The Determination and the Solubility of Water in Liquid Sulfur Dioxide

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Liquid sulfur dioxide has been used in a large scale as a selective solvent for separation of aromatic hydrocarbons in petroleum or as bleaching, fumigating, antiseptic, or refrigerating agent. Recently it has been used as a non-aqueous solvent frequently in inorganic and organic synthetic reactions just like liquid ammonia. But it has a defect as a solvent owing to the presence of a small quantity of water. The corrosion of industrial equipments is largely due to minute amount of water contained in it. The amount was therefore defined to be below 50 p. p. m. by the Sulfur Dioxide Committee[1] in U. S. A. in 1933, the required accuracy for the analytical method being 1～2 p. p. m..

It is also anticipated that the reaction process and the rate are largely affected by a minunte amount of water in sulfur dioxide in case of organic ionic reactions. The determination of water in sulfur dioxide was studied for the first time in 1931.[2,3] The method was consisted of a dehydration of water in liquid sulfur dioxide with phosphorus pentoxide. A titration method using the Karl Fischer (abridged as K. F.) reagent was proposed by Karl Fischer in 1935[4] and lately reformed by Dicaprio[5] to make the analysis of water in liquid sulfur dioxide,easier. In the dehydration method[2,3] the liquid sulfur dioxide to be analyzed was evaporated, passed through a tube containing phosphorus pentoxide and the water absorbed in the tube was determined. In this method, it was pointed out by Zavarov[3] that an intolerable amount of water yet remained in the dioxide when more than 0.01% of water was contained in the original sample.

In the Dicaprios method[5], it is difficult to pick up the sample accurately, the manipulation is inconvenient as it required a low-and constant temperature room and the K. F. reagent changes in quality by the lapse of the storing time.

The writers have devised a simple and accurate measuring method of water in liquid sulfur dioxide, improving the method of the K. F. titration.

On application of the new method, the solubility curve of water in liquid

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[1] F. A. Eustass, *Ind. Eng. Chem., Anal. Ed.*, **5**, 77 (1933).

[2] A. Scribner, *Ind. Eng. Chem., Anal. Ed.*, **3**, 255 (1931).

[3] G. V. Zavarov, *Zavodskaya. Lab.*, **5**, 1314 (1936); J. Mitchell and D.M. Smith, "Aquametry", Interscience Publishers, Inc., New York. p. 236 (1948).

[4] K. Fischer, *Angew. Chem.*, **48**, 394 (1935).

[5] B. R. Dicaprio, *Anal. Chem.*, **19**, 1010 (1947).

sulfur dioxide at ordinarily adopted temperatures has been traced. Also a convenient method for drying liquid sulfur dioxide is discussed by estimating the residual water in the dried liquid sulfur dioxide by the present analytical procedure. Two points of improvement are involved in this method as shown in the following.

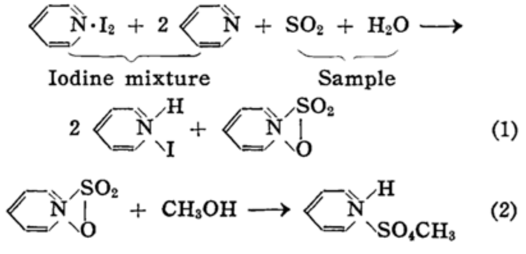
Firstly, as sulfur dioxide constitutes a component of the K. F. reagent, there is no need to use the so called K. F. reagent. It is satisfactory only to add a mixture of iodine and pyridine in methanol (abridged as iodine mixture) to the sample (liquid sulfur dioxide).

Secondly, to avoid the operative difficulties and the loss due to evaporation in sampling, weighing and titration it has been devised to take up the sample in a small glass pressure bottle to be weighed and put into a titration flask, chilled to about −40°C by dry ice.

A K. F. reagent is prepared instantly and caused to react with the water in the sample at the same moment when a definite amount of the iodine mixture is added to the titration flask. The excess of the iodine mixture is back-titrated by an aqueous methanol, of a known water-equivalent value. The iodine mixture can be kept for a long time without change. Accuracy is also raised by the direct weighing of the sample in the pressure bottle before and after the charge into the flask.

As this method is very convenient in its manipulation, it may be used as a rapid routine analysis in factories. The accuracy of this method was found to be satisfactory. The differences between added water (5 to 30 mg.) in the sample and the water found by this procedure were zero to ±0.06 mg.

In the titration flask, the following series of reaction is occurring and, even at −40°C, the K. F. reaction has been proved to proceed quantitatively⁶⁾.



The solubility of water in liquid sulfur dioxide was measured by Wickert⁷⁾ only at 22°C and no other study at different temperatures has been reported. We have measured the solubility of water in liquid sulfur dioxide at various temperatures utilizing the above-mentioned method. (cf. Table I.)

TABLE I
SOLUBILITY OF WATER IN LIQUID SULFUR DIOXIDE

Temp. °C	Solubility g. H_2O/100 g. liq. SO_2
30	2.68
22	2.29
15	1.88
5	1.50
0	1.20
−10	0.81
−20	0.55
−30	0.37
−50	0.22

One part of liquid sulfur dioxide in equilibrium with water in a pressure bottle at a definite temperature was introduced into a small pressure bottle and the water in it was determined by the above described method. Thus the solubility of water in liquid sulfur dioxide in the range between −50°C and +30°C was measured. The solubility at 22°C (2.29 g. H_2O/100 g. liq. SO_2) was well conformed with the Wickert's result (2.3 g. H_2O/100 g. liq. SO_2)⁷⁾.

From the solubility value obtained as above, a linear plot of the logarithm of the solubility as a function of the reciprocal

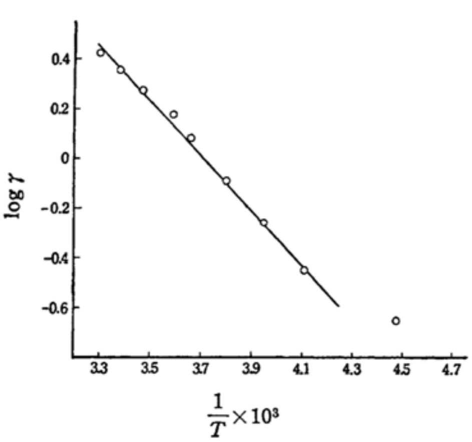


Fig. 1. Solubility of water in liquid sulfur dioxide as a function of temperature.
$\log\gamma = Q/RT + C$ (1), where, Q: heat of solution, γ: solubility, T: absolute temperature, R: gas constant and C: a constant.

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6) G. Toennies and M. Elliott, *J. Am. Chem. Soc.*, **59**, 902 (1937).

7) K. Wickert, *Z. anorg. allgem. Chem.*, **239**, 89 (1938).

of the absolute temperature is given in Fig. 1, using the following thermodynamic equation (1): the heat of solution of water in liquid sulfur dioxide is found to be 5.04 kcal./mole (endothermic) for the range between −50°C and +30°C (Table II.).

TABLE II
HEAT OF SOLUTION OF WATER IN LIQ. SO_2
$C=4.095$ in eq. (1)

Temp. °C	Heat of Soln. Q kcal./mole
30	5.08
22	5.05
15	5.03
5	4.99
0	5.01
−10	5.03
−20	5.04
−30	5.09

Mean $Q=5.04$ kcal./mole.

Method of the Measurement

(1) Reagents.—Pyridine was dehydrated with potassium hydroxide and distilled. Methanol was dried with metallic magnesium and distilled. Liquid sulfur dioxide was purified and dehydrated with concentrated sulfuric acid and distilled.

The iodine mixture was prepared by mixing the above three materials so that the molar ratio of iodine, pyridine and methanol was to be 1 : 10 : 40. It may be better to increase the quantity of methanol when the water content in the sample was very small. The methanol-water mixture to be used for the back titration was prepared by mixing 1 mole of water with 100 moles of methanol. The water-equivalent value of the iodine mixture and the content of water in aqueous methanol should be previously determined by a standard Karl Fischer's method[4].

(2) Titration apparatus and manipulation.—An ordinary K. F. titration apparatus with conductometrical titrating device was used except that the titrating flask was equipped with a inlet glass tube with a stop cock to connect a small cylindrical pressure bottle (10 cm. long and 2.5 cm. inner diameter) with a valve or cock on its top, containing the sample (Fig. 2).

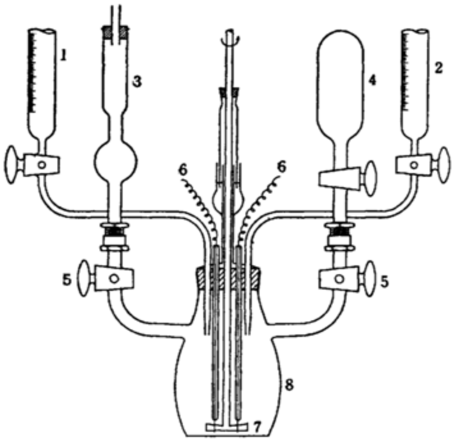

Fig. 2. Titration assembly.
1: Iodine mixture
2: Standard aqueous methanol
3: Drying tube
4: Glass pressure bottle
5: Stainless steel joint
6: Platinum electrode
7: Glass stirrer
8: Titrating flask

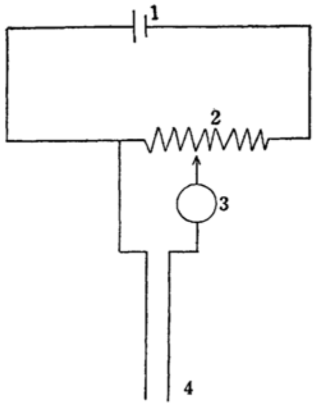

Fig. 3. Circuit diagram.
1: Battery
2: Rheostat
3: Galvanometer
4: Platinum wire electrode.

The flask and the pressure bottle were connected tightly by a couple of jointing screw pieces made of stainless steel. Liquid sulfur dioxide was condensed into this small pressure bottle with cooling and closed. After weighing, the pressure bottle was connected to the titrating flask. Space in the flask was previously replaced with perfectly dried air. The flask was cooled to −40°C with dry ice and ethanol, and the cock of the flask and the valve of the pressure bottle were carefully opened to let the sample flow into the flask. Then the valve and the cock were closed. The pressure bottle was disconnected from the flask and the weight of the empty bottle was again examined. When necessary, the sample was diluted with some more liquid sulfur dioxide of a known water content.

As the path between the cock of the flask and the valve or cock of the pressure bottle is very short and made of a thin capillary, the loss due to the wetting or the vaporization of sulfur dioxide is small. The sample was taken to make the water amount about 10 mg. After the sample had been taken up in the titration flask, known amount of iodine mixture was slowly introduced into the flask with stirring and cooling, and its excess was back-titrated with aqueous methanol. The end-point was indicated by applying the dead-stop method (initial E. M. F., 10 mV.) according to Foulk and Bawden[8,9], a rheostat, a galvanometer, a cell and two platinum electrodes being arranged as shown in Fig. 3.

(3) **Calculation.**—Water content x (g. H_2O/g. liq. SO_2 or 10^{-6} p. p. m. of liq. SO_2) is calculated by the following equation:

$$x = (\alpha A - \beta B)/G,$$

Here A, amount of iodine mixture used (cc.); α, water-equivalent of the iodine mixture (g. H_2O/cc.); B, amount of the aqueous methanol consumed for the back titration (cc.); β, water content of the aqueous methanol (g. H_2O/cc.); G, weight of the sample (g.).

Results and Discussion

(1) **Accuracy.**—To examine the accuracy of the present method, a slight amount of water (5 to 30 mg.) dissolved in methanol was titrated. The result was satisfactory as described above. The difference between the added and the found was less than ±0.06 mg.

(2) **Solubility of water in liquid sulfur dioxide.**—After equilibrium is reached by heeping a mixture of purified liquid sulfur dioxide and distilled water for four hours in a thermostat maintained at a given temperature, a part of the liquid sulfur dioxide (lower layer) was introduced into another small pressure vessel. The water was then determined by the present method. The equilibrium was obtained within three hours. The fluctuation in temperature was less than ±0.05°C at above zero degree and ±0.5°C below zero degree.

The results are shown in Table I, showing an increase in solublility as the temperature increases.

(3) **Heat of solution of water in liquid sulfur dioxide.**—A plot of $\log \gamma$ vs. T^{-1} (Fig. 1) was given as a straight line. The value of C in eq. 1 was determined as 4.095 from the plot. The heat of solution was calculated from equation 1 as 5.04 kcal./mole.

(4) **Comparison of the efficiency of various dehydrating agents for liquid sulfur dioxide.**—Liquid sulfur dioxide was dehydrated using a pressure bottle with various dehydrating agents. Namely, liquid sulfur dioxide (water content: 0.16g./100 g. SO_2) was tapped into pressure bottles filled with a definite amount of concentrated sulfuric acid, phosphorus pentoxide, active alumina, drierite and silica gel, respectively and was allowed to stand for 12 hours for dehydration.

Then the samples were taken up into measuring pressure-bottles and titrated by the present method, the results being as the following: (Table III).

TABLE III

MEASUREMENT OF WATER IN LIQUID SULFUR DIOXIDE DEHYDRATED WITH VARIOUS DRYING AGENTS

Desiccant	Added g.	Liq. SO_2 g.	H_2O p. p. m.
Sulfuric acid	30	180	110
Phosphorus pentoxide	30	180	48
Active alumina	30	180	80
Drierite	30	180	82
Silica gel	30	180	98

It was observed that phosphorus pentoxide had the most powerful dehydrating ability for liquid sulfur dioxide. In the former experiment[10], about one-meter tube filled with phosphorus pentoxide was used for the dehydration of liquid sulfur dioxide which can be replaced by phosphorus pentoxide in a pressure bottle for easier handling with satisfactory result.

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[8] C. W. Foulk and A. T. Bawden, *J. Am. Chem. Soc.*, **48**, 2045 (1926).

[9] G. Wernimont and F. J. Hopkinson, *Ind. Eng. Chem., Anal. Ed.*, **15**, 272 (1943).

[10] K. Ziegler and H. Wollschitt, *Ann.*, **477**, 90 (1930).