to be changed by overlap and, in about one-half of the cases in which overlap occurs, size measurements are possible.

An attempt was made to determine how dependent the flattening coefficient is upon drop size for No. 2 heating oil. However, no definite trends were found. If the crater coefficient varies slightly with drop size, as is reported by May, this could obscure any noticeable effect of drop size on the flattening coefficient.

CONCLUSIONS

The flattening coefficient for drops collected on glass slides treated with 0.1% Aerosol O.T. solution is dependent upon the drop composition. This flattening coefficient may be determined by other measurement procedures. The crater coefficients for water and dibutyl phthalate drops collected on MgO-coated slides are essentially the same and equal to approximately 0.82. This agrees with the results of previous studies in two ways: magnitude of the coefficient and lack of its dependence upon drop liquid. The use of MgO-coated slides for measuring drop sizes is simple, convenient, and accurate.

LITERATURE CITED

(1) May, K.R., *J. Sci. Instr.* **22**, 187 (1945).
(2) *Ibid.*, **27**, 128 (1950).
(3) Pilcher, J.M., Thomas, R.E., *Advan. Chem. Ser.* **20**, 155 (1958).
(4) Rupe, J.H., "Third Symposium on Combustion, Flame and Explosion Phenomena," p. 680, Williams and Wilkins, Baltimore, 1949.
(5) Strazhevshky, C., *Tech. Phys. USSR* **4**, 978 (1937).

RECEIVED for review January 13, 1965. Accepted July 21, 1965.

Aqueous Systems at High Temperature. XV.

Solubility and Hydrolytic Instability of Magnesium Sulfate in Sulfuric Acid–Water and Deuterosulfuric Acid–Deuterium Oxide Solutions, 200° to 350° C.

WILLIAM L. MARSHALL and RUTH SLUSHER
Reactor Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tenn.

The solubility of $MgSO_4 \cdot H_2O$ has been determined in H_2SO_4–H_2O solutions in the presence of vapor at temperatures from 200° to 350° C. and at concentrations of H_2SO_4 to 1.8 molal. Analogous solubilities of $MgSO_4 \cdot D_2O$ have been determined in D_2SO_4–D_2O over the same temperature and concentration range. In contact with solution concentrations of SO_3 (total sulfate) below approximately 10^{-2} molal at 270° to 350° C. and 0.1 molal at 200° C., the monohydrate solid (in excess) was found to be hydrolytically unstable, and converted partially either to an oxysulfate or $Mg(OH)_2$ depending upon temperature and solution concentration. Solutions of stoichiometric $MgSO_4$ in H_2O over the entire region of concentration (0.003 to 2 molal) precipitated either one or two of the solids, $MgSO_4 \cdot H_2O$ (not alone), oxysulfate, or $Mg(OH)_2$, to attain equilibrium.

IN A PREVIOUS determination of $NiSO_4$ monohydrate solubilities in H_2SO_4-H_2O and D_2SO_4-D_2O solutions at temperatures between 200° and 350° C., it was shown that $NiSO_4 \cdot H_2O$ solid, in dilute acidic solutions, converted hydrolytically to one or more nickel-oxysulfates, or to $Ni(OH)_2$ *(6)*. Since Benrath *(3)* showed that near 200° C. the apparent solubility of a $MgSO_4$ solid decreased to very low values (but that an "aufscheidungskurve" existed above the true solubility curve), it was of interest to determine the phase relationships of $MgSO_4$ in H_2SO_4-H_2O solutions between 200° and 350° C. (in the presence of vapor), and to determine whether $MgSO_4$ was similar to $NiSO_4$ in its solubility and hydrolytic characteristics. The results of this study are of particular interest to distillation processes for desalination of sea or brackish water as $Mg(OH)_2$ is one of the constituents of scale that can form on heat exchanger surfaces at high temperature. Solubility measurements were made also in D_2SO_4-D_2O solution for comparison with the previously determined, analogous solubilities of $NiSO_4 \cdot D_2O$, $Li_2SO_4 \cdot D_2O$, and Li_2SO_4 *(6, 7)*.

Previous solubility studies of $MgSO_4$ hydrates in H_2SO_4-H_2O solutions have been confined to temperatures between 0° and 55° C. These studies for the most part were concerned with the transition temperatures between the various hydrates as a function of H_2SO_4 concentration *(1-5, 8)*. Many investigators have reported on the solubility of $MgSO_4$ hydrates in H_2O from −4.0° to 240° C. References to most of this work are given and evaluated by Seidell in his compilation of solubilities *(9)*. Benrath's values are included in Seidell and Linke's supplement *(10)*.

The present paper gives the solubilities of $MgSO_4 \cdot H_2O$ and $MgSO_4 \cdot D_2O$ in solutions of H_2SO_4-H_2O and D_2SO_4-D_2O, respectively, at concentrations of acid between 10^{-2} and 2 molal and at temperatures from 200° to 350° C. In addition, the hydrolytic instability at high temperature of stoichiometric $MgSO_4$ in H_2O solution, and of $MgSO_4 \cdot H_2O$

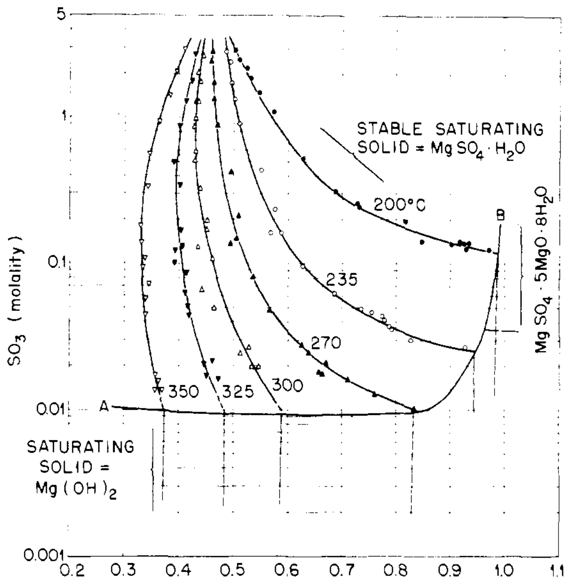

Figure 1. System $MgO-SO_3-H_2O$, 200° to 350° C.

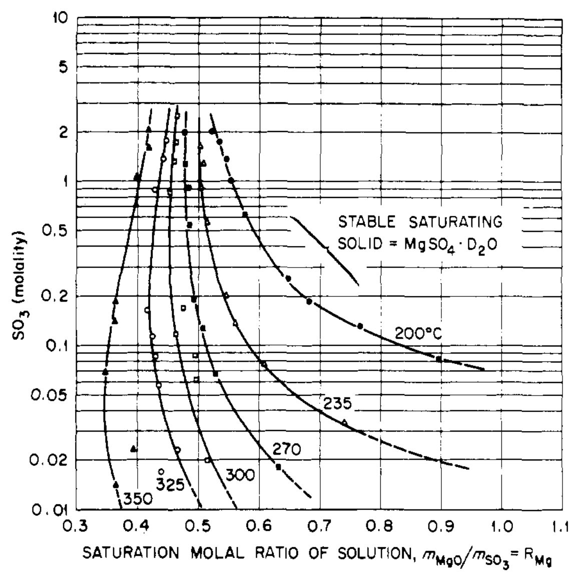

Figure 2. System $MgO-SO_3-D_2O$, 200° to 350° C.

Table I. Solubility of $MgSO_4 \cdot H_2O$ in $H_2SO_4-H_2O$ Solutions, 200° to 350° C.

H_2SO_4, m	$MgSO_4$, m	Density at 25° C.
T = 200° C.		
0.0034	0.1187	
0.0088	0.1103	1.012_6
0.0091	0.1306	
0.0099	0.1231	
0.0112	0.1287	
0.0133	0.1227	
0.0215	0.1187	
0.0351	0.1577	1.023_6
0.0646	0.1758	
0.0684	0.1820	1.027_7
0.0967	0.2216	
0.1923	0.3289	
0.468	0.636	
0.666	0.810	
0.868	0.996	
1.047	1.157	
1.240	1.307	
1.461	1.484	
T = 235° C.		
0.0020	0.0245	
0.0052	0.0249	
0.0073	0.0282	1.001_6
0.0078	0.0290	
0.0090	0.0317	
0.0097	0.0336	
0.0112	0.0350	
0.0130	0.0364	
0.0190	0.0422	
0.0351	0.0592	1.011_8
0.0656	0.0942	
0.0694	0.0925	1.017_8
0.0977	0.1319	
0.1943	0.2378	
0.443	0.465	
0.668	0.683	
0.873	0.868	
1.252	1.196	
1.477	1.401	
T = 270° C.		
0.0017	0.0084	
0.0030	0.0095	
0.0045	0 0111	0.999_4
0.0059	0.0115	
0.0061	0.0116	
0.0068	0.0138	
0.0087	0.0153	
0.0102	0.0170	
0.0205	0.0265	
0.0370	0.0427	1.009_4
0.0678	0.0668	
0.0718	0.0734	1.016_0
0.1030	0.1059	
0.2073	0.2032	
0.469	0.418	
0.718	0.623	
0.930	0.803	
1.304	1.110	
1.561	1.341	
T = 300° C.		
0.0088	0.0106	
0.0092	0.0105	
0.0117	0.0123	
0.0123	0.0138	
0.0262	0.0230	
0.0362	0.0290	1.008_2
0.0573	0.0491	
0.0718	0.0550	1.014_2
0.0937	0.0763	
0.1068	0.0877	
0.1816	0.1442	
0.2848	0.2204	
0.3237	0.2453	
0.489	0.375	1.063_8
0.547	0.417	
0.723	0.555	
0.732	0.571	1.100_2
0.993	0.785	1.134_2
1.164	0.908	
1.489	1.197	1.193_4
T = 325° C.		
0.0085	0.0076	
0.0093	0.0077	
0.0113	0.0091	
0.0116	0.0100	
0.0261	0.0191	1.000_6
0.0300	0.0215	
0.0366	0.0256	1.008_3
0.0503	0.0362	1.004_2
0.0613	0.0400	
0.0744	0.0483	1.013_1
0.0775	0.0533	1.008_0
0.0991	0.0676	
0.2064	0.1390	
0.3030	0.1968	
0.518	0.350	1.065_2
0.767	0.548	1.099_0
1.047	0.770	
1.565	1.209	1.195_6
T = 350° C.		
0.0084	0.0049	
0.0089	0.0048	
0.0100	0.0056	
0.0111	0.0062	
0.0290	0.0150	0.999_8
0.0385	0.020	
0.0468	0.025	
0.062	0.031	1.002_8
0.072	0.037	
0.094	0.045	1.008_6
0.121	0.061	1.012_2
0.218	0.115	
0.370	0.196	
0.605	0.347	1.069_2
0.882	0.552	1.104_0
1.259	0.831	1.149_4
1.798	1.262	1.210_2

solid in the presence of H_2SO_4 solutions varying from 4×10^{-4} to 0.1 molal H_2SO_4, has been studied.

EXPERIMENTAL

Magnesium sulfate·n H_2O (J.T. Baker Chem. Co. "Baker Analyzed" Reagent Grade), converted for use with D_2O to anhydrous $MgSO_4$ by heating at 400° C., and MgO (Gen. Chem. Div. of Allied Chem. Co., B. and A. Reagent Grade) were used without additional purification. Sulfuric acid (Reagent Grade) stock solutions were prepared, analyzed, and diluted to the concentrations required for the experiments. A primary stock solution of D_2SO_4 in D_2O was prepared by diluting concentrated H_2SO_4 with D_2O (containing

Table II. Equation and Coefficients for the Solubility of $MgSO_4 \cdot H_2O$ in H_2SO_4–H_2O Solution, 200° to 350° C.

(Applicable for ranges of curves shown in Figure 4)

$$m_{MgSO_4} = a_0 + a_1(m_{H_2SO_4}) + a_2(m_{H_2SO_4})^2 + a_3(m_{H_2SO_4})^3$$

T, ° C.	a_0	a_1	a_2	a_3	Std. Error of Fit, Molal Units	Number of Observations, n
200	+0.1078	+1.206	−0.2433	+0.04344	0.00765	18
235	+0.02318	+1.052	−0.1075	+0.01651	0.00524	19
270	+0.00825	+0.9024	−0.07148	+0.02356	0.00444	19
300	+0.00528	+0.7264	+0.06556	−0.01277	0.00459	20
325	+0.00348	+0.6033	+0.1589	−0.03344	0.00230	18
350	+0.00113	+0.4689	+0.2036	−0.04091	0.00266	17

Table III. Solubility of $MgSO_4 \cdot D_2O$ in D_2SO_4–D_2O Solutions, 200° to 350° C.

D_2SO_4, m	$MgSO_4$, m	Density at 25° C.	D_2SO_4, m	$MgSO_4$, m	Density at 25° C.	D_2SO_4, m	$MgSO_4$, m	Density at 25° C.
	T = 200° C.			T = 270° C.			T = 325° C.	
0.0086	0.0730	1.110_1	0.066	0.0110	1.100_3	0.0096	0.0075	
0.0308	0.1010	1.121_6	0.0312	0.0351	1.114_5	0.0120	0.0110	1.109_0
0.0608	0.1280	1.127_6	0.0640	0.0650	1.119_8	0.0330	0.0254	1.114_0
0.0901	0.1660	1.132_8	0.0973	0.0937	1.124_3	0.0490	0.0364	1.114_3
0.2672	0.363	1.168_5	0.2838	0.2660	1.157_2	0.0662	0.0485	1.119_9
0.452	0.558	1.201_1	0.478	0.445	1.188_6	0.0964	0.0692	1.122_0
0.637	0.763	1.231_0	0.678	0.622	1.217_4	0.511	0.383	1.184_5
0.826	0.945	1.256_3	1.072	0.977	1.275_1	0.774	0.614	1.222_7
1.000	1.088	1.285_7				1.006	0.813	1.255_2
				T = 300° C.				
	T = 235° C.		0.0099	0.0105			T = 350° C.	
0.0090	0.025	1.102_7	0.0313	0.0310		0.0090	0.0052	
0.0300	0.046	1.114_5	0.0454	0.0436	1.115_4	0.0140	0.0090	
0.0608	0.0780	1.120_0	0.0642	0.0551	1.119_5	0.0455	0.0240	1.115_1
0.0928	0.1110	1.126_1	0.0900	0.0820	1.122_9	0.0886	0.0506	
0.2708	0.2870	1.159_3	0.477	0.399	1.183_8	0.1230	0.0703	1.123_0
0.433	0.470	1.189_8	0.723	0.619	1.220_0	0.645	0.430	1.196_6
0.647	0.668	1.219_8	0.936	0.810	1.249_4	0.955	0.689	1.238_0
0.837	0.841	1.249_0	1.418	1.237	1.312_8	1.240	0.893	1.275_6

0.2% H_2O) and evaporating off the D_2O (with H_2O impurity) repeatedly until essentially all H_2O had been removed. All other experimental methods, procedures, and apparatus have been described and referred to previously (*6, 7*). In summary, selected mixtures of solid and solution were sealed in 60 ml. (internal volume) titanium-alloy high pressure vessels. There was no leakage during a run. Before closure, a small amount of H_2O_2 ($\sim$1 ml.) was added to each vessel; this amount decomposed to $H_2O + O_2$ at high temperature and helped prevent corrosion of the vessels. For each experimental run, eight vessels containing solution-solid mixtures were rocked at high temperature in a constant temperature aluminum block furnace. The solution phases were sampled by means of flexible capillary tubing (extending beneath the liquid level) and valves. Since the liquid phase was sampled at its equilibration temperature and subsequently analyzed, a correction for loss of water or other constituents to the vapor was unnecessary. At equilibrium, the analyses gave a composition for the liquid phase in the presence of both vapor and a solid phase (or phases). The temperature of equilibration was approached from both lower and higher temperatures; agreement of analyses was used to show that equilibrium had been attained. The times for attainment of solution saturation by the monohydrate were similar (less than 2 hours) to those found for the solubility of $NiSO_4 \cdot H_2O$, Li_2SO_4, and $Li_2SO_4 \cdot H_2O$ in H_2SO_4–H_2O (*6, 7*). Longer times (about 1 day) seemed to be necessary for attainment of equilibrium by the oxysulfate and $Mg(OH)_2$.

Solution samples were analyzed by acid-base titration both for free H_2SO_4 (or D_2SO_4) and for total acidity after removing all magnesium with Dowex-50 cation exchange resin. The difference between these two values gave the concentration of magnesium. For solution samples containing very low concentrations of magnesium and little or no free H_2SO_4, magnesium was determined by flame photometry, the results of which were reproducible to ±2 to 4%. The densities, determined at 25 ± 2° with a 1-cc. pycnometer, were used to convert molar to molal values both

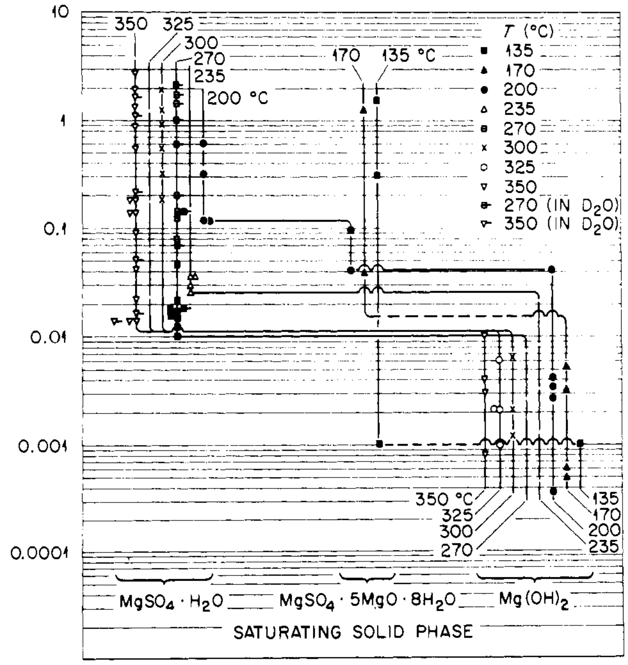

Figure 3. Solid phases in the system MgO–SO_3–H_2O and its D_2O analog, 135° to 350° C.

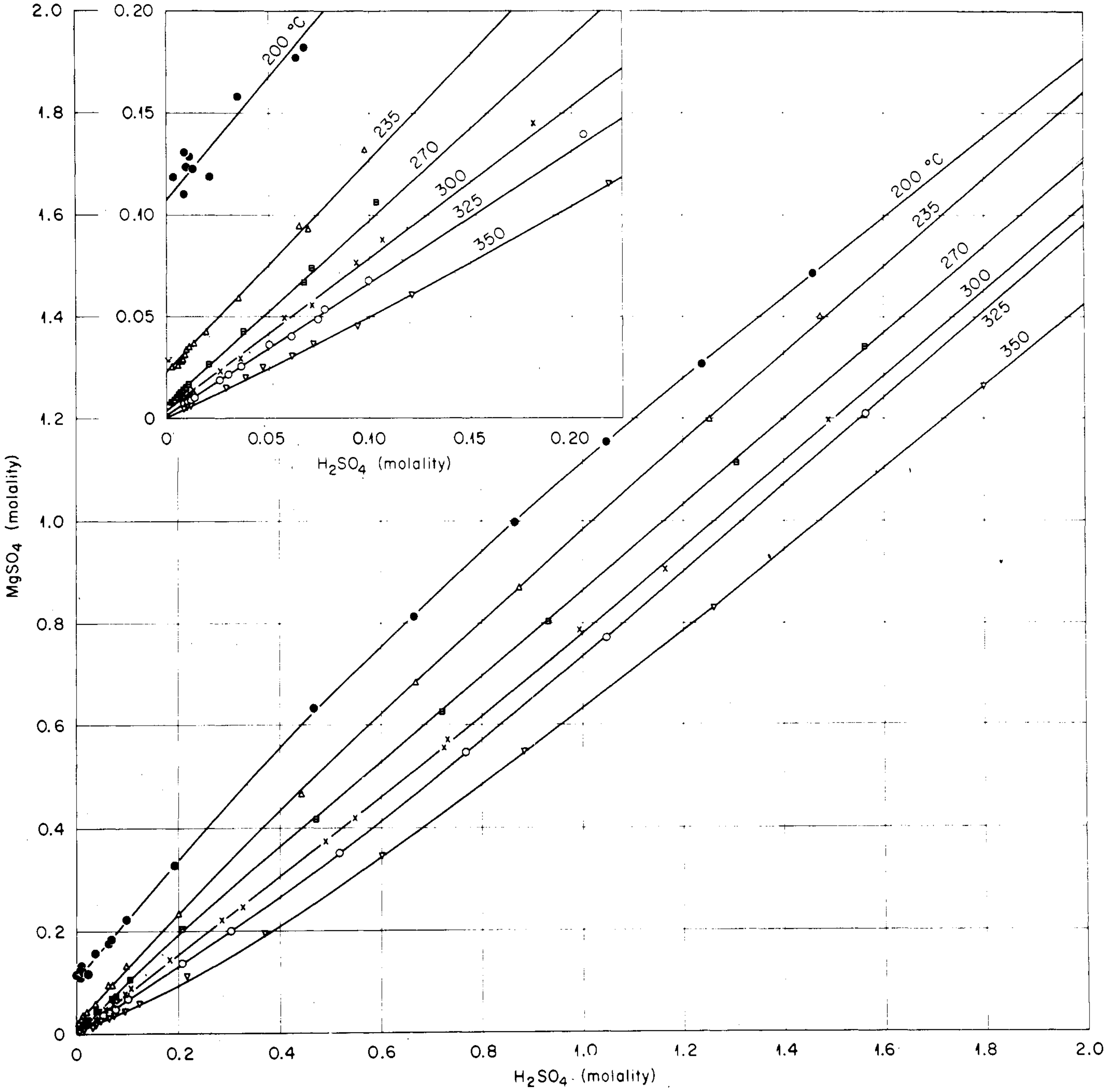

Figure 4. Solubility of $MgSO_4 \cdot H_2O$ in H_2SO_4–H_2O solutions, 200° to 350° C.

Table IV. Equation and Coefficients for the Solubility of $MgSO_4 \cdot D_2O$ in D_2SO_4–D_2O Solution, 200° to 350° C.

(Applicable for ranges of curves shown in Figure 5)

$$m_{MgSO_4} = a_0 + a_1(m_{D_2SO_4}) + a_2(m_{D_2SO_4})^2 + a_3(m_{D_2SO_4})^3$$

T, ° C.	a_0	a_1	a_2	a_3	Std. Error of Fit, Molal Units	No. of Observations, n
200	+0.05847	+1.226	−0.2468	+0.05624	0.00658	9
235	+0.01033	+1.125	−0.2055	+0.05223	0.00515	8
270	+0.00470	+0.9354	−0.04035	+0.01087	0.00166	8
300	+0.00443	+0.8190	+0.04903	−0.01012	0.00359	9
325	+0.00079	+0.7131	+0.1127	−0.02302	0.00364	9
350	−0.00162	+0.5874	+0.1441	−0.01893	0.00894	8

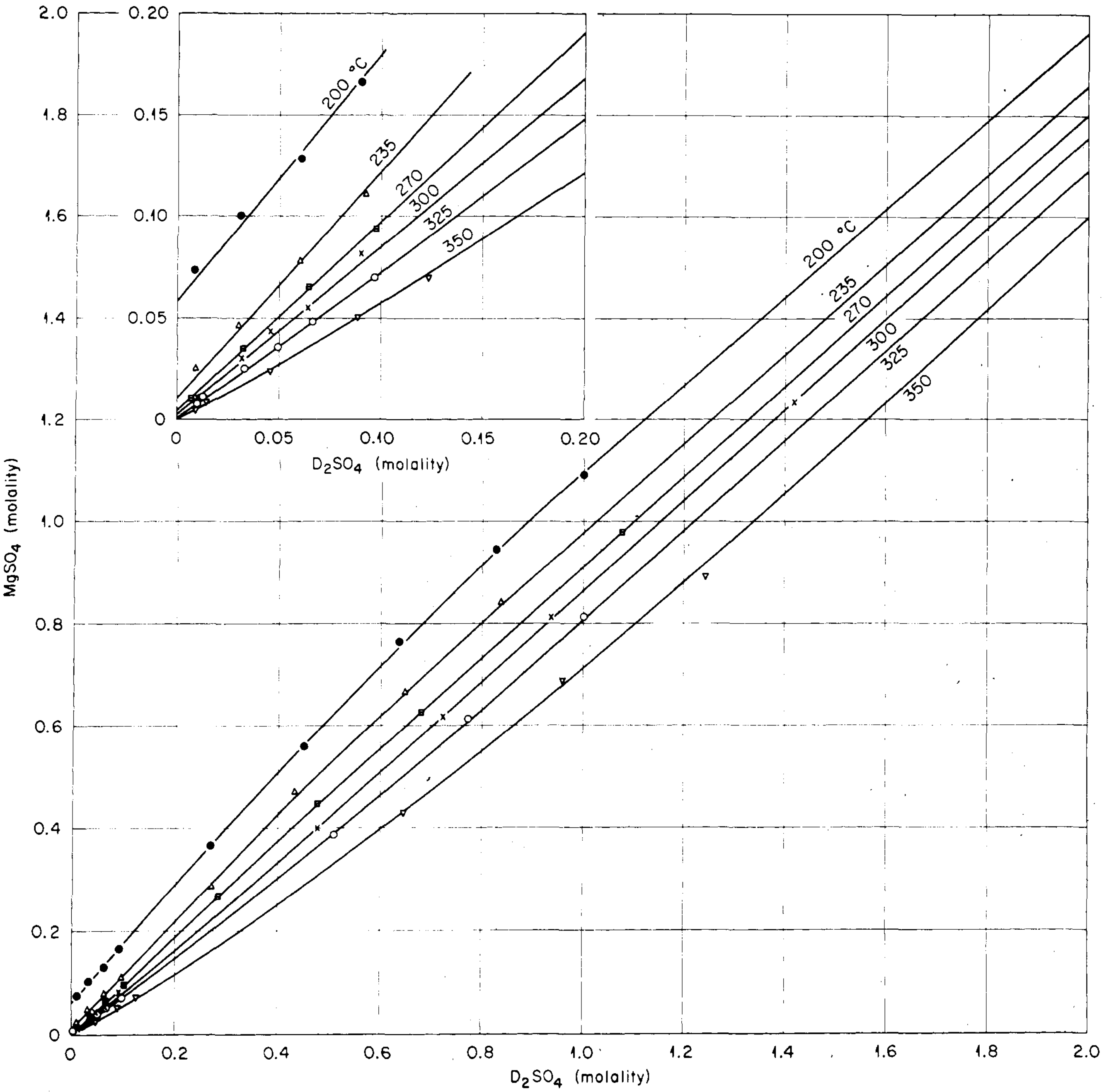

Figure 5. Solubility of $MgSO_4 \cdot D_2O$ in D_2SO_4–D_2O solutions, 200° to 350° C.

directly and by an estimation procedure similar to one described previously (*6*).

RESULTS AND DISCUSSION

General. In Figures 1 and 2, the experimental solubilities in the systems MgO-SO_3-H_2O and MgO-SO_3-D_2O at temperatures from 200° to 350° C. and at concentrations of SO_3 from 10^{-2} to 3 molal are plotted as log molality SO_3 *vs.* the saturation molal ratio, $m_{MgO}:m_{SO_3} \equiv R_{Mg}$. The saturating solid phase, $MgSO_4 \cdot H_2O$ (or $MgSO_4 \cdot D_2O$), was identified by comparison of x-ray diffraction patterns of the solid after its removal from an equilibration vessel using the methods described previously (*7*). At low concentrations of SO_3, x-ray diffraction patterns for the saturating solid phases showed lines corresponding to a magnesium oxysulfate ($MgSO_4 \cdot 5MgO \cdot 8H_2O$) reported elsewhere (*11*), and to $Mg(OH)_2$ at the lowest concentrations. Solutions (at 25° C.) of R_{Mg} greater than that drawn for a particular temperature (Figure 1) precipitated either one or two solids, $MgSO_4 \cdot H_2O$, the oxysulfate, or $Mg(OH)_2$, to reach equilibrium at that temperature. For example at 270° C., a 0.1 molal stoichiometric $MgSO_4$ solution (at 25° C.), by producing at equilibrium both $MgSO_4 \cdot H_2O$ and $Mg(OH)_2$, would reach an invariant composition (at 270° C.) along curve *AB* (Figure 1).

At SO_3 molalities lower than those of curve *AB*, different invariant points, or other compositions, were reached where the solid phase was $Mg(OH)_2$ or the oxysulfate (or both) depending upon temperature and concentration. The experimental values for R_{Mg} below curve *AB* were not sufficiently precise to be displayed; the dashed lines represent the values from approximately $\pm 5\%$ above 0.01 molal SO_3 to $\pm 15\%$ near 0.003 molal SO_3. However, in Figure 3, all identifications of solid phases in equilibrium with solution are given, including also identifications of solids from some additional experiments at 135° and 170° C. These saturating solid phases are shown as a function of solution concentration of SO_3. The positions of the cross-over lines connecting $MgSO_4 \cdot H_2O$ solid, stable at high SO_3 concentrations, to $MgSO_4 \cdot 5MgO \cdot 8H_2O$ and $Mg(OH)_2$ were estimated both from the identifications of solids and from the over-all description of the system shown in Figure 1.

Thus, the large decrease in solubility at 200° C. reported by Benrath (*3*) is attributed to hydrolytic instability of stoichiometric $MgSO_4$ solutions, similar to the behavior of $NiSO_4$ solutions (*6*).

Solubility of $MgSO_4 \cdot H_2O$ in H_2SO_4–H_2O. The data, expressed as saturation molality $MgSO_4$ *vs.* molality H_2SO_4, are given in Table I and are shown graphically in Figure 4. Like $NiSO_4 \cdot H_2O$, the solubility increases with increasing acidity but decreases with increasing temperature. The data were evaluated by the method of least squares (with a digitial computer), and are expressed by an empirical equation together with its coefficients in Table II.

Solubility of $MgSO_4 \cdot D_2O$ in D_2SO_4–D_2O. Solubilities in D_2O, expressed as molalities of $MgSO_4$ and D_2SO_4 (Table III), are shown graphically in Figure 5. They have been corrected for the approximately 2 wt. % H_2O impurity in the D_2O (resulting both from an initial 0.2% impurity and from the addition of H_2O_2 to prevent corrosion of the containment vessel) by extrapolating to 100% D_2O, using both the uncorrected values and the values in 100% H_2O (*7*). Coefficients for the empirical cubic equation expressing the data are given in Table IV. Similarly, compared with $NiSO_4 \cdot H_2O$ and $NiSO_4 \cdot D_2O$, the hypothetical stoichiometric solubility in H_2O (represented approximately by the coefficient, a_0, in Table II) is greater than in D_2O (Table IV). In moderately acidic solution, there is a crossover, and the solubility becomes comparatively greater in D_2SO_4. At 350° C., the a_0's are insufficiently precise for comparison. Like the behavior of $NiSO_4 \cdot H_2O$ (and $NiSO_4 \cdot D_2O$) and Li_2SO_4 (and its monohydrate), the comparative differences in solubility appear to be due to the differences in dielectric constant, density, and dissociation constant of the two solvents and to differences in the dissociation constant for HSO_4^- and DSO_4^-. Additional comments are given in the preceding papers (*6, 7*).

LITERATURE CITED

(1) Arditti, R., *Compt. Rend.* **196**, 1388 (1933).
(2) Batuner, L.M., *Zh. Prikl. Khim.* **11**, 391 (1938).
(3) Benrath, A., *Z. anorg. allgem. Chem.* **247**, 147 (1941).
(4) d'Ans, J., Autenrieth, H., Braune, G., Freund, H.E., *Z. Elektrochem.* **64**, 521 (1960); *Kali Steinsalz.* **3**, 15 (1960).
(5) d'Ans, J., Freund, H.E., *Kali Steinsalz.* **3**, 31 (1960).
(6) Marshall, W.L., Gill, J.S., Slusher, R., *J. Inorg. Nucl. Chem.* **24**, 889 (1962).
(7) Marshall, W.L., Slusher, R., Smith, F.J., *Ibid.*, **25**, 559 (1963).
(8) Montemartini, C., Losana, L., *L'Industria Chimica* **4**, 199 (1929).
(9) Seidell, A., "Solubilities of Inorganic and Metal Organic Compounds," 3rd ed., Vol. **I**, p. 985, Van Nostrand, New York, 1940.
(10) Seidell, A., Linke, W.F., "Solubilities of Inorganic and Metal Organic Compounds," Supplement to 3rd ed., p. 354, Van Nostrand, New York, 1952.
(11) Walter-Lévy, L., *Ann. chim.* **7** (11), 121–224 (1937).

RECEIVED for review March 8, 1965. Accepted July 8, 1965. Work sponsored jointly by the U. S. Department of the Interior, Office of Saline Water, and the U. S. Atomic Energy Commission and performed at the Oak Ridge National Laboratory, which is operated by Union Carbide Corporation for the Atomic Energy Commission. Paper XIV in J. CHEM. ENG. DATA **9**, 187 (1964).