

solubility in all the four cases studied here. Potassium iodide appears to offer no exception in this particular.

On the assumption that at one atmosphere external pressure, water in solution behaves as water under a pressure of P_e kilobars, it is possible to compute a quantity ψ_2 which may be regarded as the volume which one gram of solute occupies in solution. It has been shown¹ that for sulfates and sodium chloride ψ_2 is practically independent of the concentration, and of magnitude about 10% greater than that of the solid salt. For potassium iodide ψ_2 is also independent of the concentration, the values being given in the last column of Table II. They are, however, smaller than the volume of the solid—an observation which may throw some light on the continued increase of solubility with pressure. It is probable that on melting to form a solution, potassium iodide contracts slightly.

I am very much indebted to Mr. L. H. Adams of this Laboratory for the use of his new simplified high-pressure apparatus and for his help which made possible the direct determination of the solubility of potassium iodide at high pressures.

Summary

If it be assumed (a) that water in an aqueous solution behaves like water under a definite

hydrostatic pressure (Tammann's hypothesis) and (b) that the specific compression of a salt in solution is the same as the specific compression of the solid salt, an equation expressing the properties of water as the function of the pressure may be adapted to give an extrapolation equation whereby the effect of pressures up to 10 kb. on the solubility of four salts in water may be computed with useful accuracy from measurements made at 1 kb. As the salts investigated differ quite widely, there is no reason to believe that the method is not generally applicable. In other words, if the compressions of a salt and a series of solutions at 1 kb. are known, it is possible to calculate the change with pressure up to 10 kb. of the difference between the chemical potential of the salt in any solution and that of the pure solid salt, *i. e.*, $(\mu_2 - \mu_s)_P - (\mu_2 - \mu_s)_0$, which is equal to $\int_0^P (v_2 - v_s) dP$, and, when this change of chemical potential with pressure is known, the influence of pressure on solubility and other equilibrium relations follows immediately.

New experimental data for the densities and compressions of solutions of potassium iodide are given and the extrapolated solubility curve is checked by approximate direct determinations of the solubility of this salt in water at pressures between five and ten thousand atmospheres.

WASHINGTON, D. C.

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Equilibrium in Systems Composed of Sulfur Dioxide and Certain Organic Compounds

BY H. W. FOOTE AND JOSEPH FLEISCHER

The formation of solid addition compounds with sulfur dioxide has been reported in the literature for a number of organic compounds. The composition of such complexes formed with a series of amino compounds was investigated by Korezynski and Glebocka; similar studies were carried out with phenol by Holtzer and with pyridine by André; Baumé and Briner and Cardoso have investigated the system of sulfur dioxide and dimethyl ether; and Baumé and Pamfil the corresponding system with methyl alcohol. More recently, Hill has investigated the system formed by sulfur dioxide and aniline.¹

(1) Korezynski and Glebocka, *Gazz. chim. ital.*, **50**, I, 378 (1920); Holtzer, *J. prakt. Chem.*, [2] **25**, 463 (1882); André, *Compt. rend.*, **130**, 1714 (1900); Baumé, *ibid.*, **145**, 1322 (1909); Briner and Cardoso, *J. chim. phys.*, **6**, 641 (1907); Baumé and Pamfil, *Compt. rend.*, **152**, 1095 (1911); A. E. Hill, *This Journal*, **53**, 2598 (1931).

Since vapor pressure measurements provide an excellent means of determining the composition of such molecular complexes and at the same time furnish knowledge of the existing equilibrium relations, this type of data was obtained in the present investigation of the systems formed by a number of organic substances with sulfur dioxide. The systems studied were chosen on the basis of existing data as likely to display the formation of solid addition compounds.

The apparatus and methods employed have been described previously.² The compounds used were either of Eastman C. P. grade or were purified by customary methods. The composition of all solid addition compounds was determined after

(2) Foote and Fleischer, *ibid.*, **53**, 1752 (1931).

allowing the excess of sulfur dioxide to evaporate isothermally from the saturated solution at a pressure of one atmosphere. The temperature at which the evaporation was carried out was chosen so that the vapor pressure of the saturated solution was greater than one atmosphere, and the dissociation pressure of the addition compound was less. Under these conditions, the pure addition compound, free from solvent, remained after evaporation ceased, and was weighed. This weight, together with that of the organic component, gave the composition directly. In all determinations of composition, a small correction was applied for the weight of sulfur dioxide in the vapor phase. Vapor pressures are all expressed in centimeters of mercury at 0°.

Aniline.—Recently, and indeed while our own work was in progress, this system was investigated by Hill,¹ who found the solid compound $C_6H_5NH_2 \cdot SO_2$ and determined the vapor pressures of the saturated solutions containing an excess of SO_2 . So far as the two investigations coincide, our results confirm those of Hill. He determined the composition of the addition product by means of experiments in which equilibrium was established by adding sulfur dioxide to aniline, while our procedure consisted in removing an excess of sulfur dioxide from the system, leaving the pure compound.

When sulfur dioxide vapor is passed into aniline at room temperature, the liquid immediately attains a dark orange-red color and a bright yellow solid is precipitated, the process being accompanied by a considerable evolution of heat. A saturated solution of this compound was formed by condensing an excess of sulfur dioxide at -20° , the solution having a pale yellow color at this temperature. Evaporation of the excess solvent, through a mercury trap, from the saturated solution at 0° and atmospheric pressure, left a residue consisting of the pure solid addition product. The following data were obtained

$C_6H_5NH_2$, g.	4.957	3.221
SO_2 , g.	3.397	2.208
Ratio $C_6H_5NH_2 : SO_2$	1:0.996	1:0.996

In a sealed bulb the compound melted congruently at 65° , confirming the determination by Hill.

In any two-component system of the general type illustrated by the present case—that is, one containing a volatile component and in which a solid addition product with a congruent melting

point is formed—the vapor pressure curve of the saturated solutions in equilibrium with the solid addition compound must have a retroflex portion; in other words, it must consist of two branches meeting in a smooth curve at the melting point. This follows from the fact that at temperatures below the melting point, the addition compound can be in equilibrium with either of two solutions of entirely different concentrations and therefore of different vapor pressures. Although the complete curve could not be obtained for the present system, because the pressures at higher temperatures were too great for the apparatus, the data which were obtained indicate that this general behavior would be followed.

I (with excess SO_2)		II (with excess $C_6H_5NH_2$)	
$T, 0^\circ C.$	P , cm.	$T, 0^\circ C.$	P , cm.
-19.10	50.0	0.00	0.3
- 8.10	81.1	10.90	.9
0.00	112.9	24.00	4.7

Methylaniline.—A solid addition compound, $C_6H_5NHCH_3 \cdot SO_2$, melting congruently to a clear orange-red liquid at a temperature close to 31° , is formed in this system. The evaporation of the excess sulfur dioxide for the determination of the composition of the compound was carried out at 10° and at atmospheric pressure, the following data being obtained.

$C_6H_5NHCH_3$, g.	5.882	6.850
SO_2 , g.	3.563	4.158
Ratio $C_6H_5NHCH_3 : SO_2$	1:1.013	1:1.015

The molten compound is readily supercooled; crystallization can be effected by seeding with crystals of the aniline compound.

As the melting point of the compound is lower than that with aniline, the vapor pressures up to the melting point were sufficiently low to be determined readily and show the retroflex character of the curve (Fig. 1). The following results were obtained.

SYSTEM $C_6H_5NHCH_3 \cdot SO_2$ -SOLUTION-VAPOR						
$T, 0^\circ C.$	-19.80	-9.40	0.0	6.50	10.00	14.60
P , cm.	41.0	56.8	76.3	89.2	95.8	102.4
$T, 0^\circ C.$	18.15	22.30	25.15	28.00	30.00	29.10
P , cm.	104.6	102.3	97.5	83.0	68.4	29.9
$T, 0^\circ C.$	26.30	23.50	19.65	14.60	0.00	
P , cm.	18.2	11.7	6.7	3.5	0.6	

Ethylaniline.—This system is almost identical with the previous one, the melting point of the 1:1 compound being close to 29° . The following data for the composition of the addition product

were obtained by evaporating excess sulfur dioxide from a saturated solution at 10° and atmospheric pressure.

$C_6H_5NHC_2H_5$, g.	SO_2 , g.	Ratio	$C_6H_5NHC_2H_5:SO_2$
6.058	3.300		1:1.03

Considerable difficulty was encountered in causing the compound to crystallize; this was finally accomplished by seeding with crystals of the aniline compound.

The vapor pressures of the saturated solutions of the solid compound are given in the following table.

SYSTEM $C_6H_5NHC_2H_5:SO_2$ -SOLUTION-VAPOR					
T , °C.	-21.75	-15.00	-7.35	0.00	11.00
P , cm.	37.1	48.1	62.2	78.5	97.8
T , °C.	20.30	24.00	25.00	12.60	6.60
P , cm.	104.0	96.2	21.8	4.3	1.8

The diagram representing these data is very similar in form to Fig. 1 and is therefore omitted.

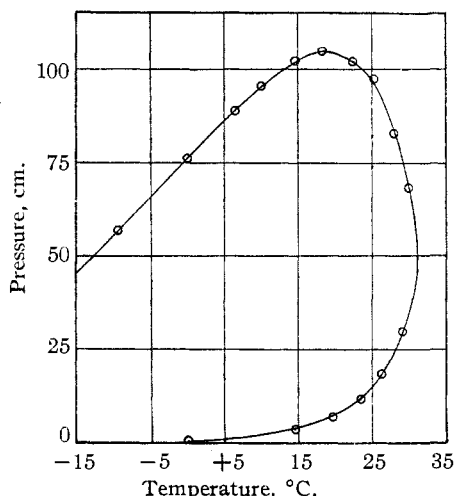


Fig. 1.—System $C_6H_5NHCH_2SO_2$, solution, vapor.

Diethylaniline.—No solid compound was found in this system at temperatures above -20° . The two liquids are miscible in all proportions, the solutions having a deep purple-red color. A vapor pressure-composition isotherm was determined at 0° , the data for which are given below and are plotted in Fig. 2.

$C_6H_5N(C_2H_5)_2$, mole %	10.9	13.8	18.3	20.7	22.6
Press., cm.	100.8	94.6	84.5	78.4	73.3
$C_6H_5N(C_2H_5)_2$, mole %	24.9	28.4	32.9	38.2	43.0
Press., cm.	67.3	58.4	47.2	35.9	27.6
$C_6H_5N(C_2H_5)_2$, mole %	46.8	54.1	65.3	74.8	90.8
Press., cm.	22.5	14.9	8.1	4.4	1.3

As sulfur dioxide is removed, the color of the solution fades until it finally reaches a faint red tint when only a trace of sulfur dioxide remains. The large negative deviations from Raoult's law, the evolution of heat on mixing the two liquids, and the deep color of the solutions all indicate the existence of chemical attraction between sulfur dioxide and diethylaniline; a solid compound could undoubtedly be obtained by lowering the temperature sufficiently.

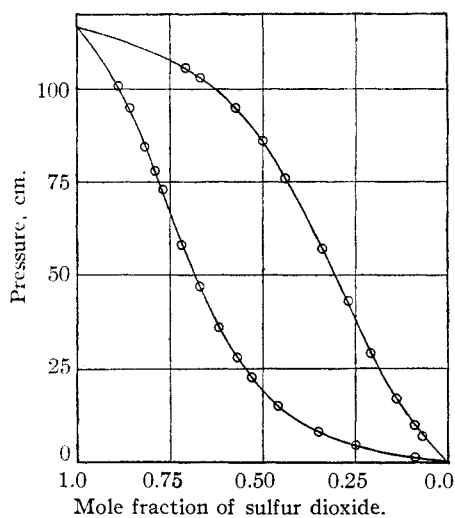


Fig. 2.— 0° isotherms: upper, SO_2 + ethylene glycol; lower, SO_2 + diethylaniline.

Diphenylamine.—Diphenylamine is readily soluble in liquid sulfur dioxide, yielding deep purple-red solutions. No solid addition compound exists above -20° , as shown by the fact that practically all the sulfur dioxide added was withdrawn at the pressure of the saturated solution in isotherms carried out at -20° and at 0° ; it seems likely that one would be formed at lower temperatures.

Korezynski and Glebocka reported having found an addition compound, $(C_6H_5)_2NH \cdot 0.5SO_2$, basing the formula on the volume of sulfur dioxide vapor absorbed at 0° and atmospheric pressure by a weighed quantity of the diphenylamine. The present results show that this absorption was due to the fact that the vapor pressure of the saturated solution of diphenylamine in liquid sulfur dioxide is below atmospheric at 0° ; furthermore, if equilibrium had been attained in their experiment, an unsaturated solution would have resulted, with the absorption of a much larger quantity of sulfur dioxide.

Vapor pressures of saturated solutions are given in the table.

DIPHENYLAMINE-SOLUTION-VAPOR					
<i>T</i> , °C.	-21.40	-20.80	-14.75	-9.00	-3.80
<i>P</i> , cm.	26.7	27.4	34.7	42.9	51.0
<i>T</i> , °C.	+ 2.00	6.30	10.00	19.60	
<i>P</i> , cm.	60.4	67.4	73.2	85.2	

p-Toluidine.—A solid bright yellow compound, C₇H₇NH₂SO₂, is formed on treating *p*-toluidine with liquid sulfur dioxide. The following data were obtained by evaporating the excess solvent from a saturated solution of the addition compound in liquid sulfur dioxide at 0° and atmospheric pressure.

C ₇ H ₇ NH ₂ , g.	SO ₂ , g.	Ratio C ₇ H ₇ NH ₂ :SO ₂
5.250	3.120	1:0.993

The following vapor pressure measurements were obtained on the two univariant systems:

C ₇ H ₇ NH ₂ :SO ₂ , soln., <i>T</i> , °C.	vapor <i>P</i> , cm.	C ₇ H ₇ NH ₂ :SO ₂ , <i>T</i> , °C.	C ₇ H ₇ NH ₂ , vapor <i>P</i> , cm.
-20.50	46.6	20.30	1.0
- 8.50	79.9		
0.00	113.5		

Korezynski and Glebocka reported the same composition for this compound.

On the basis of the results obtained with the above systems, it is evident that chemical attraction exists between sulfur dioxide and organic nitrogen bases; in several of the cases studied, this attractive force is sufficient to cause the formation of solid addition compounds in equimolecular proportions, at ordinary temperatures. It is interesting to note that the substitution of an alkyl group for hydrogen attached to nitrogen in the aniline molecule results in lowering the melting point of the addition compound formed with sulfur dioxide. This fact suggests a possible application for the use of sulfur dioxide in the separation of mixtures of aniline with mono- and di-substituted alkyl derivatives.

Naphthalene and Diphenyl.—Neither naphthalene nor diphenyl forms solid addition compounds with sulfur dioxide at temperatures above 0°, as isotherms at 0° showed that all but a trace of the sulfur dioxide added was evaporated at the pressure of the saturated solution. In both cases the saturated solutions have a greenish-yellow color.

The following results were obtained on the vapor pressures of saturated solutions.

Naphthalene, soln., <i>T</i> , °C.	vapor <i>P</i> , cm.	Diphenyl, soln., <i>T</i> , °C.	vapor <i>P</i> , cm.
-18.70	47.3	-21.50	40.6
- 8.50	74.0	- 9.50	66.5
0.00	103.4	0.00	93.8

Naphthols.—Although phenol has been reported to form a solid addition compound with sulfur dioxide, neither α- nor β-naphthol gave any evidence of forming any above -20° as shown by vapor pressure isotherms carried out at that temperature. Both are rather insoluble in liquid sulfur dioxide, producing orange colored solutions.

α-Naphthol, soln., <i>T</i> , °C.	vapor <i>P</i> , cm.	β-Naphthol, soln., <i>T</i> , °C.	vapor <i>P</i> , cm.
-20.00	46.1	-21.20	45.1
-10.00	71.5	- 9.50	76.1
0.00	106.6	0.00	112.4

Diphenyl Ether.—No solid addition compound was found to exist between sulfur dioxide and diphenyl ether at temperatures above -20°. It dissolves readily in liquid sulfur dioxide, giving greenish-yellow solutions. Evaporation of sulfur dioxide from an unsaturated solution at -15° left a residue of supercooled liquid diphenyl ether which crystallized immediately on admitting air into the bulb.

Ethylene Glycol.—Ethylene glycol is completely miscible with liquid sulfur dioxide above -20°, giving colorless solutions. A vapor pressure-composition isotherm was determined at 0°, large positive deviations from Raoult's law being obtained. The experimental data are given below and plotted in Fig. 2.

Ethylene glycol, mole %	20.3	32.7	42.5	50.1
<i>P</i> , cm.	105.5	102.8	95.1	85.7
Ethylene glycol, mole %	56.4	66.0	72.8	79.4
<i>P</i> , cm.	75.8	57.1	42.7	29.1
Ethylene glycol, mole %	86.2	90.7	93.2	
<i>P</i> , cm.	16.8	9.91	6.67	

Summary

Vapor pressure measurements have been made on the two-component systems formed by sulfur dioxide with aniline, methylaniline, ethylaniline, diethylaniline, diphenylamine, *p*-toluidine, naphthalene, diphenyl, diphenyl ether, α- and β-naphthols, and ethylene glycol between the maximum temperature limits -20 and 30°. Solid addition compounds were found to exist in this temperature range between sulfur dioxide and aniline, methylaniline, ethylaniline and *p*-toluidine, their formulas being determined.