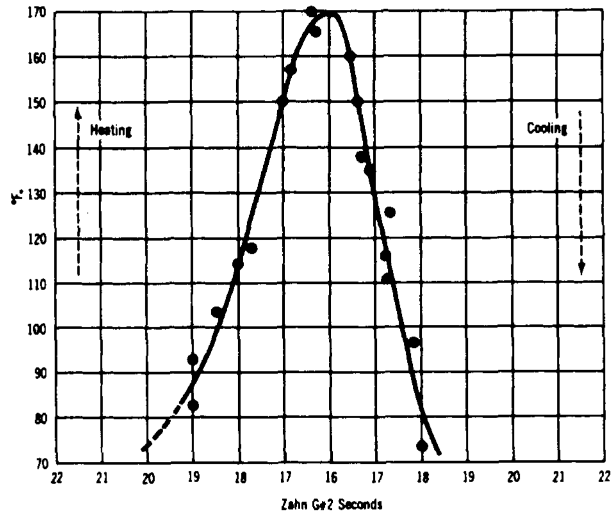

Figure 3. Changes in viscosity with increase and decrease in temperature in a PVM/MA-HA dispersion prepared at 170°F.

this point the solution became slightly more turbid and assumed an amber color (*5*).

No appreciable change in viscosity was observed when PVM/MA copolymer solutions were heated at different temperatures for varying periods of time (*5*). Thus, if the decrease in viscosity, observed in the case of solutions of the half amide, is due to oxidative degradation, it is possible that the reactivity of the tertiary hydrogen atoms is governed in part by the nature of the carboxylate groups. The replacement of carboxyl hydrogens with the amide and/or ammonium groups may favor the formation of hydroperoxides, which in turn readily decompose to bring about chain scission.

Unfortunately, no attempt was made to investigate the fundamental aspects of the observed viscosity behavior. However, the experiments reported were helpful in devising methods for the preparation of improved lithographic plate coating solutions.

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Solubility of Acidic Gases in Aqueous Monoethanolamine

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The solubility behavior of acidic gases in aqueous monoethanolamine (MEA) solution is of particular interest in the proper design and operation of amine-type units for the removal of hydrogen sulfide and carbon dioxide from gaseous systems.

Determinations of the solubility of carbon dioxide in aqueous monoethanolamine solutions, have been made by several investigators. Mason and Dodge (*4*) studied the solubility of carbon dioxide in 0.5, 2.0, 5.0, 9.5, and 12.5*N* solutions at temperatures of 0°, 25°, 50°, and 75°C. and at partial pressures of carbon dioxide ranging from about 20 to 750 mm. Reed and Wood (*7*) published a small-scale plot showing the solubility of carbon dioxide in 2.5*N* (15.3 weight %) MEA solutions at temperatures of 100°, 120°, and 140°C., and carbon dioxide partial pressures from 20 to 250 p.s.i.a. These authors did not claim high accuracy for their measurements. Similar data are given by Reed (*6*). Lyudkovskaya and Leibush (*3*) studied the solubility of carbon dioxide in 0.5, 2, and 5*N* MEA solutions at temperatures of 25°, 50°, and 75°C. and carbon dioxide partial pressures from 2.5 to 40 atm. Muhlbauer and Monaghan (*5*) recently reported data on the solubility of carbon dioxide in 2.5*N* MEA solutions at 25° and 100°C. and partial pressures of about 1 to 1000 mm.

Riegger, Tartar, and Lingafelter (*8*) measured the solubility of hydrogen sulfide in 0.6, 1.0, 1.5, 2.0, 3.0, and 5.0 molal solutions of MEA at temperatures of 25°, 45°, and 60°C. and at partial pressures of hydrogen sulfide from 25 to 700 mm. Leibush and Shneerson (*2*) reported the solubility of hydrogen sulfide in 0.93 and 2.5*N* solutions of MEA at temperatures of 15°, 25°, and 50°C. and over a partial pressure range of about 0.01 to 250 mm. Reed (*6*) included a small-scale plot showing the solubility of hydrogen sulfide at 100° and 120°C., with experimental points covering a partial pressure range of about 22 to 53 p.s.i.a. Muhlbauer and Monaghan (*5*) reported values at 25° and 100°C. for partial pressures of about 1 to 950 mm. Atwood, Arnold, and Kindrick (*1*) computed activity coefficients for the system hydrogen sulfide–MEA–water. Limited data at 25°C. on the solubility of mixtures of carbon dioxide and hydrogen sulfide in 15.3 weight % MEA have been obtained by Leibush and Shneerson (*2*). In their experiment, the hydrogen sulfide concentration was held constant at either 0.145 or 0.265 mole per mole of amine while the carbon dioxide concentration was varied from 0.025 to 0.416 mole per mole of amine. Muhlbauer and Monaghan (*5*) published data on the simultaneous solubility of hydrogen sulfide and carbon dioxide in 15.3 weight % MEA at temperatures of 25° and 100°C. Their data were obtained at hydrogen sulfide partial pressures ranging from 1 to 964 mm. and at carbon dioxide pressures from 1 to 1290 mm.

There are considerable differences in the reported values for the solubilities of hydrogen sulfide and carbon dioxide. Data in the low partial pressure, high temperature region are very meager. The data on mixtures of the two acidic gases are also limited in scope and temperature range covered.

This study was made to provide an accurate, self-consistent set of data for use in the design and optimum operation of amine-type units for removal of acidic gases.

MATERIALS AND EQUIPMENT

The amine solutions were prepared from distilled water and commercial MEA. The MEA analyzed 99.2% by acid titration and contained 0.7% of water. The physical properties of the amine and its aqueous solution were:

	d^{30}_4	n^{20}_D
Commercial MEA	1.0143	1.4541
MEA solution, 15.3 wt. %	1.0065	1.3520

Oil pumped nitrogen, bone dry carbon dioxide, and 99.9 mole % grade hydrogen sulfide were used as received. Mass spectrometer analyses of the hydrogen sulfide showed only trace amounts of methyl mercaptan, carbon disulfide, and carbon dioxide as impurities.

A sketch of the equilibrium vessel is shown in Figure 1. The vessel was constructed from a 500-cubic inch stainless steel oxygen holder. All lines, valves, and fittings were also of stainless steel. The vessel was tapped at a point on top and midway between the ends to provide a vapor sample point. Fittings were added at the ends of the vessel to provide for a liquid sample point and for a pressure gage. A 0 to 60 pound gage with 0.2 pound subdivisions was used in the low and medium pressure range and a 0 to 200 pound gage with 1-pound subdivisions was used in the high pressure range. The pressure gages were calibrated against a dead-weight tester. The equilibrium vessel was fitted into a thermostated oil bath and rocked at a rate of seven cycles per minute. The temperature was controlled to ±0.1°C. at 40°C. and ±0.5°C. at 140°C. The sample bombs were stainless steel vessels having volumes of 10 and 50 ml. and equipped with valves at each end. One end was fitted with a stainless steel line for evacuation of the sample bomb prior to collecting the sample.

EXPERIMENTAL PROCEDURE

The entire system was purged with nitrogen and a gage pressure of 5 to 10 pounds was established in the equilibrium vessel. A vessel containing 2 liters of MEA solution having predetermined carbon dioxide and hydrogen sulfide contents was attached to the liquid sample port. The nitrogen in the equilibrium vessel was used to purge air from the liquid line and amine container. The amine solution of carbon dioxide and hydrogen sulfide was forced into the vessel using nitrogen pressure and the nitrogen flow was continued until the liquid line was free of amine. The liquid sample valve was then closed and the liquid and vapor sample bombs were attached. For the vapor samples collected at 60°C. and above, a drying tube containing carbon dioxide-saturated magnesium perchlorate was placed before the sample container to remove most of the water vapor and to prevent water condensation in the sample bomb.

The vessel was lowered into the constant temperature bath and connected to the rocking device. The system usually attained the temperature of the bath and indicated a constant gage pressure after about 1 hour. The vessel was rocked for an additional hour after a constant pressure was indicated, to ensure equilibrium of the system. The rocking was stopped with the solution covering the liquid sample port and a sample of the solution was taken into the weighed and evacuated sample bomb. A sample of the vapor was taken at the temperature and pressure of the system.

The concentrations of carbon dioxide and hydrogen sulfide in the vapor were determined on a dry basis by mass spectrometer analyses. The partial pressures of carbon dioxide and hydrogen sulfide above the amine solution were computed, employing (1) the mass spectrometer analysis, (2) the calculated value for the vapor pressure of a 15.3 weight % amine solution at the experimental temperature, and (3) the gage and atmospheric pressures.

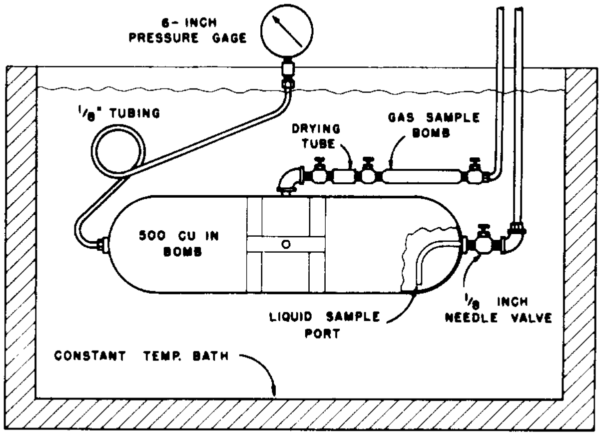

Figure 1. Equilibrium vessel

The amount of sample in the liquid phase sample bomb was determined by weight. The bomb was then chilled to ice temperature and the solution was washed into a 250-ml. volumetric flask containing about 50 ml. of cold water. The solution was diluted to almost 250 ml., allowed to warm to room temperature, and diluted to the mark with distilled water. When the amine solutions contained high concentrations of acidic gases, about 50 ml. of 15.3 weight % amine were placed in the flask instead of water to prevent the loss of acidic gases.

The hydrogen sulfide content of the liquid was determined by adding a suitable aliquot of the amine solution to an excess of acidified iodine solution. The excess iodine was back-titrated with standard thiosulfate solution. The hydrogen sulfide content of the original sample was then computed and expressed as moles of hydrogen sulfide per mole of amine.

Aliquots of the amine solution were used for carbon dioxide determinations which were made by two procedures: by precipitation as carbonate with barium chloride and by a modified Knorr (*9*) procedure. In the latter method, an aliquot of the sample is acidified with sulfuric acid and the solution is heated. The released carbon dioxide is swept from the reaction flask with nitrogen and passed in series through a drying tube and a tared absorption tube containing a carbon dioxide absorbent, Caroxite. When hydrogen sulfide was present, acidified potassium permanganate was used to remove hydrogen sulfide from the gas stream. The two analytical methods gave check values for the carbon dioxide content of the solution in regions where carbamates were not formed. When the total carbon dioxide plus hydrogen sulfide content of the solution was high, the barium chloride precipitation method generally gave low results, apparently because of the formation of carbamates in the solutions at the higher acid gas loadings. The analyses by acid evolution were used in most cases to compute the carbon dioxide content of the liquid phase.

RESULTS AND DISCUSSION

Carbon Dioxide. The experimentally determined solubility data for carbon dioxide in 15.3 weight % MEA at temperatures of 40°, 60°, 80°, 100°, 120°, and 140°C. are tabulated in Table I. A plot of these data (carbon dioxide partial pressure vs. moles of carbon dioxide per mole of MEA) shown in Figure 2 illustrates the changes in the partial pressure of carbon dioxide with temperature. Smoothed values of the data at selected partial pressures are presented in Table II. These values were obtained from large scale plots similar to Figure 2.

Certain experimental determinations were made to check the reproducibility of the data. The liquid phases for Nos. 6 and 31 were sampled before and after taking a vapor sample. The experimental values for moles of carbon dioxide per mole of MEA were 0.493 and 0.497 for No. 6 and 0.449 and 0.454 for No. 31. Determinations 7 and 8 represent values from duplicate samplings of the same solution 24 hours apart. In these tests, values for the carbon dioxide partial pressure differed by 2.4% and for the carbon dioxide content of the liquid by 0.5%. The same procedure was used in Nos. 28 and 29. The carbon dioxide partial pressures differed by 0.1% and the carbon dioxide content of the liquid by 0.6%. Replicate determinations of the carbon dioxide content of the same solution usually agreed within 0.5%. For partial pressures less than about 1 mm., the mass spectrometer analyses are probably not accurate to better than about 20%.

The data given in Table I and shown graphically in Figure 2 provide an accurate representation of the solubility behavior of carbon dioxide over the regions investigated. The isotherms in Figure 2 show only moderate curvature at 100 °C. and above in the region of medium and high carbon dioxide partial pressures. However, at low carbon dioxide partial pressures, the carbon dioxide content of the solution must decrease much faster than an extrapolated straight line value would indicate, since the partial pressure at zero concentration is zero. The pressure at which this deviation occurs increases as the temperature is increased. There appears to be no sharp break as the concentration of carbon dioxide increases past the stoichiometric concentration of 0.5 mole per mole of amine.

Table I. Solubility of Carbon Dioxide in 15.3 Weight % MEA

Detn. No.	Temp., °C.	Vapor Compn., Partial Press. CO_2, Mm. Hg	Liquid Compn., Mole CO_2/Mole MEA
1	40	0.56	0.305
2	40	0.74	0.312
3	40	2.18	0.404
4	40	2.50	0.412
5	40	14.9	0.485
6	40	17.5	0.495
7	40	165	0.599
8	40	169	0.602
9	40	563	0.684
10	40	570	0.685
11	40	905	0.713
12	60	17.8	0.437
13	60	268	0.571
14	60	271	0.567
15	60	1215	0.665
16	80	48.4	0.398
17	80	70.7	0.427
18	80	90.2	0.437
19	80	143	0.460
20	80	192	0.484
21	80	260	0.498
22	80	385	0.520
23	80	501	0.538
24	80	924	0.578
25	80	4073	0.694
26	80	6206	0.728
S	100	0.02	0.017
S	100	0.1	0.039
S	100	0.6	0.076
S	100	2.0	0.111
S	100	4.0	0.140
S	100	6.0	0.160
27	100	42.0	0.266
28	100	98.4	0.347
29	100	98.5	0.345
30	100	174	0.380
31	100	428	0.452
32	100	974	0.502
33	100	3242	0.602
34	100	4346	0.627
35	100	5426	0.649
36	120	89.4	0.215
37	120	242	0.301
38	120	425	0.343
39	120	1038	0.417
40	120	2396	0.492
41	120	4491	0.531
42	120	6983	0.599
43	140	138	0.133
44	140	366	0.211
45	140	464	0.232
46	140	690	0.265
47	140	3346	0.420
48	140	4862	0.460

Smoothed values interpolated from 10 and 20 wt. %.
MEA solution values obtained by gas saturation method.

The data of Mason and Dodge (*4*) and of Lyudkovskaya and Leibush (*3*) were interpolated to give values for a 15.3 weight % MEA solution at 40°C. In the range of 20 to 760 mm. partial pressure of carbon dioxide, the agreement between the authors' data and those of Mason and Dodge is good. The close agreement in this region is evidence that no appreciable errors were introduced into these determinations by the use of nitrogen to provide superatmospheric pressures to facilitate sampling. The values at low carbon dioxide partial pressures have not been previously determined. The data of Lyudkovskaya and Leibush generally were obtained at higher partial pressures than those of this study.

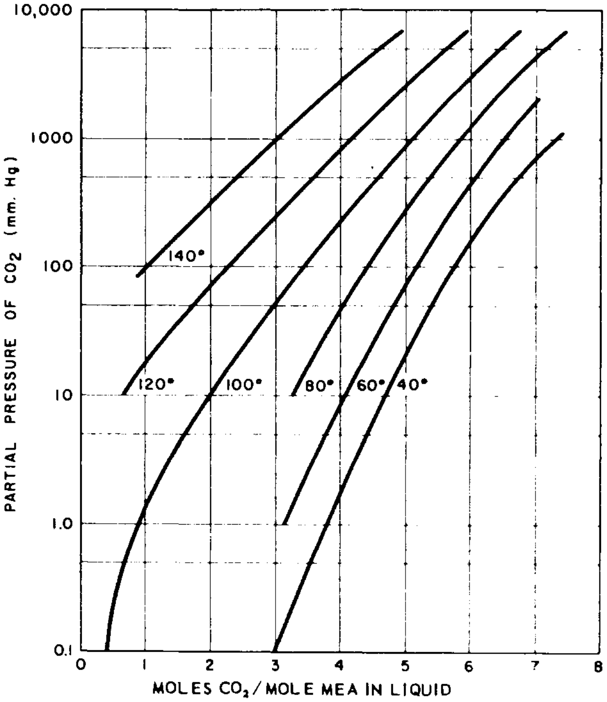

Figure 2. Solubility of carbon dioxide in 15.3 weight % monoethanolamine at various temperatures

Table II. Smoothed Values for Solubility of Carbon Dioxide in 15.3 Weight % MEA

Partial Press. CO_2, Mm. Hg	Mole Carbon Dioxide per Mole MEA 40° C.	60° C.	80° C.	100° C.	120° C.	140° C.
1	0.383	...	...	0.096	...	...
5	0.438	...	...	0.152	...	...
10	0.471	0.412	...	0.194	...	...
30	0.518	0.459	0.379	0.265	...	...
50	0.542	0.482	0.405	0.299	...	...
70	0.558	0.498	0.422	0.322	0.200	...
100	0.576	0.516	0.442	0.347	0.227	0.109
200	0.614	0.552	0.481	0.393	0.281	0.162
300	0.639	0.574	0.505	0.423	0.314	0.194
400	0.657	0.591	0.523	0.442	0.336	0.219
500	0.672	0.605	0.538	0.458	0.355	0.237
600	0.686	0.615	0.550	0.472	0.370	0.254
760	0.705	0.631	0.566	0.489	0.390	0.275
1000	0.727	0.650	0.584	0.509	0.413	0.300
2000	...	0.702	0.637	0.562	0.476	0.366
3000	...	...	0.669	0.596	0.513	0.408
5000	...	...	0.712	0.641	0.562	0.464
7000	...	...	0.742	0.672	0.597	0.500

The data of this study would extrapolate to yield somewhat lower values of partial pressure at the same solution loadings.

The agreement at 100°C. between the authors' data and those of Muhlbauer and Monaghan (*5*) is good at partial pressures above 200 mm. At lower partial pressures, the present data show higher solution loadings for the same partial pressures.

Hydrogen Sulfide. The experimentally determined solubility data for the system hydrogen sulfide–15.3 weight % MEA at 40°, 60°, 80°, 100°, 120°, and 140°C. are given in Table III. A plot of the hydrogen sulfide partial pressure versus moles of hydrogen sulfide per mole of MEA in the liquid phase is shown in Figure 3. This plot shows graphically the changes in partial pressure of hydrogen sulfide with temperature. Smoothed values of the data at selected partial pressures are given in Table IV. These values were obtained from large scale plots similar to those shown in Figure 3.

The general operability of the experimental apparatus has been discussed previously. Determinations 16 and 17 represent duplicate sampling of the liquid and vapor phases from the same solution taken 24 hours apart. The hydrogen sulfide contents of the two liquid layers in these duplicate runs agreed within 1%. The values obtained for the vapor compositions also were within this limit. Generally, the deviations of the experimental points from the smooth curve were also within 1%.

The data given in Table III and shown graphically in Figure 3 are believed to provide an accurate representation of the solubility of hydrogen sulfide in the regions investigated. The isotherm of 40°C. has a pronounced S-shape (Figure 3). However, above 60°C. the isotherms appear to follow smooth curves with no S-shape characteristics.

Table III. Solubility of Hydrogen Sulfide in 15.3 Weight % MEA

Temp., °C.	Vapor Compn., Partial Press. H_2S, Mm. Hg	Liquid Compn., Mole H_2S/Mole MEA
40	0.96	0.125
	3.0	0.208
	9.1	0.362
	43.1	0.643
	59.7	0.729
	106	0.814
	143	0.842
	188	0.884
	261	0.920
	409	0.948
	600	0.965
60	7.1	0.202
	11.2	0.251
	36.3	0.419
	125	0.636
	433	0.849
	436	0.842
	847	0.952
80	6.7	0.119
	32.1	0.251
	88.8	0.403
	228	0.569
	515	0.711
100	2.1	0.041
	6.7	0.066
	48.0	0.199
	230	0.396
	719	0.612
120	5.1	0.036
	22.1	0.088
	130	0.206
	513	0.394
140	4.9	0.025
	34.5	0.077
	296	0.197

Table IV. Smocthed Values for Solubility of Hydrogen Sulfide in 15.3 Weight % MEA

Partial Press. H_2S, Mm. Hg	Mole Hydrogen Sulfide per Mole MEA					
	40° C.	60° C.	80° C.	100° C.	120° C.	140° C.
1	0.128	...	...	0.029	...	...
3	0.212	0.137	...	0.050	0.025	0.016
5	0.271	0.171	...	0.065	0.036	0.025
10	0.374	0.240	0.141	0.091	0.056	0.040
30	0.579	0.386	0.243	0.160	0.101	0.072
50	0.683	0.472	0.314	0.203	0.139	0.091
70	0.750	0.534	0.364	0.238	0.153	0.106
100	0.802	0.600	0.422	0.279	0.182	0.124
200	0.890	0.722	0.545	0.374	0.256	0.167
300	0.931	0.790	0.617	0.439	0.312	0.200
400	0.949	0.836	0.666	0.490	0.357	0.226
500	0.959	0.871	0.706	0.536	0.393	...
600	0.970	0.900	0.738	0.575	0.426	...
700	0.980	0.921	...	0.607	0.453	...
800	...	0.942	...	0.636	...	...

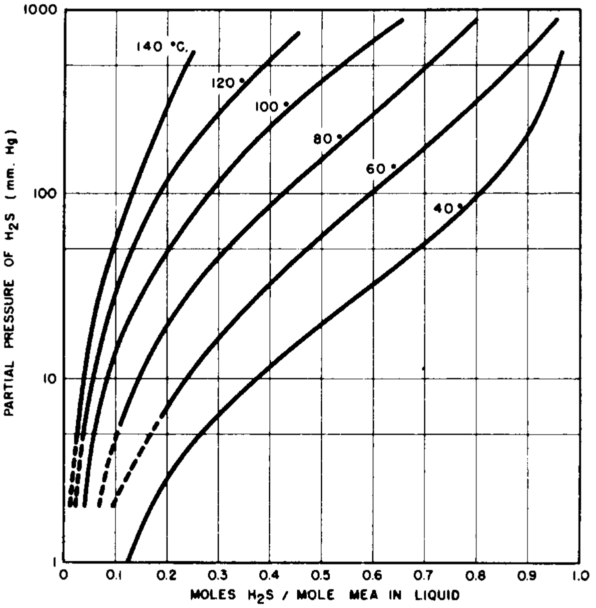

Figure 3. Solubility of hydrogen sulfide in 15.3 weight % monoethanolamine at various temperatures

The interpolated data of Riegger and others (*8*) at 40°C. cross the authors' curve at about 65-mm. partial pressure of hydrogen sulfide. At lower partial pressures their values are below the curve and at higher concentrations above the curve. At most, the liquid loading expressed as moles of hydrogen sulfide per mole of amine for a given partial pressure above 65 mm. differs from the authors' by about 2%. Because of the steepness of the solubility curve, however, this causes the partial pressures at a given liquid composition to deviate by as much as 25%. At 60°C., the data of Riegger and others cross the authors' curve at about 50-mm. partial pressure of hydrogen sulfide. Their data at partial pressures above 50 mm. are below the authors' curve. The maximum deviation in liquid loading at a given partial pressure of hydrogen sulfide is less than 5%. Because the curve is flatter than the 40°C. curve, the partial pressures at constant liquid loading differ from the authors' by less than 20%. Below 10-mm. partial pressure at 40°C., the agreement with Leibush and Shneerson (2) is good. Above 10-mm. partial pressure, however, the values of Leibush and Shneerson deviate from those of this investigation, the deviation becoming greater as the partial pressure becomes larger. Part of the deviation is probably caused by the presence of carbon dioxide in the solutions used by Leibush and Shneerson.

At 100°C., the data of this study agree closely with those of Muhlbauer and Monaghan at partial pressures above 100 mm. Below this value, data of this paper yield higher solution loadings at the same measured partial pressures. The values for the partial pressure of hydrogen sulfide determined in this investigation are much lower than those of Reed (*6*) at comparable liquid compositions.

Mixtures of Carbon Dioxide and Hydrogen Sulfide. The experimentally determined solubility data for the system carbon dioxide–hydrogen sulfide–15.3 weight % MEA at 40°, 60°, 100°, and 120°C. are given in Table V. A plot of the data at 40°C. (hydrogen sulfide partial pressure *vs.* moles of hydrogen sulfide per mole of MEA) is shown in Figure 4. Lines are drawn representing constant ratios of hydrogen sulfide to carbon dioxide in the liquid phase. A cross plot of the data at selected partial pressures is shown in Figure 5. Figures 6 and 7 are analogous plots based on the ratio of hydrogen sulfide to carbon dioxide in the vapor phase. Table VI contains interpolated values for hydrogen sulfide concentrations in MEA at selected partial pressures and ratios of hydrogen sulfide to carbon dioxide in the liquid phase at temperatures of 40°, 60°, 100°, and 120°C. A similar tabulation is given in Table VII at constant ratios of hydrogen sulfide to carbon dioxide in the vapor phase.

Because the same basic equilibrating, sampling, and analytical procedures were used as in the previous work, it is assumed that the precision and accuracy of these studies are comparable. The only change was in the method for the determination of the carbon dioxide content of the liquid phase in which the hydrogen sulfide was removed by the use of acidified potassium permanganate. Check determinations for the carbon dioxide contents of six different solutions by the modified Knorr method and by precipitation of barium carbonate agreed within 1% when carbamates were absent. The

Table V. Solubility of Hydrogen Sulfide Plus Carbon Dioxide in 15.3 Weight % MEA

Temp., °C.	Vapor Compn., Mm. Hg		Liquid Compn., Mole/Mole MEA		Mole Ratio H_2S/CO_2	
	PP. H_2S	PP. CO_2	H_2S	CO_2	Vapor	Liquid
40	1.1	1.4	0.0164	0.387	0.78	0.042
	2.1	3.1	0.0214	0.424	0.68	0.051
	2.2	1.9	0.0282	0.400	1.2	0.071
	5.2	13.4	0.0248	0.480	0.39	0.052
	5.4	13.3	0.0272	0.472	0.41	0.058
	5.7	2.5	0.0612	0.392	2.3	0.156
	5.8	5.4	0.0436	0.436	1.1	0.100
	7.6	1.4	0.101	0.349	5.4	0.289
	8.7	434	0.0056	0.652	0.020	0.0086
	8.8	43.2	0.0199	0.527	0.20	0.038
	15.2	26.2	0.0488	0.488	0.580	0.100
	16.8	7.5	0.106	0.412	2.2	0.257
	19.6	455	0.0123	0.658	0.043	0.019
	43.0	17.8	0.149	0.424	2.42	0.351
	55.8	3.0	0.361	0.200	18.7	1.81
	76.4	7.8	0.351	0.293	9.8	1.20
	108	18.5	0.314	0.335	5.86	0.937
	117	45.6	0.235	0.415	2.58	0.566
	128	522	0.0712	0.620	0.245	0.115
	131	532	0.0716	0.620	0.246	0.116
	337	148	0.327	0.414	2.28	0.790
	842	353	0.425	0.406	2.39	1.05
	1409	578	0.495	0.398	2.44	1.24
60	0.95	10.7	0.0074	0.406	0.12	0.023
	5.2	2.8	0.0597	0.290	1.8	0.206
	5.9	0.8	0.107	0.166	7.4	0.644
	10.2	435	0.0070	0.594	0.023	0.012
	14.4	130	0.0200	0.529	0.111	0.038
	21.9	41.9	0.0569	0.452	0.523	0.126
	23.2	14.2	0.0878	0.381	1.63	0.230
	71.5	9.6	0.255	0.274	7.4	0.930
	80.2	753	0.0396	0.606	0.107	0.065
	396	374	0.238	0.460	1.06	0.517
	1496	3504	0.235	0.570	0.427	0.412
100	2.8	57.4	0.0053	0.293	0.049	0.018
	5.2	322	0.0050	0.420	0.016	0.012
	7.0	13.0	0.0272	0.171	0.54	0.159
	15.4	281	0.0140	0.412	0.055	0.034
	25.6	59.3	0.0460	0.272	0.432	0.169
	37.5	570	0.0245	0.456	0.066	0.054
	57.4	30.2	0.112	0.180	1.90	0.622
	150	77.5	0.178	0.238	1.93	0.748
	280	640	0.140	0.405	0.438	0.346
	467	98.2	0.366	0.175	4.75	2.09
120	6.6	328	0.0059	0.322	0.020	0.0183
	10.1	7.7	0.0405	0.0393	1.3	1.03
	14.9	28.9	0.0344	0.106	0.516	0.324
	15.3	66.3	0.0264	0.178	0.231	0.148
	39.3	286	0.0361	0.298	0.138	0.121
	72.9	141	0.104	0.202	0.517	0.515
	77.5	154	0.104	0.200	0.502	0.520
	108	316	0.0940	0.280	0.340	0.336

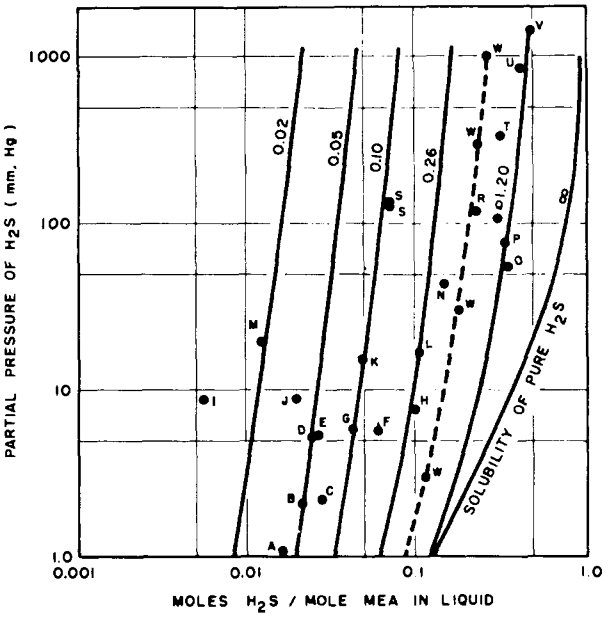

Figure 4. Solubility of hydrogen sulfide in 15.3 weight % monoethanolamine containing carbon dioxide at 40°C.

(Lines at constant mole ratios H_2S/CO_2 in liquid, R_L)

	R_L		R_L		R_L
A.	0.042	*I*.	0.0086	*Q*.	0.937
B.	0.051	*J*.	0.038	*R*.	0.566
C.	0.071	*K*.	0.100	*S*.	0.115
D.	0.052	*L*.	0.257	*S*.	0.116
E.	0.058	*M*.	0.019	*T*.	0.790
F.	0.156	*N*.	0.351	*U*.	1.05
G.	0.100	*O*.	1.81	*V*.	1.24
H.	0.289	*P*.	1.20	*W*.	0.50 (interpolated)

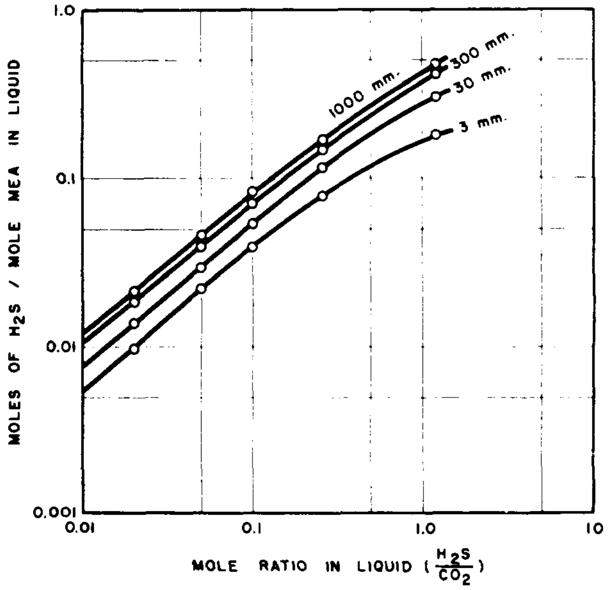

Figure 5. Effect of liquid mole ratio (H_2S/CO_2) on hydrogen sulfide content of 15.3 weight % monoethanolamine containing carbon dioxide at 40°C.

(Lines at constant pressures of hydrogen sulfide)

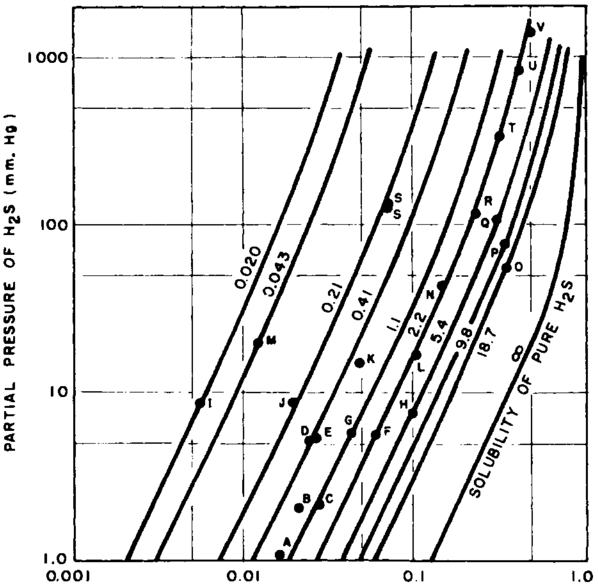

Figure 6. Solubility of hydrogen sulfide in 15.3 weight % monoethanolamine containing carbon dioxide at 40° C.

(Lines at constant mole ratios H_2S/CO_2 in vapor, R_V)

	R_V		R_V		R_V
A.	0.78	*I*.	0.020	*Q*.	5.86
B.	0.68	*J*.	0.20	*R*.	2.58
C.	1.2	*K*.	0.580	*S*.	0.245
D.	0.39	*L*.	2.2	*S*.	0.246
E.	0.41	*M*.	0.043	*T*.	2.28
F.	2.3	*N*.	2.42	*U*.	2.39
G.	1.1	*O*.	18.7	*V*.	2.44
H.	5.4	*P*.	9.8		

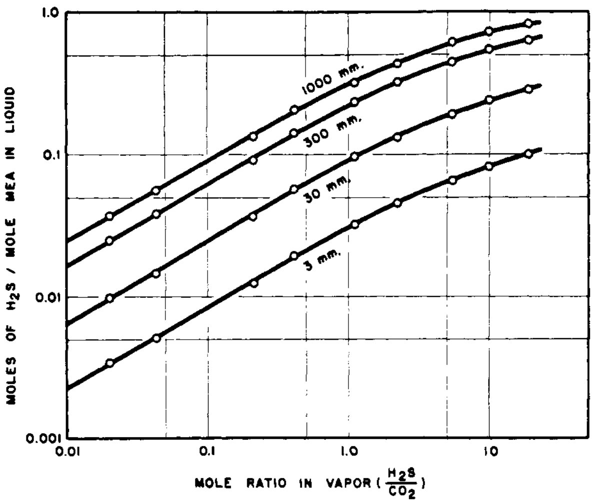

Figure 7. Effect of vapor mole ratio (H_2S/CO_2) on hydrogen sulfide content of 15.3 weight % monoethanolamine containing carbon dioxide at 40 °C.

(Lines at constant pressures of hydrogen sulfide)

precision of the determination of the hydrogen sulfide and carbon dioxide contents of the solutions was to better than 1%.

In addition to the experimental values given in Table V, the mole ratios of hydrogen sulfide to carbon dioxide in both the liquid phase, (R_L), and vapor phase, (R_V), are tabulated. The manner in which these mole ratios are used to correlate the data is illustrated using the 40°C. data. The partial pressure of hydrogen sulfide is plotted against the hydrogen sulfide content of the solution (see Figure 4). Lines are drawn representing constant ratios of hydrogen sulfide to carbon dioxide in the liquid phase. The limiting line is the solubility curve for pure hydrogen sulfide in 15.3 weight % MEA. This line represents an infinite ratio of hydrogen sul-

Table VI. Hydrogen Sulfide Partial Pressure over Monoethanolamine Solutions Containing Carbon Dioxide and Hydrogen Sulfide

Temp., °C.	Partial Press. H_2S, Mm.	Mole H_2S per Mole MEA					
		$R_L{}^a = 0.01$	$R_L = 0.05$	$R_L = 0.10$	$R_L = 0.50$	$R_L = 1.0$	$R_L = \infty$
40	1	0.0047	0.0190	0.0327	0.0863	0.1140	0.128
	3	0.0055	0.0225	0.0395	0.1160	0.1630	0.212
	10	0.0066	0.0263	0.0468	0.1510	0.2220	0.374
	30	0.0077	0.0301	0.0540	0.1820	0.2720	0.579
	100	0.0092	0.0351	0.0619	0.2120	0.3260	0.802
	300	...	0.0399	0.0710	0.2350	0.3720	0.931
	1000	...	0.0464	0.0830	0.2700	0.4250	1.00
60	1	0.0037	0.0145	0.0237	0.0650	0.0775	0.085
	3	0.0046	0.0184	0.0304	0.0845	0.1130	0.137
	10	0.0059	0.0234	0.0396	0.1125	0.1600	0.240
	30	0.0074	0.0288	0.0492	0.1450	0.2120	0.386
	100	0.0092	0.0355	0.0605	0.1840	0.2750	0.600
	300	...	0.0431	0.0730	0.2190	0.3230	0.790
	1000	...	...	0.0910	0.2620	0.3840	0.970
100	1	0.0024	0.0067	0.0103	0.0220	0.0247	0.029
	3	0.0036	0.0101	0.0155	0.0340	0.0407	0.050
	10	0.0056	0.0155	0.0239	0.0540	0.0675	0.091
	30	0.0082	0.0228	0.0349	0.0810	0.1040	0.160
	100	...	0.0343	0.0524	0.1250	0.1650	0.279
	300	...	0.0503	0.0762	0.1800	0.2430	0.439
	1000	...	...	...	0.2480	0.3340	0.680
120	1	0.0016	0.0031	0.0040	0.0072	0.0088	0.012
	3	0.0030	0.0059	0.0078	0.0146	0.0184	0.025
	10	0.0059	0.0120	0.0163	0.0312	0.0393	0.056
	30	0.0110	0.0228	0.0308	0.0590	0.0750	0.101
	100	...	0.0424	0.0558	0.1075	0.1400	0.182
	300	...	...	0.0935	0.1800	0.2325	0.312
	1000	...	...	...	0.3120	0.4050	0.520

$^aR_L = \dfrac{\text{mole } H_2S/\text{mole MEA}}{\text{mole } CO_2/\text{mole MEA}}$.

Table VII. Hydrogen Sulfide and Carbon Dioxide Partial Pressures over Monoethanolamine Solutions Containing Hydrogen Sulfide and Carbon Dioxide

Temp., °C.	Partial Press. H_2S, Mm.	Mole H_2S per Mole MEA						
		R_V[a] = 0.01	$R_V = 0.05$	$R_V = 0.10$	$R_V = 0.50$	$R_V = 1.0$	$R_V = 10$	$R_V = \infty$
40	1	0.0013	0.0035	0.0050	0.0120	0.0178	0.0500	0.128
	3	0.0022	0.0057	0.0084	0.0208	0.0300	0.0825	0.212
	10	0.0039	0.0100	0.0149	0.0380	0.0540	0.1450	0.374
	30	0.0064	0.0166	0.0250	0.0630	0.0910	0.2400	0.579
	100	0.0107	0.0279	0.0415	0.1050	0.1510	0.3900	0.802
	300	0.0167	0.0430	0.0638	0.1550	0.2200	0.5500	0.931
	1000	...	0.0625	0.0920	0.2170	0.3050	0.7300	1.00
60	1	0.0019	0.0049	0.0070	0.0172	0.0239	0.0643	0.085
	3	0.0029	0.0074	0.0108	0.0260	0.0363	0.0940	0.137
	10	0.0044	0.0115	0.0172	0.0414	0.0565	0.1420	0.240
	30	0.0066	0.0175	0.0260	0.0621	0.0850	0.2080	0.386
	100	0.0102	0.0272	0.0405	0.0980	0.1360	0.3140	0.600
	300	...	0.0410	0.0610	0.1480	0.2040	0.4320	0.790
	1000	...	...	0.0940	0.2170	0.2900	0.5500	0.970
100	1	0.0017	0.0034	0.0046	0.0095	0.0118	0.0224	0.029
	3	0.0030	0.0061	0.0082	0.0163	0.0207	0.0390	0.050
	10	0.0056	0.0114	0.0155	0.0301	0.0381	0.0720	0.091
	30	0.0098	0.0200	0.0270	0.0525	0.0665	0.1260	0.160
	100	0.0176	0.0360	0.0483	0.0945	0.1200	0.2250	0.279
	300	...	0.0585	0.0780	0.1510	0.1910	0.3700	0.439
	1000	...	...	...	0.2250	0.2880	0.5820	0.680
120	1	0.0013	0.0024	0.0031	0.0058	0.0078	0.0115	0.012
	3	0.0026	0.0050	0.0065	0.0122	0.0160	0.0245	0.025
	10	0.0056	0.0107	0.0140	0.0265	0.0352	0.0520	0.056
	30	0.0110	0.0210	0.0278	0.0535	0.0705	0.0980	0.101
	100	...	0.0429	0.0573	0.1110	0.1380	0.1800	0.182
	300	...	...	0.1010	0.1850	0.2250	0.3020	0.312
	1000	...	...	...	0.3000	0.3630	0.5000	0.520

[a] $R_V = \frac{\text{pp. } H_2S}{\text{pp. } CO_2}$.

fide to carbon dioxide and aids in establishing the shape of the nearby constant R_L lines. To establish the position of even-interval R_L lines, a cross plot is prepared as shown in Figure 5. The lines represent the selected constant partial pressures of hydrogen sulfide. From these curves, interpolated values may be read for even-interval lines. Figure 6 is a plot similar to that shown in Figure 4, except that lines are drawn for constant R_V values. Figure 7 is the corresponding cross plot.

From Figure 5, for example, curves can be derived which show the partial pressures of hydrogen sulfide in equilibrium with solutions containing varying amounts of hydrogen sulfide at any predetermined ratio of hydrogen sulfide to carbon dioxide in the liquid. To illustrate the use of those charts, assume that the ratio of hydrogen sulfide to carbon dioxide in the solution is 0.5. Reading from Figure 5 at $R_L = 0.5$ gives the following:

Partial Pressure of H_2S, mm. of Hg	Moles H_2S/Mole MEA (Liquid)
3	0.116
30	0.182
300	0.236
1000	0.270

These values are marked W on Figure 4. Large scale plots such as these were made at liquid ratios of 0.01, 0.05, 0.10, 0.50, and 1.00. Partial pressures and solution loadings as read from such curves are tabulated in Table VI.

The data were similarly treated, using Figures 6 and 7 to yield even-interval R_V lines. Data read from these curves are given in Table VII. In a similar manner, the data at 60°, 100°, and 120°C. were treated to yield the interpolated values that are given in Tables VI and VII for these temperatures. Data are not included in these tables which would represent partial pressures of hydrogen sulfide less than 1 mm. or total solution loadings of more than 1 mole of acidic gas per mole of MEA, because the experimental data did not extend into these regions.

From plots similar to Figures 4, 5, 6, and 7, one can obtain equilibrium concentrations of hydrogen sulfide (or carbon dioxide) when either the composition of the gas phase or solution is known. When sufficient constant ratio lines are obtained and plotted similarly to those of Figure 4 or 6, graphical interpolation on these plots may be made without resorting to further use of Figures 5 or 7. For example, if the concentrations of hydrogen sulfide and carbon dioxide in the liquid phase are known, the ratio, R_L, is fixed. Then using the concentration of hydrogen sulfide in the liquid and the R_L value, the partial pressure of hydrogen sulfide is read from the R_L plot (Figure 4). With a plot similar to Figure 6 and the vapor and liquid concentrations of hydrogen sulfide the value for $R_V \; \frac{ppH_2S}{ppCO_2}$ is obtained. The partial pressure of carbon dioxide is then given by dividing the hydrogen sulfide pressure by R_V. When the values of the vapor composition are known, the values for the liquid composition are obtained by a similar process starting with the R_V chart.

The data and smoothed values in this paper have been expressed in terms of the concentration of hydrogen sulfide in both the liquid and vapor phase, because the hydrogen sulfide concentration has prime importance in treating natural gas. A second series of plots was prepared in terms of the partial pressure of carbon dioxide with lines drawn at both constant liquid and vapor ratios. These curves with their cross plots and the hydrogen sulfide plots were used to check the consistency of the data. Random liquid and vapor compositions were assumed over the entire range of this study, and the corresponding vapor or liquid compositions were obtained using both the hydrogen sulfide and carbon dioxide plots. In no case was the deviation between the values obtained by the two sets of plots more than 10%. The maximum deviations were in those regions where small differences in the liquid composition caused large differences in the partial pressure of the acidic gas.

A comparison of the data from this paper and those of Muhlbauer and Monaghan (*5*) at 100°C. was made. Because data in the two studies were not obtained at the same liquid or vapor compositions, comparison values were derived as follows. The various partial pressures of hydrogen sulfide and solution loadings (from *5*) were obtained from a large scale plot provided in a preprint. The authors' values were derived from a series of correlation graphs for 100°C. similar to Figures 4 and 5 of this report. R_L values were computed from the solution loadings of Muhlbauer. Lines representing these R_L values were then constructed from the authors' data. The hydrogen sulfide contents of the liquid phases were read from these lines at selected partial pressures of hydrogen sulfide. A comparison was made in the region of 80- to 800-mm. partial pressure, because this was the region in which most of the data of (*5*) were obtained.

The agreement between the two sets of values is good, considering the experimental difficulties of handling this system at the elevated temperature. When carbon dioxide is present, the authors' computed values for the hydrogen sulfide contents of the equilibrium solutions are consistently higher at given partial pressures of hydrogen sulfide than those reported by Muhlbauer and Monaghan. The authors believe that the differences in the computed solution loadings are caused in part by the different analytical techniques used to determine the carbon dioxide content of the liquid phase.

The method of correlation using mole ratios appears to be more useful than those employed by other investigators. A wide range of concentrations of the acidic gases can be studied with a comparatively few carefully selected experimental determinations.

CONCLUSIONS

This study provides accurate solubility data for the system carbon dioxide-hydrogen sulfide-15.3 weight % MEA over temperature and concentration ranges of particular interest in the design and operation of amine units. An empirical correlation is presented by which either the solution loading or vapor composition of an equilibrium system can be obtained when the composition of either phase is known.

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Solubility of Nitrogen in Freon-114

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Nitrogen has been injected into the cell coolant systems at various times to lower the condenser heat transfer coefficient on the Freon side, thus making it possible to increase water velocity. However, difficulty has been encountered in removing the injected nitrogen by venting, and results of analyses of Freon in the cells indicate that an appreciable amount of nitrogen dissolves in the liquid phase. The objective of this study was to determine the equilibrium solubility of nitrogen in Freon-114 at various temperatures.

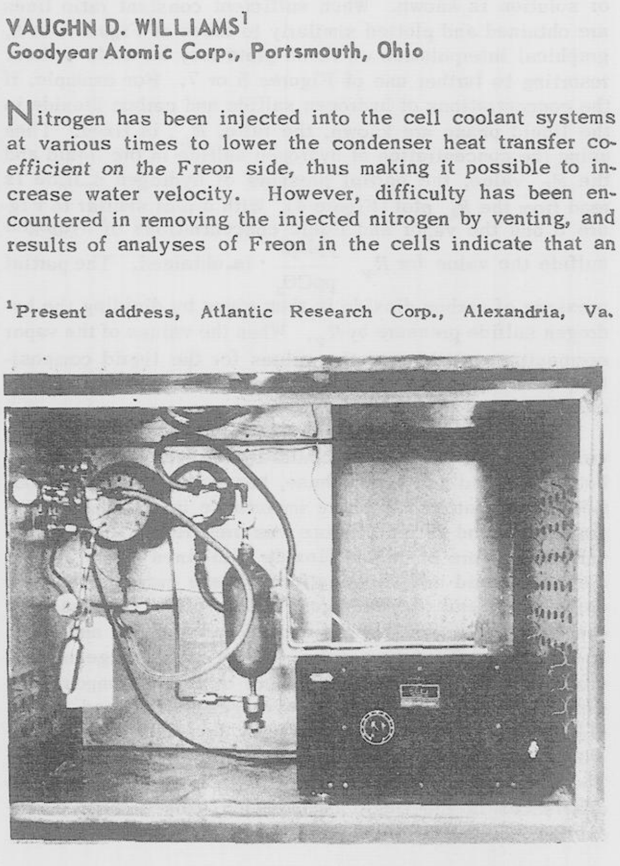

Figure 1. Apparatus for determining the concentration of nitrogen in liquid and vapor phases at different temperatures

PROCEDURE

Concentration of Nitrogen in Liquid and Vapor Phases. A method similar to that used by Parmelee (*1*) to determine the solubility of air in Freon-12 and Freon-22 was used. The apparatus, shown in Figure 1, consists of a Harshaw bomb, a sampling manifold, and pressure gages.

As is indicated schematically in Figure 2, a 1000-cc. Harshaw bomb, *A*, with a three-way diaphragm Hoke valve at the top and a normal diaphragm Hoke valve at the bottom, was fitted with a

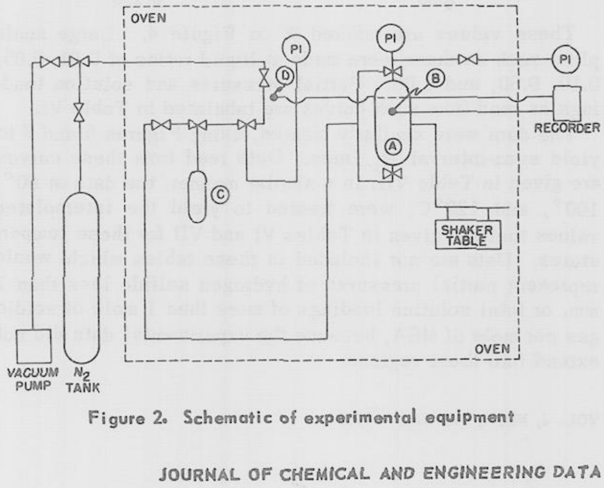

Figure 2. Schematic of experimental equipment

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