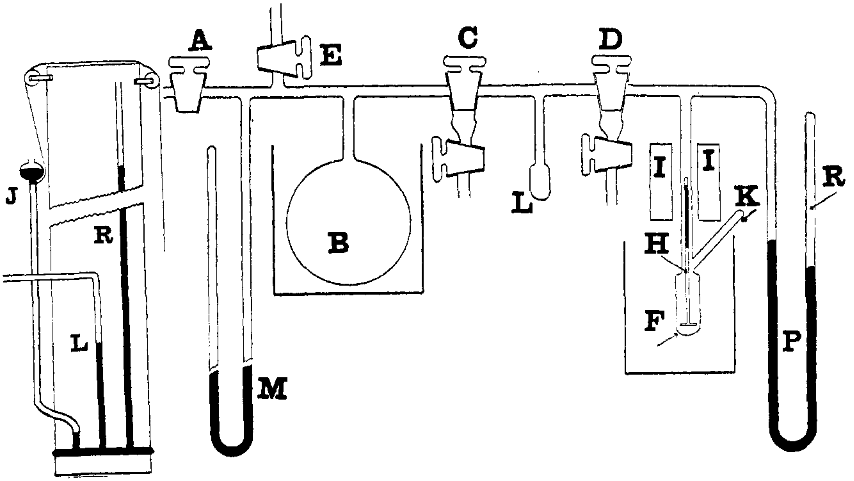

Fig. 2.

The usual form of manometer (M) served to measure the pressures in the apparatus from A to D and a pressure manometer P on which pressures up to twenty atmospheres could be read was employed to measure the vapor pressures of the solutions. The closed arm R of manometer P instead of being evacuated was filled with air at atmospheric pressure when the mercury was level in both arms of the manometer. Before the manometer was put together the volumes of R were carefully measured for various positions of the mercury in this arm and these results plotted on a graph. A glass mirror scale made it possible to read the mercury levels to 0.1 mm. and a thermometer placed beside R gave the temperature T, °C., of the enclosed air.

However, at the higher pressures, when solutions of water in sulfur dioxide were examined, this did not register pressure changes accurately enough. Hence another

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[8] Maass and Boomer, THIS JOURNAL, **44**, 1727 (1922).

[9] Maass and Morrison, *ibid.*, **45**, 1677 (1923).

[10] Maass, *Trans. Roy. Soc.* (*Canada*), **11**, 137 (1917).

type of manometer was constructed which was then also used in the redetermination of values found by means of the enclosed air manometer.

The manometer consisted of two arms, R and L, one of which was 4 meters long, fastened to a scale and attached to a wooden framework. A ladder placed a foot away, in front of the scale, made it possible to read the position of the mercury column at any height. The long arm of the manometer was open at the top so that atmospheric pressure had to be added to the pressure as read by the difference in level between the mercury columns in the two arms. Thermometers were placed at intervals along the mercury column so that the temperature of the latter could be reduced to 0°. J was a leveling bulb connected to the bottom of the manometer (shown in Fig. 2) by a thick, stout rubber tube. This leveling bulb was held by a rope which passed over a pulley at the top of the wooden framework. As the sulfur dioxide warmed up and the pressure in F rose, the leveling bulb was raised by means of the rope to keep the mercury in the short arm at a constant level.

When the sulfur dioxide in bulb F was at the temperature of carbon dioxide–ether, its pressure was only a few centimeters of mercury. This, combined with the fact that the long arm was open to the atmosphere, made it necessary for the short arm to be at least 80 cm. long to prevent the mercury from being forced into F by atmospheric pressure. Each time the bulb F was cooled down by carbon dioxide and ether, care had to be taken to lower the mercury.

The procedure followed in the vapor pressure measurements was then as follows. Through side arm K a known weight of water was placed in bulb F by means of a specially constructed weight pipet. K was then sealed off and the water frozen by surrounding bulb F with liquid air. All taps except A were then opened so that the apparatus could be completely evacuated through tap E.

Tap D was then closed and the water in F was allowed to melt. Any air occluded in the ice bubbled into the evacuated space above the water. The water was frozen again and the space once more evacuated. The freezing of the water expelled all the air and at the low pressure none of this redissolved, as could be shown by repeating the process, when no occluded bubbles could be observed in the ice. This process, then, ensured that the water was quite free from dissolved air.

Taps E and D were then closed and the rest of the apparatus filled (through A) with sulfur dioxide to a pressure p, as registered by manometer M. The volume from A to D, including tubing, flask B, bulb L, etc., was accurately known, having been previously determined. By means of a carbon dioxide–ether mixture a small amount of sulfur dioxide was condensed in bulb L and tap C closed. After the sulfur dioxide had been allowed to warm up to room temperature, the stirrer was started and tap D was opened so that the sulfur dioxide from bulb L distilled into the water. Tap D was then closed, tap C opened and the pressure p_2 read on the manometer. The amount of sulfur dioxide which had passed through D could therefore be calculated with great accuracy by means of the equation developed in the preceding section and by making use of the data given here.

The sulfur dioxide which had passed through tap D may be divided into two portions, that which enters into the water and the quite appreciable amount which fills the tubing above leading to manometer P. The pressure registered was practically all due to the partial vapor pressure of the sulfur dioxide, as the vapor pressure of water over the temperature range where experiments were carried out is relatively very small. The volume of bulb F and the tubing leading to the left arm of the manometer P was accurately known and hence the amount of sulfur dioxide above the liquid in bulb F could be calculated. Hence the concentration of the solution formed in bulb F could be evaluated with great precision.

A few words are now in place with regard to the function of the magnetic stirrer. Naturally it takes time for equilibrium to be established between a liquid and a gaseous phase. Indeed, it was found that without "a stirring" which both broke the surface of the liquid and circulated the gas above its surface true equilibrium was not established for several hours. As it was, even with the splendid stirring of the magnetic stirrer, which moved through the whole body of the liquid and right out of the surface in each stroke, it required five minutes for complete equilibrium to be established. Once this was established the vapor pressure registered had a definite value which remained unaltered. After reading the pressure for a given temperature and then altering the pressure by changing the temperature, it was found that on returning to the original temperature the original pressure was again registered exactly. The temperatures of the solutions were governed by a well stirred bath surrounding bulb F, the temperature being read by a Reichsanstalt thermometer. In some of the solutions a trace of sugar was added for reasons which are apparent from the section on analysis of sulfurous acid. It was found that a trace of sugar did not alter the pressures.

Again a sample calculation will be given in order that from the quantities involved the accuracy of the results may be judged. All pressures are given in cm. of mercury corrected to 0°. The weight of water placed in bulb L as given by weight pipet and corrected to vacuum was 5.472 g.; initial pressure, p_1, 75.41; final pressure, p_2, 56.65; volume of flask B, bulb L and tubing up to manometer, 0.3891 liter; temperature of gas, 25.8°; apparent molecular weight of sulfur dioxide at 25.8°, 65.23; weight of sulfur dioxide

$$\frac{(75.41 - 56.65)}{76}\left\{64.06 + \frac{(65.23 - 64.06)}{76}(75.41 + 56.65)\right\}\frac{0.3891}{0.08209 \times 298.9} = 0.2587 \text{ g.}$$

Upward movement of manometer M during pressure change caused displacement of sulfur dioxide calculated from volume of tubing to be 0.0173 g.; weight of sulfur dioxide passing tap D, 0.276 g.; pressure registered by manometer P calculated to be 24.3 cm., giving 0.014 g. as the amount of sulfur dioxide above the solution when the volume of the tubing and the temperature were taken into account. Hence the percentage of sulfur dioxide in the solution is given by 0.262/(5.472 + 0.262) = 4.57%. The pressure of 24.3 cm. was registered when the solution was kept at 10°.

In this way the values of the vapor pressures of solutions at various concentrations and pressures were measured. When the solution of sulfur dioxide in water reached a certain concentration, a second liquid phase separated out, the solution of water in sulfur dioxide. The pressure registered by this two-phase system is, of course, independent of the relative amounts of water and sulfur dioxide present. Its pressures were measured over a temperature range, 10–27°. The vapor pressures of pure sulfur dioxide were also determined over the same temperature range. For this, bulb F was first carefully dried *in vacuo* and then filled with pure sulfur dioxide.

TABLE III

TOTAL VAPOR PRESSURES OF SULFUR DIOXIDE SOLUTIONS AT DIFFERENT TEMPERATURES AND CONCENTRATIONS

T, °C.	Concn., %	Press., cm. of Hg at 0°	*T*, °C.	Concn., %	Press., cm. of Hg at 0°
10.0	4.57	24.3	22.0	4.40	37.8
	8.19	45.2		7.88	69.3
	11.64	67.4		11.17	102.2
	14.75	87.4		14.04	132.6
	18.91	124.5		18.22	178.3
	19.86	128.8	22.0	19.14	186.1
	23.10	154.3		22.32	222.2
16.5	4.48	31.0	25.0	6.9	66.2
	8.03	57.2		22.4	246.9
	11.42	84.4	27.0	4.32	44.8
	14.31	111.4		7.71	81.0
	18.57	151.9		10.95	118.3
	19.52	156.0		13.74	152.8
	22.71	188.4		17.85	206.9
				21.86	255.6

TABLE IV

VAPOR PRESSURES OF TWO PHASE SYSTEM SULFUR DIOXIDE–WATER

T, °C.	Press., cm. of Hg at 0°	*T*, °C.	Press., cm. of Hg at 0°	*T*, °C.	Press., cm. of Hg at 0°
10.0	166.6	22.7	258.9	16.0	204.4
11.3	175.2	25.0	277.4	18.0	219.6
16.5	209.8	27.0	297.3	19.9	234.8
22.0	254.1	11.0	172.2		

TABLE V

VAPOR PRESSURES OF PURE SULFUR DIOXIDE

T, °C.	Press., cm. of Hg at 0°	*T*, °C.	Press., cm. of Hg at 0°	*T*, °C.	Press., cm. of Hg at 0°
1.3	123.5	22.0	264.1	15.0	207.0
2.25	127.6	27.0	314.2	18.0	230.5
10.0	173.3	0.2	117.27	22.6	269.8
16.5	218.8	9.1	168.17		

In Fig. 3 the values of the vapor pressures contained in Table III are plotted against concentration. The determinations carried out at the same temperature are connected by lines, which show that the pressures increase more gradually with concentration, to become finally nearly linear, at the higher concentrations. The values in Table IV are plotted as horizontal lines, being independent of the concentration. Fig. 4 shows the relation of vapor pressure to temperature of pure sulfur dioxide (Curve I) and the two liquid phase system (Curve II). The curves in this figure were drawn from the points marked with circles, which were determined by the open-end manometer. The values found by the enclosed air manometer are marked in by crosses. It will be seen that in the case of the pure sulfur dioxide these crosses lie on the curve. In Curve II the crosses lie slightly above the curve.

Vapor pressures of aqueous solutions of sulfur dioxide have been determined by Schoenfeld,[11] Sims[12] and Hudson.[3g] By recalculation and extrapolation, the results of the two latter investigators at low concentrations are found to be in good agreement with those of the authors, although the experimental methods employed were quite different. In the present work a larger range of concentration and pressure was covered and the temperature range, 10–27°, was more fully investigated.

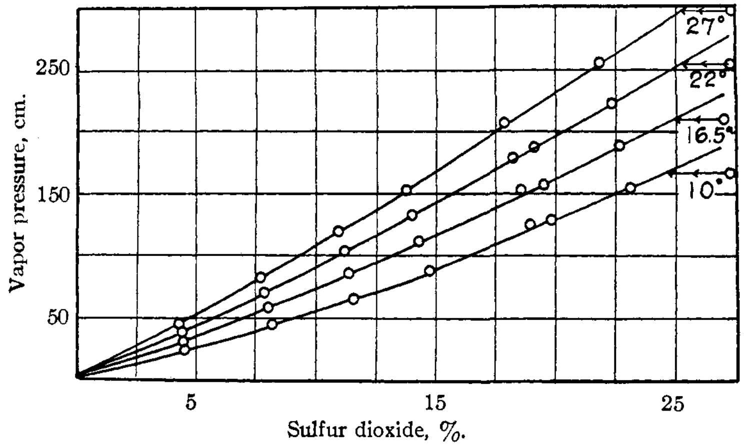

Fig. 3.—Variation of vapor pressure with concentration of sulfurous acid solutions at four different temperatures.

With regard to the vapor pressure of pure sulfur dioxide, the authors' value at 0° is in agreement with that obtained by Cardoso[13] and Regnault.[14] At higher temperatures Cardoso's values differ in an irregular way from those obtained in the work described.

Roozeboom[15] measured a few pressures of the hydrate $SO_2 \cdot 7H_2O$, when in equilibrium with the liquid phase. He found that the vapor pressure of this hydrate at the quadruple point, 12.1°, was 177.3 cm. This should correspond to the vapor pressure of the two liquid phase system at 12.1°. The curve in Fig. 6 gives a slightly higher value, 179.0 cm.

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[11] (a) Schoenfeld, *Ann.*, **95**, 1 (1855); (b) Landolt-Börnstein, Tables, 5th ed., **1923**, p. 762.

[12] Sims, *Trans. Chem. Soc.*, **14**, 1 (1862).

[13] Ref. 1, p. 835.

[14] Regnault, "Relation des Experiences," II, p. 581.

[15] Roozeboom, *Z. physik. Chem.*, 1, 206 (1887).

Concentrations in the Two Liquid Phase System Sulfur Dioxide–Water

The vapor pressures contained in Tables III and V can be used in connection with the determination of the solubility of sulfur dioxide in the water phase of the two liquid phase system. This is made plain by a consideration of the curves in Fig. 3. As sulfur dioxide is added to the water, the solution becomes increasingly stronger and the pressure correspondingly higher. When the water phase reaches its saturation concentration, a second liquid phase separates out—a solution of water in sulfur dioxide. Further addition of sulfur dioxide results in a readjustment of the relative amounts of the two phases to a new equilibrium but the percentage composition of both phases remains unaltered. That is, the percentage composition of the water phase does not change after its saturation concentration has been reached, and its pressure therefore remains constant. The constant pressure corresponds to the horizontal line of the graph. The percentage corresponding to the point where this line cuts the extrapolated pressure concentration curve gives the solubility of sulfur dioxide at that temperature.

This is a sensitive and novel method of estimating the concentrations of the aqueous liquid phases. In Table VI these values (probably correct to 0.1%) are given.

TABLE VI

TEMPERATURE VARIATION OF CONCENTRATION IN THE AQUEOUS PHASE

T, °C.	10.0	16.5	22.0	27.0
SO_2 in aqueous phase, %	24.60	24.92	25.24	25.20

The concentrations of the aqueous phases are definitely known. However, the value at 12.1° is only 24.7% of SO_2, notably different from the concentration of the liquid phase at the quadruple point as measured by Roozeboom, namely, 31%.[15] It was therefore deemed advisable to check one of the concentrations by direct analysis.

On account of the high vapor pressure of the system after true equilibrium has been established, it is a matter of great difficulty to remove one of the liquid phases without upsetting this equilibrium. This is a general experimental problem met with in the examination of systems of this type, for instance in the system H_2O–Cl_2. The solving of this problem as described below is therefore of some importance.

In Fig. 5 tap A leads to the sulfur dioxide purification apparatus and tap E to a vacuum pump. A tube B is connected to the system by a glass tube with a constriction. A side tube C on B leads through a capillary D to a smaller tube F of about 2 cc. capacity, the top of which ends in a closed capillary, H. Ten cc. of water had been placed in B before it was sealed on. This water was frozen and the apparatus evacuated through E. Approximately 10 g. of sulfur dioxide was then condensed on top of the ice in B and B sealed off at the constriction. It was then placed in a water-bath and allowed to warm up to the desired temperature. The liquid layers which formed in the bottom of B were well shaken up, care being taken that no liquid entered C. The tube was allowed to stand at constant temperature until the two layers were quite separate and then the tube was carefully tilted until some of the liquid in the upper layer ran into C, filling it with some 4 cc. of liquid which was held in place by the sulfur dioxide vapor in F. The tube B was then tilted back into a position as indicated in the second part of the diagram (Fig. 5). On gradually immersing F in a cooling bath the contraction of the sulfur dioxide vapor in E caused some of the liquid in C to flow through the capillary. Before all the liquid from C had entered F, F was plunged quickly into a carbon dioxide–ether mixture so that the liquid flowing through the capillary was frozen. This was the essential feature of the whole method because the liquid in F was trapped and represented the true equilibrium condition corresponding to the temperature of the water-bath. The bottom of tube B was then immersed in a second carbon dioxide–ether bath, the tube F still being kept in the first one. All the liquid remaining in tube C above the frozen part in the capillary distilled back into C. The capillary was then sealed off at K. Tube F was allowed to warm up, weighed, cooled again in a carbon dioxide–ether mixture and the capillary tubes were broken off. The ends of the capillaries were then placed beneath the surface of a sodium hydroxide sugar solution and the contents of F allowed to warm up and dissolve. The glass was washed, dried and weighed.

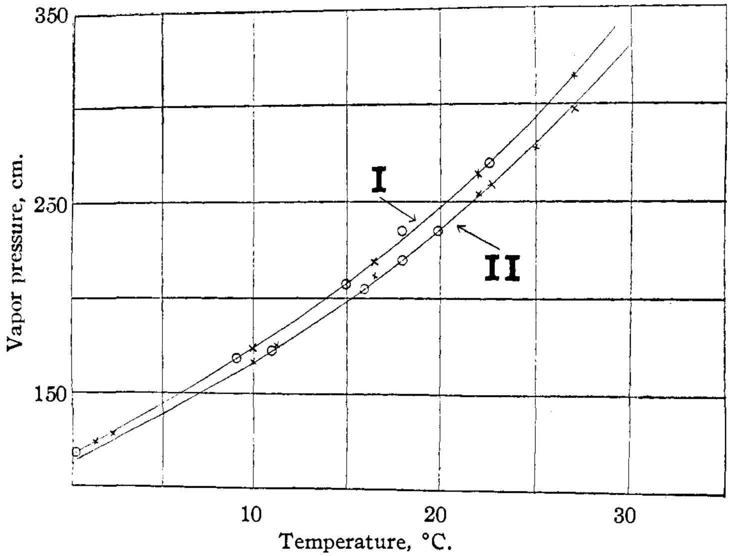

Fig. 4.—Variation of vapor pressure with temperature. I. Sulfur dioxide. II. The two phase system sulfur dioxide–water.

The analysis of the solution was carried out as described in a former section. A sample calculation is given below.

Temperature of water-bath, 20°

Weight of solution trapped in F, 1.525 g.

Solution in NaOH made up to 250 cc.

One cc. of iodine, equivalent to 0.002717 g. of SO_2, was found to oxidize 1.720 cc. of the solution in NaOH

Total SO_2 was, therefore, 0.2951 g.

SO_2 vapor trapped in F, 0.0121 g.

SO_2 in aqueous phase, 25.10%

Three other determinations carried out at the same temperature gave practically identical values, thus confirming the results given in Table IV to within 0.1% SO_2.

An approximate estimate of the water in the sulfur dioxide phase of the two phase system can be derived by means of the vapor pressure curves shown in Fig. 4. In the two liquid phase system, the vapor pressure can be regarded as due either to the water or to the sulfur dioxide phase, since these phases are in equilibrium. If the pressure is regarded as exerted by the sulfur dioxide phase, it follows from the proximity of the two curves that the vapor pressure of pure sulfur dioxide is only slightly lowered by the dissolved water and that this can only be present in small amount in this phase. Since the solution is only a dilute one, calculations can be made by means of Raoult's law to deduce the amount of water dissolved.

This can be written

$$\frac{m}{M_{H_2O}} \times \frac{M_{SO_2}}{W} = \ln \frac{p}{p^1}$$

where m and W are the weights of the water and sulfur dioxide, respectively. Hence

$$\%\ H_2O = \frac{m}{W+m} = \frac{\frac{18}{64}\,2.3\ \lg \frac{p}{p^1}}{1 + \left(\frac{18}{64}\,2.3\ \lg \frac{p}{p^1}\right)}$$

This equation is based on the assumption that water is not associated when dissolved in liquid sulfur dioxide. The percentages calculated in this way must, therefore, represent the minimum possible water concentration.

TABLE VII

PERCENTAGE OF WATER IN SULFUR DIOXIDE PHASE OF TWO LIQUID PHASE SYSTEM, CALCULATED FROM VAPOR PRESSURE DATA OF FIG. 6

T, °C.	Vapor press. of pure SO_2, cm. of Hg at 0°	Vapor press. of two phase system, cm. of Hg at 0°	Water in soln., %
5.0	143.4	138.2	1.02
10.0	173.9	165.7	1.33
18.0	230.5	219.6	1.34
22.0	264.3	251.8	1.34
25.0	292.2	277.5	1.42
27.0	314.2	297.2	1.52

Since the above values had been obtained only by calculation, some direct experimental method of determining them was sought. The method employed was again based on the measurement of the vapor pressures, this time of solutions of water in sulfur dioxide. Due to the slight solubility of water in liquid sulfur dioxide, the difficulty in this procedure lay in making up solutions of known concentrations. The following device was finally used. A piece of ordinary glass tubing was drawn out into a capillary, at the end of which a small, thin walled bulb of about 3 mm.

diameter was blown. The bulb and tubing were then accurately weighed. Water was introduced into the bulb through the capillary by alternately heating and cooling the former, thus driving the air out of it. In this way enough water to fill the bulb (about 50 mg.) entered, and the capillary was then sealed off as close above the surface of water as possible. The piece of tubing was carefully dried and again weighed with the filled bulb. Thus the weight of water was definitely known. The little bulb was placed in tube F (see Fig. 2) through side arm K. The magnetic stirrer was kept down while the small bulb slipped past it down to the bottom of F. Side arm K was sealed off, tube F evacuated and surrounded with carbon dioxide–ether mixture. When the water was frozen, the bulb was broken by means of the magnetic stirrer, which acted as a hammer. The freezing of the water was important, as was found by experience. If the water bulb is broken in the evacuated space, the water will spatter all over the tube and evaporate into the space. After the bulb was broken, measured quantities of sulfur dioxide were added to the tube and the resulting pressures measured at 18°.

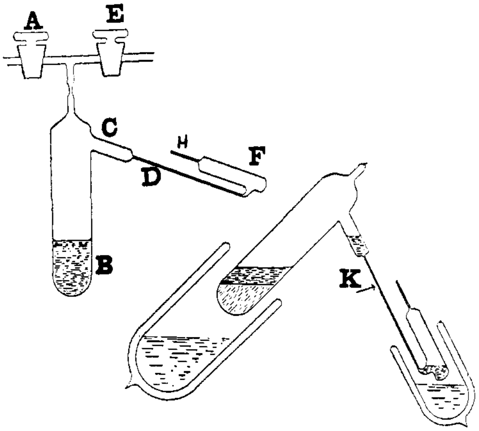

Fig. 5.

From the values contained in Table VII it was known that the saturation concentration of the water in sulfur dioxide would be small, in the neighborhood of 1 or 2%. The percentage of the solution calculated after the first addition of sulfur dioxide was about 5% of H_2O. This, of course, did not exist, and the amount of water left over, above the amount required to form a saturated solution of water in the sulfur dioxide, separated out to form a small amount of second phase, a solution of sulfur dioxide in water. The pressure registered at this point, then, was that due to the two liquid phase system at that temperature and agreed with the value found for this in Fig. 4.

As further quantities of sulfur dioxide are added, the pressure remains constant until a point is finally reached at which the amount of sulfur dioxide present is just sufficient to give the saturated solution of water. The second phase disappears and the pressure registered is due only to this saturated solution. Further addition of more sulfur dioxide raises the pressure until it nearly reaches the pressure of pure sulfur dioxide. This value is never quite reached, however, as no matter how much sulfur dioxide is present the original amount of water remains. The values obtained are given in Table VIII.

Table VIII

Vapor Pressures for Two Phase System, Water–Sulfur Dioxide

Temp., °C.	H_2O in SO_2, %	Press., cm. of Hg at 0°
18	4.23	219.6
	2.16	219.7
	1.096	221.7
	0.735	224.9
	.494	226.8

These results are shown graphically in Fig. 6. At 18° the vapor pressure of pure sulfur dioxide was found to be 230.5 cm. and that of the two liquid phase system was found to be 219.6 (see Fig. 4). It will be seen from the figure that the last three values are almost in a straight line which, when produced in one direction, meets the zero percentage of water, that is, pure sulfur dioxide, at 230.5 cm. and cuts the 219.6 cm. isobar at 1.33% of water; 1.33% must, therefore, be the percentage of water dissolved in the liquid sulfur dioxide, that is, the saturated solution.

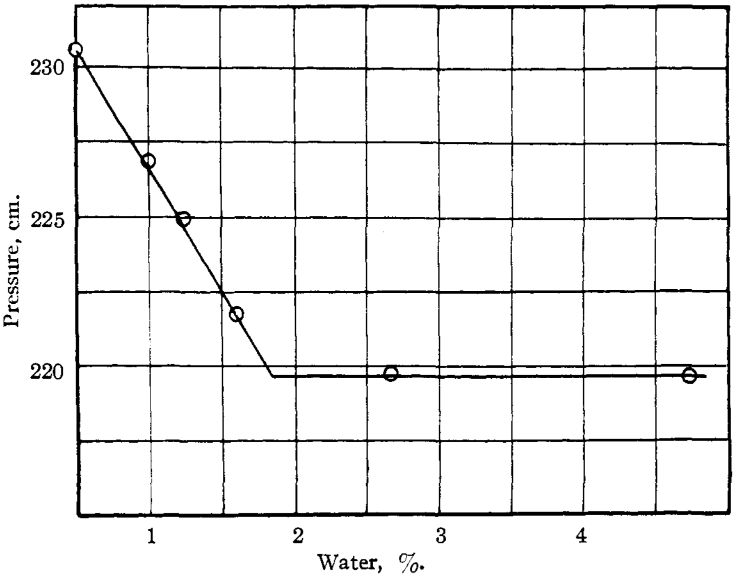

Fig. 6.

The value calculated from Raoult's equation is based on the assumption of unassociated molecules; this is justified by the experimental results. The agreement of 1.34% calculated from the equation, with 1.33% found experimentally, is better than the accuracy of the measurements.

Further measurements of the pressures of a 0.49% H_2O solution were made over a temperature range. Table IX contains the results obtained.

TABLE IX

TEMPERATURE VARIATION OF VAPOR PRESSURE OF A 0.49% H_2O SOLUTION

Temp., °C.	3.0	7.0	11.0	18.0	20.0
Vapor pressure, cm. of Hg at 0°	130.2	151.5	175.9	226.9	243.7

In the measurements just given, the concentration was so low that the pressure differences of solvent and solution were small and the error correspondingly large. Using the pressures in Table IX in Raoult's equation to determine the percentage, a mean value of 0.51% was given, which agrees remarkably well with the value 0.49%.

It is seen that the saturation solubilities of sulfur dioxide in water, and water in sulfur dioxide, do not vary appreciably with the temperature, namely, about 1% per 30° in the case of the former and 1% in 40° in the case of the latter. It will be interesting to determine the rest of the solubility curves for the higher temperatures. It is probable that complete mutual solubility will not occur before a temperature is reached not far removed from the critical temperature of sulfur dioxide, 155°.

Water is a substance which has a great tendency to associate. It does not do so in substances of similar nature. In these cases, however, there is far greater solubility than is shown by water in sulfur dioxide. Hence it is more probable that the water in the solution is combined with the sulfur dioxide to form sulfurous acid. The results obtained by Raoult's Law would be the same, within experimental accuracy, whether the water is present as unassociated water or as sulfurous acid. These are the only two possible conditions of the water and, from what has been said above, the existence of the water as sulfurous acid is the more probable.

Acknowledgment is made to the Research Council of Canada for a Bursary and Studentship awarded to one of us during the period in which this work was carried out.

Summary

A procedure for accurately analyzing solutions of sulfurous acid is described.

The apparent molecular weights of sulfur dioxide were measured over the temperature range −5 to 35°. An equation is developed in terms of apparent molecular weight which gives the most convenient and accurate evaluation of the weight of any gas taken out of a known volume when the initial and final pressures are measured.

A convenient method for measuring vapor pressures of solutions containing one volatile component is described. The vapor pressures of aqueous solutions of sulfur dioxide were measured over the temperature range 10–27°. All possible concentrations were covered. The vapor pressures of pure sulfur dioxide were measured over the range 1–27°. The vapor pressures of the two liquid phase system were measured over the range

10–27°. A comparison of values found by other investigators is included. It is shown that the concentration of the volatile component in the water, phase can be determined by means of the vapor pressure measurements and the concentration of water in the sulfur dioxide phase, approximately calculated by using Raoult's Law.

A method was designed for separating a portion of one liquid phase from any three phase system (liquid–liquid–gas) which is in equilibrium at pressures which are so great that there is difficulty in obtaining accurate analysis of the equilibrium concentration. This method was employed for measuring the concentration of sulfur dioxide in the aqueous phase and the values deduced from the vapor pressure measurements for the range 10–27° were confirmed at the temperature where measurements were made,

A method was devised by means of which the concentration of water in the sulfur dioxide phase can be more exactly determined. This method consisted in the measurement of vapor pressures of solutions of water in sulfur dioxide, and gave values agreeing very closely with those calculated.

MONTREAL, CANADA

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

CERIC SULFATE AS A VOLUMETRIC OXIDIZING AGENT, III. THE TITRATION OF IODIDE

BY H. H. WILLARD AND PHILENA YOUNG[1]

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Introduction

Previous work with ceric sulfate as a volumetric oxidizing agent[2] suggested the importance of investigating potentiometrically the iodide-ceric salt reaction. Lange[3] stated that since ceric sulfate, even in the most dilute solutions, set free iodine from potassium iodide, it might be used as an oxidizing agent in volumetric analysis. Numerous investigators have made use of this reaction[4] as an iodimetric method for ceric cerium, their procedure being to treat the ceric salt with excess iodide in acid solution and to titrate the iodine liberated with thiosulfate. The direct titration of iodide with ceric sulfate, however, or the reverse reaction appears not

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[1] From a dissertation submitted by Philena Young to The Graduate School of the University of Michigan in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry.

[2] Willard and Young, THIS JOURNAL, **50**, 1322, 1334 (1928).

[3] Lange, *J. prakt. Chem.*, **82**, 129 (1861).

[4] Bunsen, *Ann. Chem.*, **86**, 285 (1853); Hartley, *J. Chem. Soc.*, **41**, 202 (1882); Browning, Hanford and Hall, *Z. anorg. Chem.*, **22**, 297 (1899); Browning, *Am. J. Sci.*, **158**, 451 (1899); Power and Shedden, *J. Soc. Chem. Ind.*, **19**, 636 (1900); Meyer and Koss, *Ber.*, **35**, 3740 (1902); Brauner, *Z. anorg. Chem.*, **34**, 207 (1903).