by Fordyce and Chapin[1] in their study of the emulsion copolymerization of styrene and acrylonitrile. In their work the value of R was 0.367 and the temperatures were 60 and 75°. The results of this calculation are given in Table IV.

Table IV

Acrylonitrile Contents of the Oil Phases Present During the Emulsion Copolymerization Studies of Fordyce and Chapin[1]

Initial mole %	8.24	9.36	14.86	17.90	18.83	24.93	32.92	36.32	45.68	66.25	94.64
Equilibrium mole %	5.76	6.63	10.9	13.4	14.1	19.4	26.5	29.7	38.9	60.5	93.6

The values given for the initial mole %'s in the table are the acrylonitrile contents of the oil phases before adding to the emulsion while the values for the equilibrium mole %'s are the acrylonitrile contents of the oil phases present in the emulsions during the polymerization. These latter values were calculated from the initial values using equation 4 and values of the partition coefficient, α, given by Fig. 1.

Having calculated the compositions of the oil phases actually present during the emulsion copolymerizations, it is now possible to compare the compositions of copolymers produced in emulsion with those produced in bulk from oil phases of identical composition. The data of Fordyce and Chapin[1] so treated are shown in Fig. 2. It is seen that this correction of the compositions of the emulsion oil phases makes the emulsion and bulk copolymerization composition curves identical within the accuracy of the data. Thus, the suggestion of Fordyce and Chapin that the consistent difference which they found was due to the water solubility of the acrylonitrile is substantiated by this investigation.

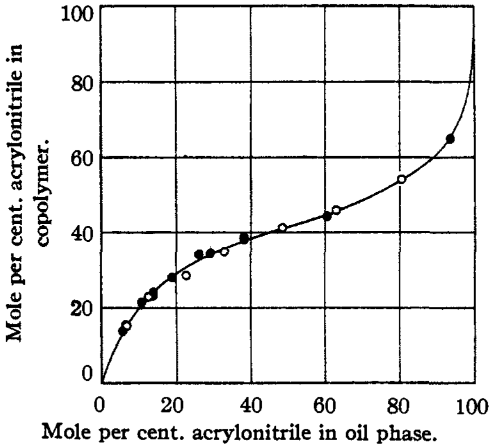

Fig. 2.—Monomer-polymer composition curve for styrene–acrylonitrile with correction for water solubility of the acrylonitrile: bulk polymerization, ○; emulsion polymerization, ●.

Summary

The compositions of styrene–acrylonitrile solutions in equilibrium with water–acrylonitrile solutions have been determined. These equilibrium compositions have been used to calculate the acrylonitrile contents of the oil phases present in the emulsion copolymerization experiments of Fordyce and Chapin. It is shown that when this is done the above authors' emulsion data are identical with their bulk polymerization data in regard to composition of polymer produced from a given oil phase.

Passaic, New Jersey Received July 12, 1947

[Contribution from School of Mines and Metallurgy, University of Missouri]

Some Equilibrium Relations in the System Magnesium Oxide–Sulfur Dioxide–Water (Acid Region) at Pressures below Atmospheric[1]

By Frank H. Conrad and Donat B. Brice

I. Introduction

This is a report of the study of the equilibrium $MgSO_3 \cdot 6H_2O$ + solution + vapor, in the system magnesium oxide–sulfur dioxide–water. It presents the pressure–composition relations at constant temperature (15 and 25°). The liquid phase of this system consists of a solution of the bisulfite of magnesium containing a small amount of the monosulfite. The vapor phase consists of SO_2 and water vapor.

These relations were desired because of the contemplated use of magnesia base cooking liquors in the "Sulfite Pulping Process" in place of calcium base liquor. Hatch[2] has pointed out that magnesia base liquor has the advantages: (a) the spent liquor may be used to recover both the magnesia and the sulfur dioxide; (b) heat is supplied to the process from the burning of the organic solids in the evaporated spent liquor; and perhaps most important; (c) the problem of disposing of the spent liquor is eliminated.

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[1] This paper is based on a Dissertation presented by Donat B. Brice in May, 1947, to the Faculty of the Graduate School of the School of Mines and Metallurgy, University of Missouri, Rolla, Missouri, in candidacy for the degree of Master of Science in Chemical Engineering.

[2] R. S. Hatch, *Paper Trade J.*, **122**, No. 11, 54-56 (March 14, 1946).

II. The Experimental Part

The materials used were "C. P. Analyzed" magnesium oxide containing negligible quantities of sulfate and calcium. The sulfur dioxide and water were treated as described by Conrad and Beuschlein.[3]

The apparatus used in determining the equilibrium pressures was almost identical to that described in "reference 3." The materials for making the equilibrium mixture were prepared in the same manner with the exception of the magnesium oxide.

After equilibrium was obtained, as shown by constant pressure readings, the solid was allowed to settle and a portion of the saturated solution was withdrawn to a weighing pipet. The solution (9 to 12 g.) was drained and washed into a volumetric flask nearly full of water. The tip of the pipet was kept below the surface of the water to prevent the loss of sulfur dioxide. The flask was then filled to volume and the aliquots were withdrawn in a manner similar to the removal of water from a wash bottle. This method was used to avoid the loss of any sulfur dioxide.

Aliquots were analyzed for the total and combined sulfur dioxide by the Hohn method the essentials of which are given by Birchard.[4] The free sulfur dioxide is obtained by subtracting the combined sulfur dioxide from the total sulfur dioxide. The free sulfur dioxide is the actual free sulfur dioxide plus half of the sulfur dioxide in the bisulfite of magnesium, and is more properly called the "available sulfur dioxide" as it indicates the sulfur dioxide in excess of that required to form the monosulfite. The combined sulfur dioxide represents that required to form the monosulfite. These definitions are as set forth by the Technical Association of Pulp and Paper Institute.[5] The standard solutions used in these analyses were sodium thiosulfate and iodine of approximately 0.1 *N* and sodium hydroxide approximately 0.2 *N*. Standardizations of the iodine and thiosulfate were made by the appropriate use of sodium oxalate and potassium permanganate. Since these solutions were standardized frequently the potassium permanganate was used. The sodium hydroxide was standardized against potassium acid phthalate.

The equations for the chemical reactions during analysis and for calculation of the combined sulfur dioxide are similar to those of "reference 3," only replacing the calcium atom by magnesium.

Before making any tests on the ternary system and in order to test the reliability of the results with the particular apparatus used in these experiments, the vapor pressure of water was determined at two temperatures. The vapor pressures obtained agreed with values read from the "International Critical Tables"[6] within 0.5 mm. pressure in all cases. As a further check on both the accuracy of the pressure readings and the analytical reagents used in analysis, the solubility of sulfur dioxide in water at 25° was determined at various pressures. The equilibrium flask was charged with water and sulfur dioxide, agitated at constant temperature in a thermostat, connected to the manometer and pressure readings obtained. It was noted that after two or three minutes the pressure remained constant although tests were allowed to stand for one and one-half hours to ensure that equilibrium had been attained. These data were in good agreement with those given in the "International Critical Tables,"[7] as well as the data of reference 3. The maximum deviation of any one point was 0.1 g. of sulfur dioxide per 100 g. of water. It was concluded from these preliminary tests that the apparatus and method would give results which were sufficiently accurate for the ternary system.

III. Experimental Results

Results of analysis of the liquid phase at 25 and at 15° are given in tabular form in Tables I and II, respectively, and are shown in graphical form in Figs. 1 and 2.

TABLE I

ANALYSIS OF THE LIQUID PHASE OF THE SYSTEM MAGNESIUM OXIDE–SULFUR DIOXIDE–WATER EQUILIBRIUM AT 25°

		Grams per 100 grams of water		
Expt.	Total pressure, mm.	Total SO_2	Free SO_2	Combined SO_2
1	130.2	28.2	14.0	14.2
2	154.4	28.0	13.15	14.85
3	213.2	35.6	17.4	18.2
4	264.3	35.2	17.3	17.9
5	288.0	37.5	18.75	18.75
6	326.5	40.7	20.35	20.35
7	410.9	42.1	20.8	21.3
8	560.7	50.3	24.9	25.4
9	638.4	51.6	25.3	26.3
10	726.8	50.7	24.85	25.85
11	728.4	52.0	25.8	26.2
A[a]	728.7	50.1	24.4	25.7

[a] Experiment A made at 35°.

TABLE II

ANALYSIS OF THE LIQUID PHASE OF THE SYSTEM MAGNESIUM OXIDE–SULFUR DIOXIDE–WATER EQUILIBRIUM AT 15°

	Grams per 100 grams of water		
Total pressure, mm.	Total SO_2	Free SO_2	Combined SO_2
75.5	30.4	14.7	15.7
87.5	28.05	13.3	14.75
110.7	29.65	14.6	15.05
156.8	32.9	16.0	16.9
162.3	31.4	14.85	16.55
245.5	39.9	18.9	21.0
419.3	46.9	23.35	23.55
448.7	44.8	22.4	22.4
726.8	54.6	26.8	27.8
730.3	53.3	26.55	26.75

It was possible to remove only one sample of clear saturated liquid without disturbing the equilibrium in the flask. Duplicate analytical determinations made on some samples checked to within 0.6 g. of sulfur dioxide per 100 g. of water.

Saturation of the liquid phase, with respect to both gas and solid, was approached from both the supersaturated and the unsaturated conditions. In all experiments at 25° except those at atmospheric pressure the temperature at which the gas was admitted was three to five degrees below the final equilibrium temperature. Also, in order to remove any insoluble gaseous impurities admitted with the sulfur dioxide, solutions were boiled at reduced pressures. As sulfur dioxide is more soluble at low temperatures and high pressures, these experiments were approached from supersaturation with respect to the gas.

Equilibrium at 15° was approached from the unsaturated state with respect to both gas and

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(3) F. H. Conrad and W. L. Beuschlein, THIS JOURNAL, **56**, 2554 (1934).

(4) W. H. Birchard, *Paper Industry*, **8**, 793 (1926).

(5) T. A. P. P. I. Standards, "Analysis of Bisulfite Cooking Liquor," T 604 m-45, corrected, Sept., 1945.

(6) "International Critical Tables," Vol. III, McGraw-Hill Book Company, New York, N. Y., 1928, p. 212.

(7) *Ibid.*, Vol. III, p. 302.

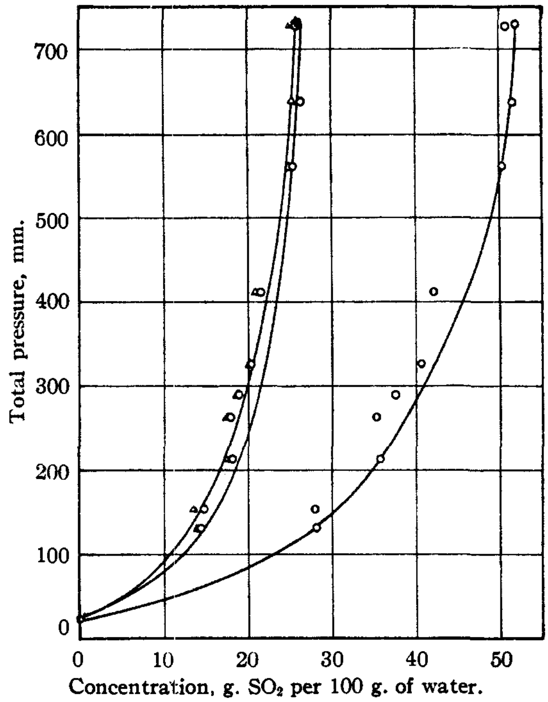

Fig. 1.—Pressure–concentration curves for liquid phase of system $MgO–SO_2–H_2O$; temperature, 25°.

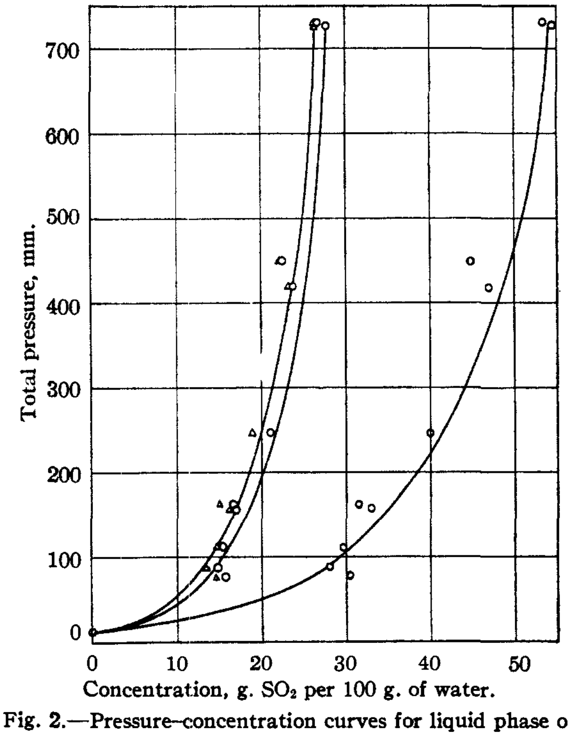

Fig. 2.—Pressure–concentration curves for liquid phase of system $MgO–SO_2–H_2O$; temperature 15°.

solid. The temperature at which the gas was admitted was five to eight degrees higher than the equilibrium temperature. The pressure was greater when the flask was placed in the thermostat than at final equilibrium. Thus these experiments were approached from the unsaturated side with respect to the gas.

In experiments 4 and 6 of Table I sulfur dioxide was added until all the solid phase was dissolved. After the solid was dissolved the solution was subjected to vacuum until solid phase reappeared. When the solid was again present the flask was placed in the thermostat and treated in the same manner as other experiments. Experiments 4 and 6 of Table I thus were approached from the supersaturated condition with respect to both gas and solid.

The curves of Figs. 1 and 2 have been constructed from data obtained. The correlation of these data by smooth curves is good.

In order to show the effect of temperature upon the concentration of sulfur dioxide, experiment "A" (Table I) was made at 35° and atmospheric pressure (in this case 728 mm.). The results of this experiment and the corresponding values at the same pressure (the 15° run was at 727 mm.), read from the curves in Figs. 1 and 2 are plotted in Fig. 3. The temperature concentration relations for the system calcium oxide–sulfur dioxide–water from "reference 3" are also plotted for comparison. It should be noted that the amount of sulfur dioxide in a solution is much greater for the magnesia system than for the calcium system at the same pressure. In the magnesia system the amount of combined sulfur dioxide was always greater than the free, in contrast to that for the calcium oxide system where it was much less. The amounts of combined and free were very nearly equal, the combined being always greater,

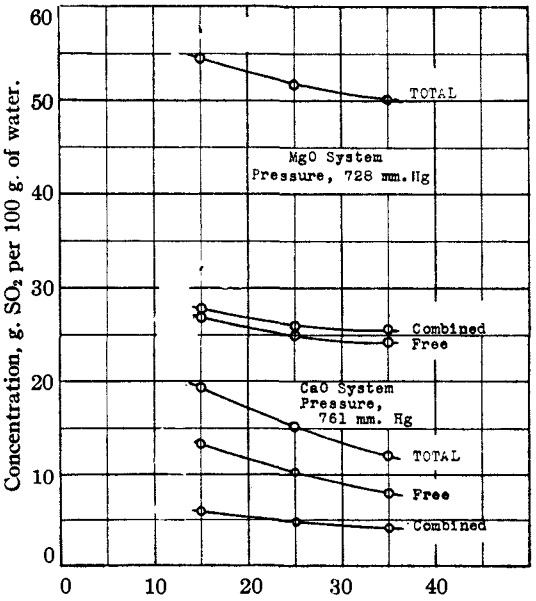

Fig. 3.—Temperature–concentration curves for liquid phase of the systems $MgO–SO_2–H_2O$ and $CaO–SO_2–H_2O$ at atmospheric pressure.

representing slightly more than 0.5 of the total. The combined was never more than 0.52 of the total.

IV. Analysis of the Solid Phase

Samples of the solid, assumed to be $MgSO_3 \cdot 6H_2O$, were removed from the equilibrium flask and analyzed. Samples for experiments 1, 2 and 3, Table III, were drained with suction and then dried to constant weight over 67% sulfuric acid in an atmosphere of carbon dioxide. Hartog[8] reports that crystals of $MgSO_3 \cdot 6H_2O$ are deposited when a solution of $Mg(HSO_3)_2$ is concentrated *in vacuo* at temperatures below 100° and then cooled. The magnesium oxide was determined by the pyrophosphate method and the sulfur dioxide by the Hohn method as previously referred to in the analysis of the liquid.

The mole ratio magnesium oxide to sulfur dioxide indicated a compound containing one mole of magnesium oxide to one of sulfur dioxide, but the amount of magnesium oxide was somewhat high in samples 1 and 2. It was thought that possibly oxidation was taking place in spite of all precautions. It was therefore decided, as other solid samples were removed from the equilibrium flask, to wash them with distilled water until free of solution and analyze a portion immediately for sulfur dioxide and magnesium oxide. Another portion of these same samples was dried as described and analyzed for the magnesium oxide content. It is thus possible to calculate from the weight of the dried sample and the magnesium oxide–sulfur dioxide ratio of the same sample, the amount of magnesium sulfite it would contain and to obtain the hydrate water by difference. Results of these analyses and calculations are shown for samples 5 to 8 (Table III).

TABLE III

COMPOSITION OF THE SOLID PHASE FOR THE SYSTEM MAGNESIUM OXIDE–SULFUR DIOXIDE–WATER

Expt.	MgO. g.	SO_2, g.	Mole ratio MgO/SO_2	Moles water / Mole $MgSO_3$
1	0.1081	0.143	1.20	..
2	.1031	.135	1.21	..
3[a]	.0860	.128	1.06	..
4[a]	.0730	.1043	1.11	..
5	.0290	.0395	1.17	6.22
6[a]	.1086	.0294	1.002	5.77
7	.0522	.0615	1.35	6.35
8[a]	.0280	.0416	1.07	5.68
9[a]	.0362	.054	1.06	..
$MgSO_3 \cdot 6H_2O$	40.32	64.06	1.000	6.00

[a] Equilibrium approached from supersaturation.

Samples of solids were obtained from solutions in which the equilibrium had been approached from both the unsaturated and the supersaturated conditions as in the liquid phase investigation. The time allowed for equilibrium to be reached in the preparation of the solid samples was identical with that used in the liquid phase work. Also constancy of pressure readings was likewise used as a criterion of equilibrium, and hence the tests should be comparable with those for the liquid phase. Examination of the results in Table III shows that solids obtained from experiments approached from the supersaturated side have close to the theoretical ratio of one to one for magnesium oxide to sulfur dioxide. The fact that this ratio is slightly greater than one may indicate a small amount of oxidation even though the samples were analyzed for sulfur dioxide without drying. Those approached from the unsaturated side deviated considerably more and the ratio varied from one run to another. It is the opinion of the authors that although equilibrium in the liquid phase was established, such that pressure–concentration curves could be constructed, there was actually some magnesium oxide occluded by the magnesium monosulfite in the solids prepared from the unsaturated side.

Sulfur dioxide was permitted to react with a suspension of magnesium oxide in water, which amounted to having a particle of magnesium oxide as the core with magnesium hydroxide covering the oxide. The sulfur dioxide reacted with the hydroxide and formed a coating of magnesium monosulfite hexahydrate around the magnesium oxide. These particles then after long standing were in equilibrium with the solution of bisulfite of magnesium. Thus, even if occluded magnesium oxide were present it would have little effect upon the liquid phase investigation.

It is realized that the removal of the solid phase from equilibrium with the liquid and gaseous phases may in some cases change the composition of the solid. Attempts were made to obtain data satisfactory for the construction of a modified Schreinemakers diagram as used by Conrad and Beuschlein[3] but the intersections were at such acute angles and so erratic as to make the method of little value.

Summary

1. The total pressure–composition relationships have been determined for the system magnesium oxide–sulfur dioxide–water in the acid region up to atmospheric pressure at 15 and 25°.
2. The total, free and combined sulfur dioxide has been determined for saturated solutions in equilibrium with solid magnesium monosulfite hexahydrate at total pressures of sulfur dioxide and water vapor from the vapor pressure of water to atmospheric pressure for the temperatures 15 and 25°.
3. The temperature–composition relationship has been determined for the total pressure of 728 mm. at temperatures of 15, 25 and 35°.
4. The analysis of the solid removed from the equilibrium is in agreement with the assumed formula of $MgSO_3 \cdot 6H_2O$.

ROLLA, MISSOURI

RECEIVED AUGUST 4, 1947

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[8] Hartog, *Compt. rend.*, **104**, 1793 (1887).