Δt = rise in temperature of calorimeter, K

ΔE_a = energy released by formation of nitric acid, cal

ΔE_w = energy released by combustion of fuse wire, cal

ΔE_c = energy that would have been released by combustion of residual carbon, cal

ΔE_{co} = energy that would have been released by combustion of residual carbon monoxide, cal

W = sum of the terms in the correction of the internal energy of combustion to standard states that are essentially constant for all experiments on one explosive, cal; W is designated as ΔE_{Σ} in ref. 5

ΔE_c^{o} = standard internal energy of idealized combustion reaction at 298K, cal/mol

M = molecular weight of explosive, g/mol (2)

ΔH_c^{o} = standard enthalpy of idealized combustion reaction at 298K, cal/mol

a, b, c, d = subscripts in the formula $C_aH_bO_cN_d$ of an explosive

ΔH_f^{o} = standard enthalpy of formation at 298K, cal/mol

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Gas Sweetening Data: Equilibrium Solubility of Hydrogen Sulfide and Carbon Dioxide in Aqueous Monoethanolamine and Aqueous Diethanolamine Solutions

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Equilibrium solubility data for hydrogen sulfide, carbon dioxide, and mixtures of the two acid gases in methane are collected for water solutions of monoethanolamine (MEA) and also diethanolamine (DEA). The experimental procedures, experimental apparatus, and analytical methods are described. The resulting equilibrium solubility data are presented for 15 wt % MEA and 25 wt % DEA over ranges of temperature and acid gas composition encountered in commercial MEA and DEA gas treating units. Some of the data are plotted and compared to data from other sources.

Knowledge of the equilibrium solubility of hydrogen sulfide, carbon dioxide, and their mixtures in water solutions of monoethanolamine (MEA) and diethanolamine (DEA) is essential in the design of natural gas and refinery gas absorption systems which remove these acid gases. The equilibrium solubility of the acid gases determines the amount of amine feed solution to be circulated to treat a given feed gas and the maximum amount of residual acid gases which can be present in the regenerated amine feed solution to the contactor to produce the desired acid gas specification for the treated gas. The equilibrium solubility of either acid gas is a function of temperature, hydrogen sulfide and carbon dioxide partial pressure in the vapor phase, amine type (MEA or DEA), and amine concentration in the liquid phase. The data presented provide a partial definition of the effects of these variables upon acid gas solubility.

Several investigators have measured hydrogen sulfide and carbon dioxide solubility in MEA and DEA solutions. Much of the past work, however, has limited utility for engineering design because the concentration and temperature ranges of the data are too narrow, the data are not consistent with other independent work, and/or the data are for only hydrogen sulfide or only carbon dioxide, but not for mixtures of the two acid gases. The most usable data collections are those of Jones et al. (7), Muhlbauer and Monaghan (19), Atwood et al. (2), Bocard (3), Leibush and Shneerson (15), Dow (6), Pearce (22), Mason and Dodge (17), and Lee et al. (11). Other solubility data are presented by Atadan (1), Bottoms (4), Lyndkovskaya and Leibush (16), Murzin et al. (20, 21), Reed (24), Reed and Wood (25), Lee et al. (10–14), and Riegger et al. (26).

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Experimental

Materials. Amine solutions were prepared from distilled water and commercial grade MEA and DEA. Both amines checked better than 99% by acid titration. Methane at 99 mol % minimum, 99.5 mol % hydrogen sulfide, and 99.99 mol % carbon dioxide were used as received. Mass spectrometer analyses were made to check purities. Distilled water for use in analysis was filtered through a bed of activated charcoal to remove oxidants.

The equilibrium cell is shown in Figure 1. The cell body was a nominal 1-l. stainless-steel cylinder supplied with a sample port at each end. A third connection was welded to the top of the cylinder to provide a gas-sampling port. All fittings and valves were made of stainless steel. The equilibrium cell was suspended in an oil bath and rocked at 14 cycles/min. The temperature was controlled to $\pm0.2°F$ at $100°F$ and $\pm1.0°F$ at $300°F$. A zero to 1000 psi gauge with 5 psi subdivisions and a zero to 200 psi gauge with 1 psi subdivisions were used. The pressure gauges were calibrated with a dead weight tester.

Sample containers were of three types. Liquid samples and some vapor samples were taken in nominal 10-ml type 304 stainless-steel sample cylinders having stainless-steel valves at each end. Other vapor samples were taken in either nominal 25-ml glass sampling containers or a special 200-ml gas sampling bottle. The gas sampling bottle is shown in Figure 2.

Loading and sampling equilibrium cell. The equilibrium cell was cleaned, assembled, and evacuated. About 600 g of amine solution were added, and the cell was lowered into the oil bath. Predetermined amounts of hydrogen sulfide and/or carbon dioxide were added; then methane was charged to the cell to achieve the desired total pressure. The cell mixture was rocked for a minimum of 16 hr.

Before taking a liquid sample for analysis, a small flush sample was taken to void any "dead space" liquid in the sampling line upstream of the liquid sampling valve. Liquid samples were then taken in a weighed nominal 10-ml sample cylinder with valves at each end. The lines and cylinder were first evacuated to the equilibrium cell sample valve. After sampling, the cylinders were reweighed to determine liquid sample weight.

Vapor-phase samples were taken by different methods depending upon acid gas concentration. For high acid gas concentrations, the vapor phase of the equilibrium cell was sampled into the evacuated 10-ml sample cylinder, as described above for liquids, except no flush sample was needed. The total sample cylinder pressure was chosen to avoid water condensation in the cylinder at room temperature. The sample was submitted for mass spectrometer analysis. For lower hydrogen sulfide concentrations, vapor-phase samples were taken in the 25-ml glass sample containers because of suspected appreciable loss of hydrogen sulfide from the vapor sample by reaction or adsorption on the stainless-steel sample cylinders. The glass containers were closed by two-way oblique bore stopcocks and were kiln fired before use. The container and sample line were connected to the equilibrium cell, evacuated, and then filled with sample to slightly above atmospheric pressure.

When the vapor-phase hydrogen sulfide concentration was near or below the mass spectrometer detection limit, the 200-ml gas sampling bottle was used. Before sampling, the container was charged with zinc acetate and sodium hydroxide solutions, evacuated to about 6 mm Hg pressure, and filled with vapor sample to atmospheric pressure. The container was then chilled in ice water and shaken to absorb the acid gas into the liquid. The methylene blue color was developed directly in the absorbing liquid. The larger glass sampling container was subsequently used for higher hydrogen sulfide concentrations with 25 wt % DEA as the absorbing medium. This sampling technique avoided the long contact time between vapor sample and sample container, which was un-
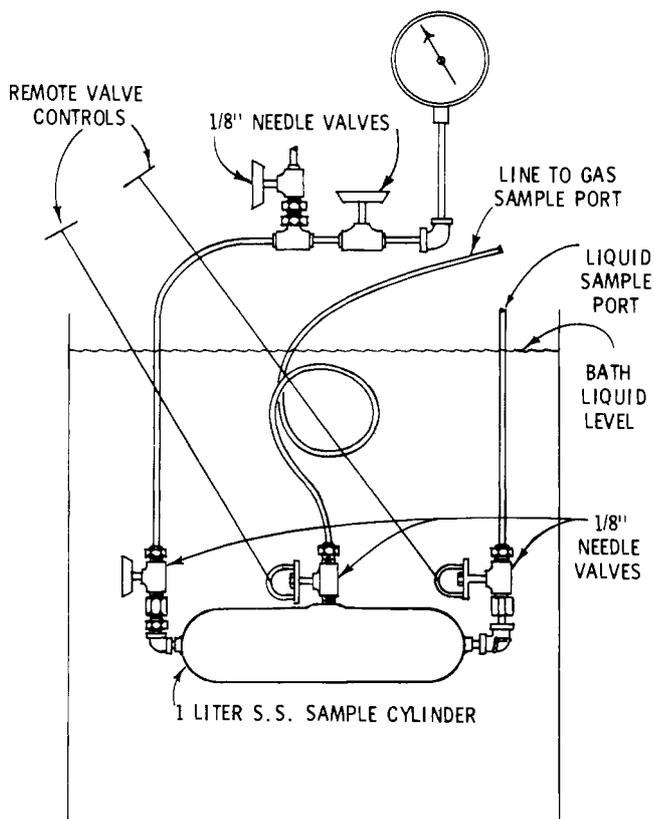
Figure 1. Equilibrium cell
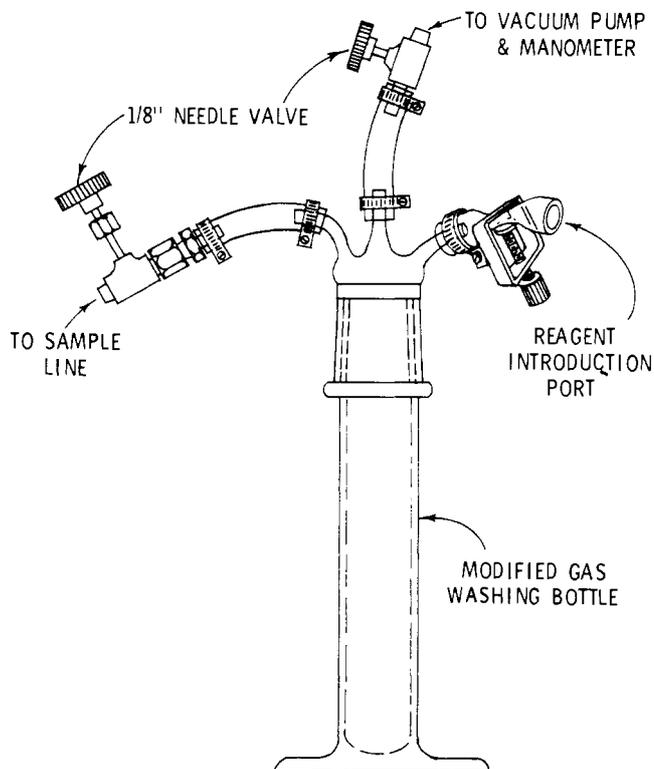
Figure 2. Gas sampling bottle

avoidable with the mass spectrometer analysis, and therefore limited sampling errors caused by contamination, adsorption, and reaction.

Analytical methods. Vapor-phase analyses were routinely done by mass spectrometry. When long delays in mass spectrometer service were anticipated, duplicate vapor samples were analyzed by absorption of the acid gases into 25 wt % DEA and electrometric titration by 0.1N ammoniacal nitrate for sulfide of water diluted aliquot portions. A silver–silver sulfide electrode was used. The analytical method is outlined by Willard and Fenwick (29) and in the text of Kolthoff and Furman (8). No significant interference is caused by chloride, sulfide, sulfate, thiosulfate, or polysulfides, but mercaptans do interfere because silver mercaptides are precipitated when sulfide concentrations become low.

The carbon dioxide content of the duplicate samples was found by the Knorr method as given by Scott (28) in which carbon dioxide is stripped from solution and then selectively absorbed in a tarred, carbon dioxide selective adsorbant filled tube. Reweighing gives carbon dioxide weight. For this work, a modification was made to remove hydrogen sulfide from the evolved gases by addition of a slight excess of 1.0N silver nitrate to the reaction flask before adding acid and the use of a scrubber containing sulfuric acid plus silver nitrate ahead of the adsorption tube. Very low vapor-phase carbon dioxide concentrations below the detection limit of the mass spectrometer and modified Knorr method were not measured.

Extremely low concentrations of vapor-phase hydrogen sulfide were measured by the methylene blue method as outlined by Claytor and Jones (5). In this method, sulfide and p-

Table I. Solubility of H_2S in 25 Wt % DEA

Temp, °F	Liquid compn, mol H_2S/ mol amine	Vapor compn, partial press H_2S, mm Hg	Temp, °F	Liquid compn, mol H_2S/ mol amine	Vapor compn, partial press H_2S, mm Hg
100	0.0038	0.011	150	0.515	302.
	0.0043	0.007		0.591	358.
	0.0044	0.009		0.644	500.
	0.0112	0.073		0.894	1910.
	0.0157	0.053		0.942	3960.
	0.0526	0.84		0.991	3000.
	0.0755	1.3		1.230	14000.
	0.133	3.3		1.25	17900.
	0.177	6.5		1.315	20140.
	0.196	7.1		1.432	23600.
	0.197	12.0	175	0.180	56.
	0.217	13.5		0.314	153.
	0.230	15.4		0.582	786.
	0.230	13.8		0.918	3430.
	0.234	11.5		1.212	14700.
	0.258	10.9	200	0.0039	0.10
	0.319	21.7		0.0153	1.1
	0.457	59.0		0.0208	1.7
	0.481	69.0		0.0319	3.2
	0.652	160.		0.132	65.
	0.855	760.		0.178	93.
	0.830	803.		0.201	136.
	0.975	2210.		0.211	163.
	1.082	2070.		0.212	131.
	1.043	2010.		0.315	275.
	1.107	10500.		0.565	1060.
	1.395	15600.		0.894	4450.
	1.412	17100.		0.896	4600.
	1.582	20000.		1.116	17900.
125	0.180	12.4		1.295	26300.
	0.317	42.0	225	0.169	167.
	0.588	198.		0.306	435.
	0.958	1920.		0.563	1450.
	1.241	13400.		0.856	5520.
150	0.0045	0.08		1.134	19300.
	0.0069	0.06	250	0.0143	3.4
	0.0092	0.10		0.0151	3.1
	0.0100	0.26		0.169	297.
	0.0151	0.21		0.192	349.
	0.0301	1.20		0.202	370.
	0.0488	1.61		0.295	740.
	0.124	19.7		0.531	2480.
	0.143	20.6		0.600	3770.
	0.179	27.2		0.768	6320.
	0.205	46.3		0.841	6200.
	0.207	45.8		1.095	21100.
	0.252	64.3		1.241	27800.
	0.255	57.3	275	0.162	460.
	0.256	38.1		0.496	3360.
	0.257	54.0		0.766	7590.
	0.264	35.0	300	0.151	820.
	0.318	85.		0.455	3740.
	0.446	210.		0.587	8030.
	0.462	196.			

Table II. Solubility of CO_2 in 25 Wt % DEA

Temp, °F	Liquid compn, mol CO_2/ mol amine	Vapor compn, partial press CO_2, mm Hg	Temp, °F	Liquid compn, mol CO_2/ mol amine	Vapor compn, partial press CO_2, mm Hg
100	0.408	15.	200	0.376	682.
	0.526	80.		0.390	820.
	0.823	1792.		0.418	907.
	0.861	2180.		0.583	3280.
	0.873	2420.		0.689	7480.
	1.013	9240.		0.784	12900.
	1.167	27100.		0.820	17300.
150	0.410	120.		0.950	31400.
	0.410	125.	225	0.389	1600.
	0.494	350.		0.520	4440.
	0.664	1390.		0.684	16400.
	0.756	3500.	250	0.321	2150.
	0.784	4710.		0.330	2140.
	0.914	13600.		0.340	2520.
	1.000	20000.		0.445	5730.
	1.072	30100.		0.592	11900.
175	0.627	2210.		0.715	20800.
	0.844	10900.		0.760	32800.
	0.872	15700.			
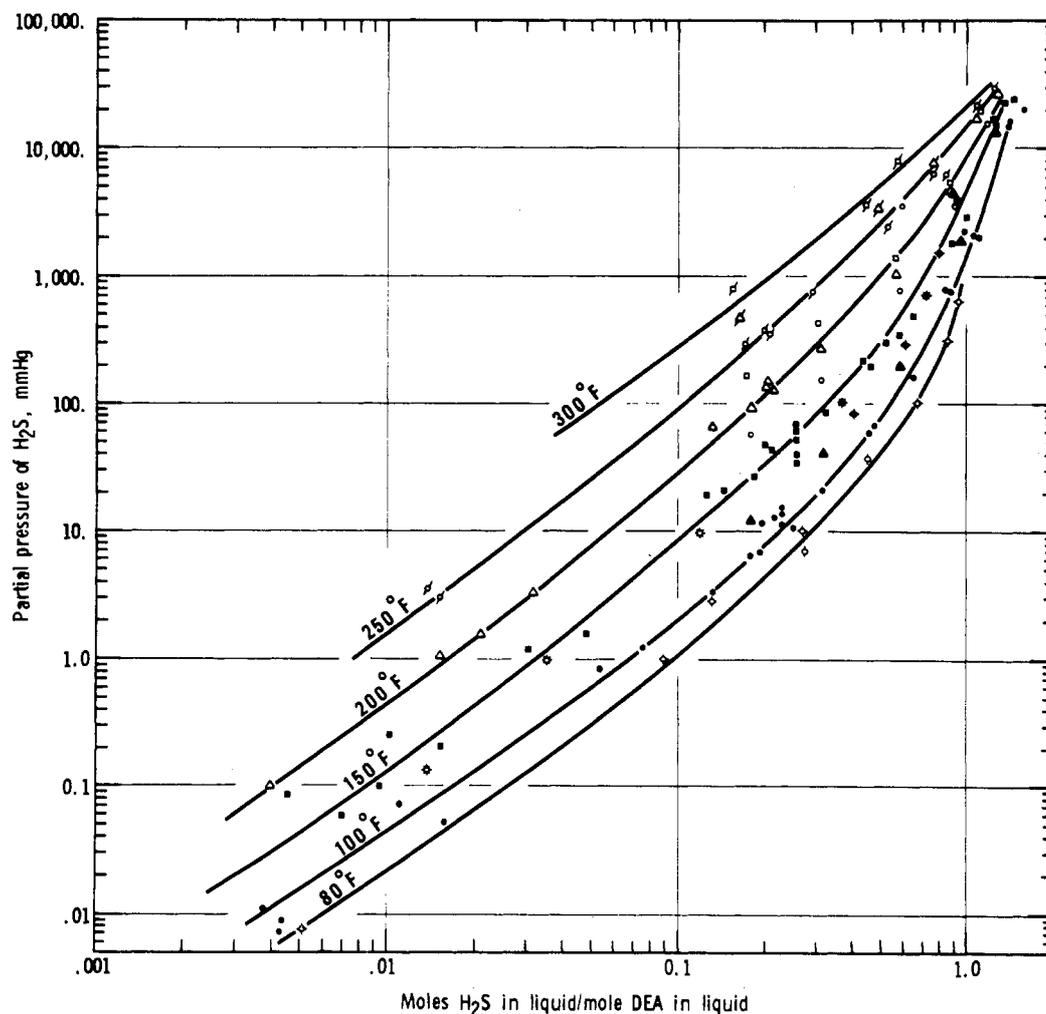
Figure 3. Solubility of H_2S in 25 wt % DEA–H_2S mixtures

Data of this study
- ● 100°F
- ▲ 125°F
- ■ 150°F
- ○ 175°F
- △ 200°F
- ▢ 225°F
- ⬭ 250°F
- ⬠ 275°F
- ▯ 300°F

Girdler (2, 3)
- ⬡ 80°F
- ✿ 120°F
- ⬢ 140°F

Lee et al. (10)
- ⬡ 77°F
- ◆ 122°F (from smoothed curve)

aminodimethylaniline react to form methylene blue, and color intensity is read using a spectrophotometer calibrated on standard sulfide solutions. A wavelength of 665 mμ was used.

Most of the liquid-phase hydrogen sulfide analyses were done on aliquot portions of diluted sample using the electrometric titration with silver nitrate. Early in the experimental project, duplicate analyses were done using an iodine–thiosulfate titration. The duplicate determinations usually checked within 3%. Liquid-phase carbon dioxide concentration was determined by the modified Knorr method performed on aliquot portions of diluted sample.

Accurate analyses were sometimes limited to certain acid gas concentration ranges. The modified Knorr method for carbon dioxide was accurate only when the amount of CO_2 detected was large enough compared to the differential weights recorded for blank runs of about 0.5 mg. This limited accurate vapor-phase carbon dioxide determinations to those above about 20 mm Hg partial pressure. The methylene blue method was considered as accurate as its calibration down to about 2 μg of hydrogen sulfide/100 ml of reaction solution. This corresponded to a lower limit of about 10 ppm of hydrogen sulfide by volume for vapor-phase analyses. However, some methylene blue tests were of questionable accuracy because of inadequate color development of off-color solu-

Table III. Solubility of H_2S Plus CO_2 in 25 Wt % DEA

Temp, °F	Liquid compn, mol/mol amine		Vapor compn, partial press, mm Hg	
	H_2S	CO_2	H_2S	CO_2
100	0.0042	0.0676	0.10	...
	0.0045	0.0990	0.13	...
	0.0074	0.130	0.19	...
	0.0077	0.081	0.20	...
	0.0095	0.212	0.55	...
	0.0125	0.113	0.39	...
	0.0122	0.230	1.0	...
	0.058	0.221	5.3	...
	0.059	0.214	4.1	...
	0.062	0.109	2.5	...
	0.106	0.734	970.	2430.
	0.111	0.715	267.	1290.
	0.120	0.478	63.	102.
	0.124	0.211	23.	...
	0.124	0.227	16.	17.
	0.127	0.118	10.	...
	0.152	0.605	163.	406.
	0.220	0.930	2500.	9500.
	0.237	0.310	69.	25.
	0.239	0.527	280.	370.
	0.251	0.160	27.	...
	0.384	0.630	1730.	2400.
	0.442	0.112	86.	...
	0.442	0.216	167.	58.
	0.441	0.410	664.	460.
	0.523	0.600	2850.	3150.
	0.585	0.381	1590.	810.
	0.607	0.281	610.	165.
	0.631	0.258	1060.	150.
	0.635	0.144	330.	26.
	0.861	0.264	9140.	3010.
	0.966	0.688	15000.	11500.
	1.020	0.119	6400.	1010.
125	0.250	0.890	2550.	10600.
	0.997	0.277	8500.	3900.
	1.050	0.161	7500.	1450.
150	0.0040	0.065	0.49	...
	0.0041	0.080	0.65	...
	0.0097	0.109	1.6	...
	0.0099	0.062	1.1	...
	0.0126	0.107	0.93	...
	0.0128	0.238	3.2	...
	0.0291	0.074	3.4	...
	0.0294	0.127	3.8	...
	0.0512	0.233	12.	30.
	0.0594	0.115	4.9	...
	0.105	0.654	360.	2950.
	0.113	0.457	145.	450.
	0.114	0.495	123.	375.
	0.118	0.215	47.	50.
	0.120	0.108	32.	11.
	0.147	0.596	310.	1180.
	0.209	0.452	450.	770.
	0.214	0.666	1180.	4540.
	0.252	0.285	214.	118.
	0.256	0.842	2500.	14000.
150	0.257	0.129	107.	23.
	0.375	0.567	1800.	3600.
	0.413	0.410	1020.	997.
	0.437	0.207	440.	183.
	0.443	0.116	321.	45.
	0.510	0.506	2850.	3800.
	0.526	0.252	1250.	560.
	0.576	0.298	1610.	920.
	0.624	0.114	730.	86.
	0.636	0.218	1030.	.320.
	0.855	0.156	6500.	3340.
	0.924	0.547	16500.	15900.
	0.990	0.118	8840.	1940.
	0.976	0.272	10200.	4100.
	1.010	0.140	9000.	1990.
175	0.255	0.770	2300.	1400.
	0.920	0.238	10500.	5200.
	0.920	0.139	9500.	2050.
200	0.0113	0.214	6.1	172.
	0.0125	0.109	4.6	...
	0.0314	0.054	2.6	...
	0.0327	0.085	7.1	30.
	0.0334	0.063	6.8	...
	0.0710	0.122	40.	64.
	0.107	0.543	445.	3950.
	0.114	0.353	220.	880.
	0.129	0.123	101.	117.
	0.129	0.533	420.	2840.
	0.156	0.474	560.	2750.
	0.183	0.354	456.	1220.
	0.196	0.245	287.	390.
	0.196	0.117	230.	152.
	0.255	0.710	2200.	13500.
	0.496	0.207	2000.	1480.
	0.881	0.395	16400.	16500.
	0.915	0.123	10400.	2630.
	0.935	0.230	11300.	5700.
225	0.172	0.730	1500.	14500.
	0.870	0.127	10700.	3210.
	0.922	0.210	12300.	6300.
250	0.0056	0.185	6.4	680.
	0.0135	0.107	10.1	...
	0.0391	0.349	233.	3100.
	0.0472	0.378	171.	3380.
	0.0532	0.448	280.	4750.
	0.0627	0.197	210.	918.
	0.0736	0.238	185.	1420.
	0.0874	0.650	650.	14700.
	0.124	0.282	331.	900.
	0.126	0.273	590.	2360.
	0.157	0.132	520.	750.
	0.176	0.070	570.	320.
	0.488	0.218	3410.	3190.
	0.825	0.117	11000.	3500.
	0.840	0.210	12400.	7200.
	0.822	0.405	15100.	17200.

tions. This occurred mostly in the higher temperature tests where, apparently, one or more interfering substances were produced.

The mass spectrometer analyses were considered accurate to within 1% of the reported value for hydrogen sulfide and carbon dioxide down to concentrations of about 1 mol % with a steady deterioration in accuracy to about ±50% at a concentration of 0.1 mol %. Alternate analyses were made whenever possible to provide a check on mass spectrometer analyses when measuring low concentrations of hydrogen sulfide. Some of the mass spectrometer analyses were considered invalid because of an unavoidably long lag time between sampling and analysis.

The limitations of the analytical methods were considered when comparing duplicate runs and culling out some data which were considered to be inconsistent.

Safety. In addition to the normal precautions which should be used to protect personnel from hydrogen sulfide poisoning, any high-pressure equipment used to contain mixtures similar to those used in this study should be inspected monthly for corrosion. At the conclusion of this study, the equilibrium cell was severely corroded almost to the point of failure around the weld of the vapor sample port.

Calculations. Laboratory measurements were used to calculate the liquid-phase concentration of acid gases in terms of moles of acid gas in the liquid-phase per mole of amine in the liquid-phase and vapor-phase acid gas concentrations in terms of partial pressure of each acid gas. Acid gas partial pressure is a convenient concentration measure because it is essentially independent of the total system pressure.

Certain assumptions were made in the calculations. The liquid-phase water/amine ratio at equilibrium was assumed to be the same as the water/amine ratio of solution charged to the equilibrium cell. Vapor-phase mass spectrometer analyses were reported in mol % on a water-free basis; therefore, an accounting for water partial pressure was made using values of vapor pressure for the particular water/amine mixture free of acid gas. A vapor-phase compressibility factor was estimated using the Redlich-Kwong (23) equation of state, together with the mass spectrometer analysis to calcu-
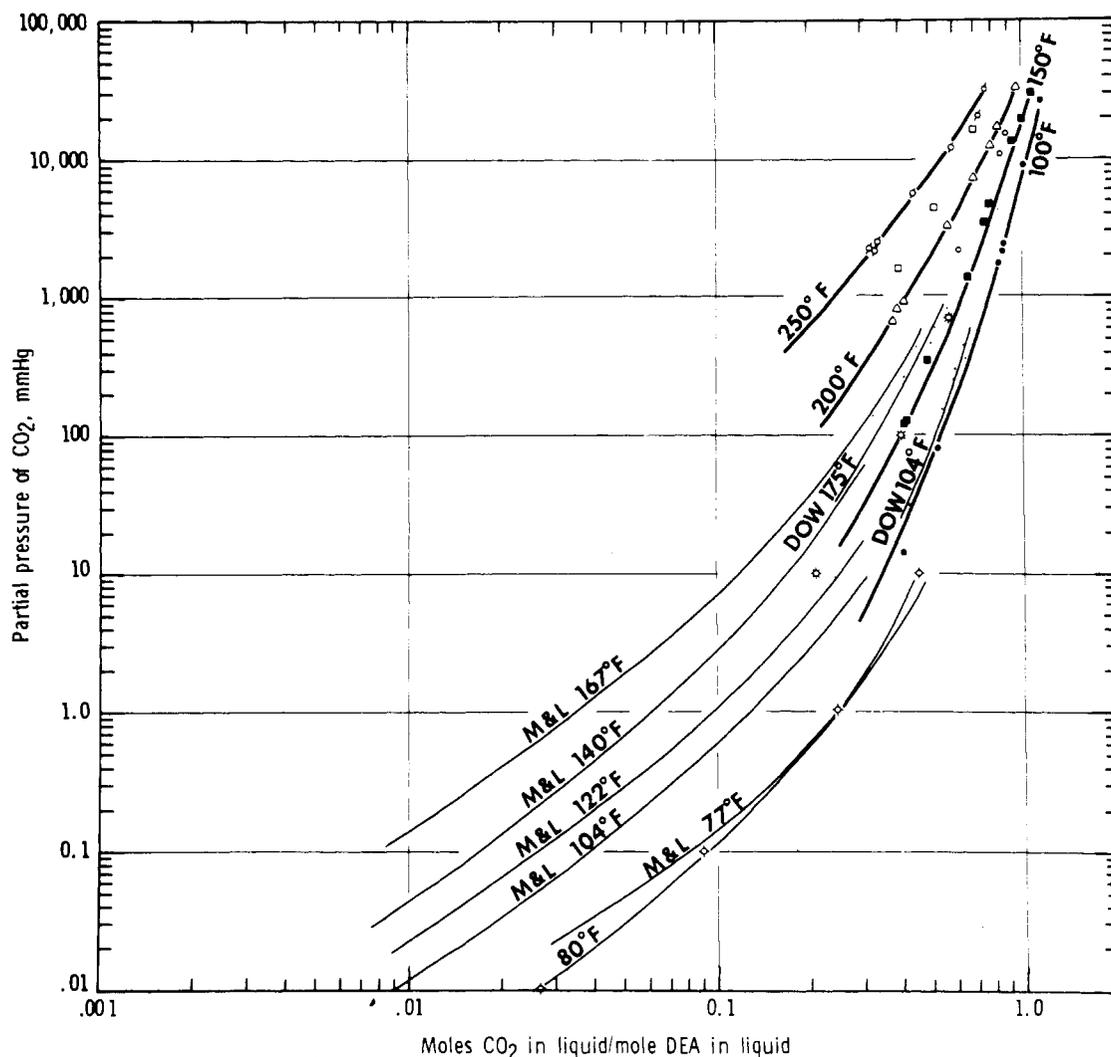
Figure 4. Solubility of CO_2 in 25 wt % DEA–CO_2 mixtures

Data of this study		Girdler (3)	
●	100°F	◇	80°F
▲	125°F	◖	140°F
■	150°F		
○	175°F	Dow (6, 22)	
△	200°F	**DOW**	
□	225°F		
◔	250°F	Murzin and Leites (20)	
		M&L	

late acid gas partial pressures in the duplicate vapor samples analyzed by electrometric titration, methylene blue, and modified Knorr methods.

Results

The experimental program was designed to obtain data for 25 wt % DEA and to extend the Jones et al. (7) data on 15 wt % MEA into regions of very low and very high hydrogen sulfide concentrations. Also, some data were collected on 30 wt % MEA and 50 wt % DEA to use as a guide in determining the effect of amine concentration on acid gas solubility. Amine weight percentages refer to acid gas-free, water-amine solutions.

Table I shows solubility data for H_2S, Table II for CO_2, and Table III for the mixed acid gas system for 25 wt % DEA. Isotherms established from the data of this study are plotted in Figure 3 for the H_2S system and Figure 4 for the CO_2 system along with data from other sources for comparison. Figure 5 shows the effect of carbon dioxide liquid-phase content on hydrogen sulfide solubility at 100°F.

Data for 15.2 wt % MEA for hydrogen sulfide, carbon dioxide, and their mixtures are given in Tables IV–VI. Figure 6 shows the comparison of isotherms prepared from the data of this study and also that of Jones et al. (7) to data from other sources for the hydrogen sulfide–nominal 15 wt % MEA system. Figure 7 shows comparisons for the CO_2–nominal 15

wt % MEA system. The additional data gathered for more concentrated amine solutions are listed in Tables VII and VIII.

Accuracy of data. The overall accuracy of the data of this study, as indicated by duplicate or near-duplicate runs, depended upon the concentration of hydrogen sulfide and carbon dioxide and temperature. In general, accuracy increased as acid gas concentration increased and as temperature decreased. When each acid gas concentration was fairly high, e.g., above 100 mm Hg, the measurement for gas- and liquid-phase hydrogen sulfide content was judged to be good usually to within about 10%. However, when hydrogen sulfide partial pressures were much below 20 mm Hg, data scatter was more than 10% from smoothed curves. Also, as temperature was increased beyond 200°F, the reproducibility of duplicate runs was not as close as those runs at 100–150°F. The standard deviation of experimental points from smoothed curves for 67 of the runs of the 25 wt % DEA–hydrogen sulfide system was 16%, and for 30 runs of the 25 wt % DEA–CO_2 system was 9%. This accuracy level seems reasonable after considering the difficulty in obtaining and preserving representative samples for analysis. Also, some compromise in accuracy is necessary when a comparatively small amount of data is collected by several different techniques to describe solubility behavior over the broad ranges of concentration encountered in this study.

Comparisons to data from other sources. Agreement be-
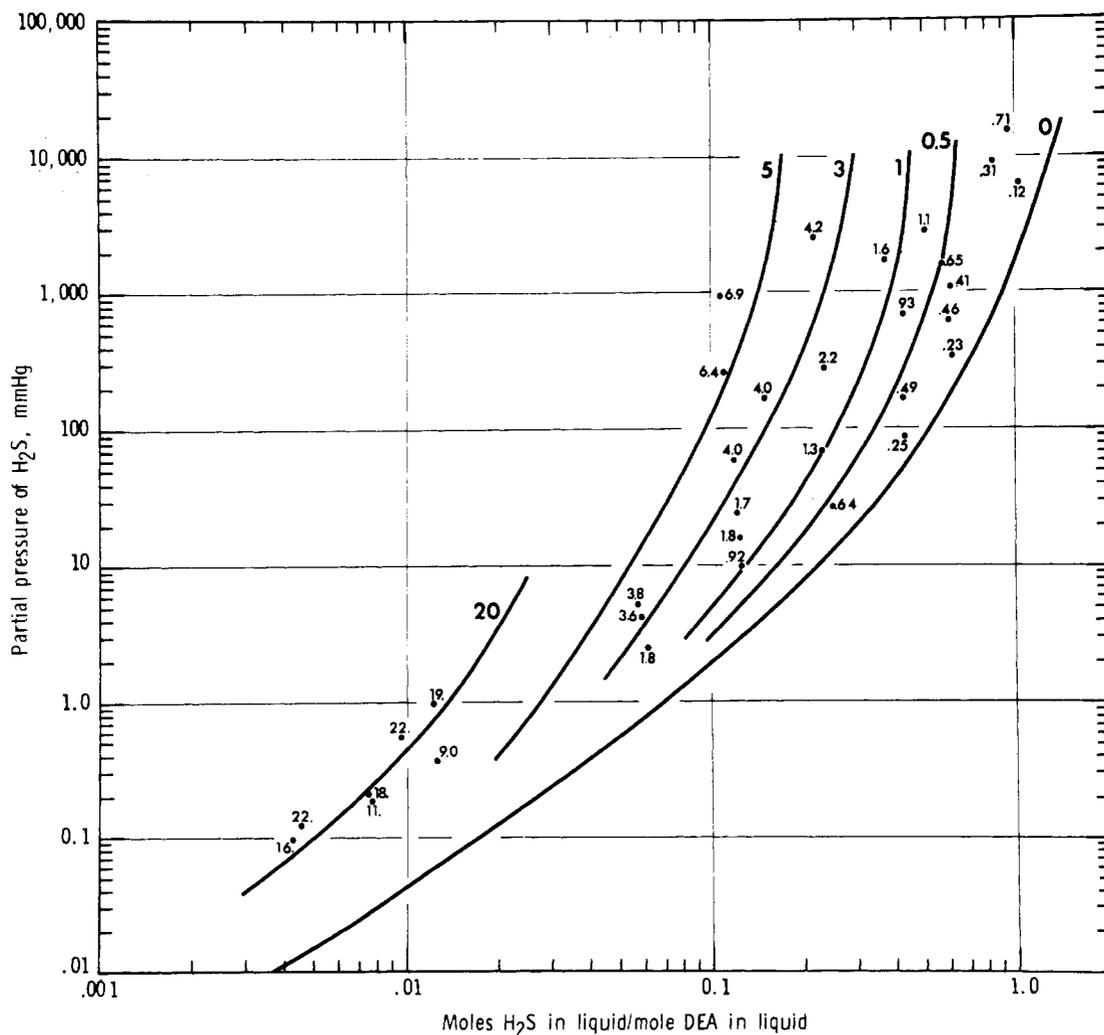
Figure 5. Solubility of H_2S in 25 wt % DEA–H_2S–CO_2 mixtures at 100°F. Parameter: mol CO_2 in liquid per mol H_2S in liquid

tween data from this study and from independent sources is shown in Figures 3, 4, 6, and 7. In Figure 3 the Girdler data of Atwood et al. (2) and Bocard (3) and data of Lee et al. (10) are shown to agree over the entire hydrogen sulfide concentration range for the 77–140°F temperatures. Figure 4 shows general agreement of all data plotted except for the low concentration data of Murzin and Leites (20) and Bocard (3). No data for higher temperatures were available for comparisons in the 25 wt % DEA systems.

More acid gas solubility data are available for MEA than DEA, and several comparisons are available for the nominal 15 wt % MEA–hydrogen sulfide system as shown in Figure 6. The data agree well except for the lower hydrogen sulfide concentration data of Muhlbauer and Monaghan (19) at

212°F and Leibush and Schneerson (15) at 122°F. Figure 7 compares the available data for the nominal 15 wt % MEA–CO_2 system. Again, good agreement is achieved at the higher carbon dioxide concentrations. The low concentration Girdler data of Bocard (3) indicate higher carbon dioxide partial pressures than does the 140°F Jones et al. (7) isotherm, but lower carbon dioxide partial pressures than the 104°F Jones et al. (7) isotherm. Data from other sources are available for the separate hydrogen–sulfide and carbon dioxide–amine systems, but direct graphical comparisons cannot be made because of differences in amine concentration.

A direct comparison is available for the 15 wt % MEA–mixed acid gas system at 212°F between the data of this work and Jones et al. (7) to that of Muhlbauer and Monaghan

Table IV. Solubility of H_2S in 15.2 Wt % MEA

Temp, °F	Liquid compn, mol H_2S/ mol amine	Vapor compn, partial press H_2S, mm Hg
104	0.0140	0.012
	0.0147	0.014
	0.0329	0.08
	0.0396	0.19
	0.0590	0.31
	0.0591	0.27
	0.0789	0.55
	0.0795	0.49
	0.373	11.
	0.380	9.3
	1.026	1920.
	1.049	1800.
	1.099	4260.
	1.116	4340.
	1.633	18600.
140	0.0052	0.009
	0.0141	0.074
	0.0339	0.28
	0.0406	0.44
	0.0593	0.74
	0.0805	1.1
	0.384	34.
	0.392	35.
	0.997	2590.
	1.114	4500.
	1.526	24500.
176	0.0055	0.028
	0.0143	0.094
	0.0349	0.74
	0.0418	1.16
	0.382	85.
	0.385	90.
	0.993	3500.
	1.028	6500.
	1.468	24300.
212	0.0058	0.047
	0.0143	0.31
	0.0633	4.7
	0.0793	5.6
	0.121	13.8
	0.376	230.
	0.384	230.
	0.952	6980.
	1.015	7580.
	1.358	28900.
248	0.0653	17.
	0.0812	18.
	0.122	32.
	0.383	480.
	0.386	505.
	0.923	7400.
	0.939	9300.
	1.36	28700.
284	0.0610	34.
	0.0749	40.

Table V. Solubility of CO_2 in 15.2 Wt % MEA

Temp, °F	Liquid compn, mol CO_2/ mol amine	Vapor compn, partial press CO_2, mm Hg
104	0.673	450.
	0.679	460.
	0.998	10400.
140	0.661	950.
	0.665	950.
	0.929	13000.
176	0.631	1810.
	0.635	1620.
	0.888	15900.
212	0.177	10.
	0.599	2780.
	0.601	2970.
	0.807	18400.
248	0.115	22.
	0.187	49.
	0.565	4400.
	0.589	4600.
	0.726	20900.
274	0.110	74.
284	0.173	230.

Table VI. Solubility of H_2S Plus CO_2 in 15.2 Wt % MEA

Temp, °F	Liquid compn, mol/mol amine		Vapor compn, partial press, mm Hg	
	H_2S	CO_2	H_2S	CO_2
77	0.155	0.413	5.1	...
	0.303	0.398	145.	23.
	0.431	0.321	94.	...
	0.533	0.505	1195.	352.
104	0.0059	0.174	0.041	...
	0.0135	0.191	0.11	...
	0.367	0.233	40.	...
	0.493	0.394	1490.	...
140	0.0057	0.176	0.17	...
	0.0064	0.386	2.4	...
	0.0130	0.191	0.53	...
	0.244	0.595	910.	1490.
212	0.0054	0.389	8.6	217.
	0.0057	0.167	0.61	...
	0.0073	0.186	2.1	15.
	0.0131	0.194	1.3	...
	0.0411	0.233	17.	30.
	0.0757	0.082	25.	...
248	0.0545	0.0675	28.	12.
	0.133	0.166	251.	255.
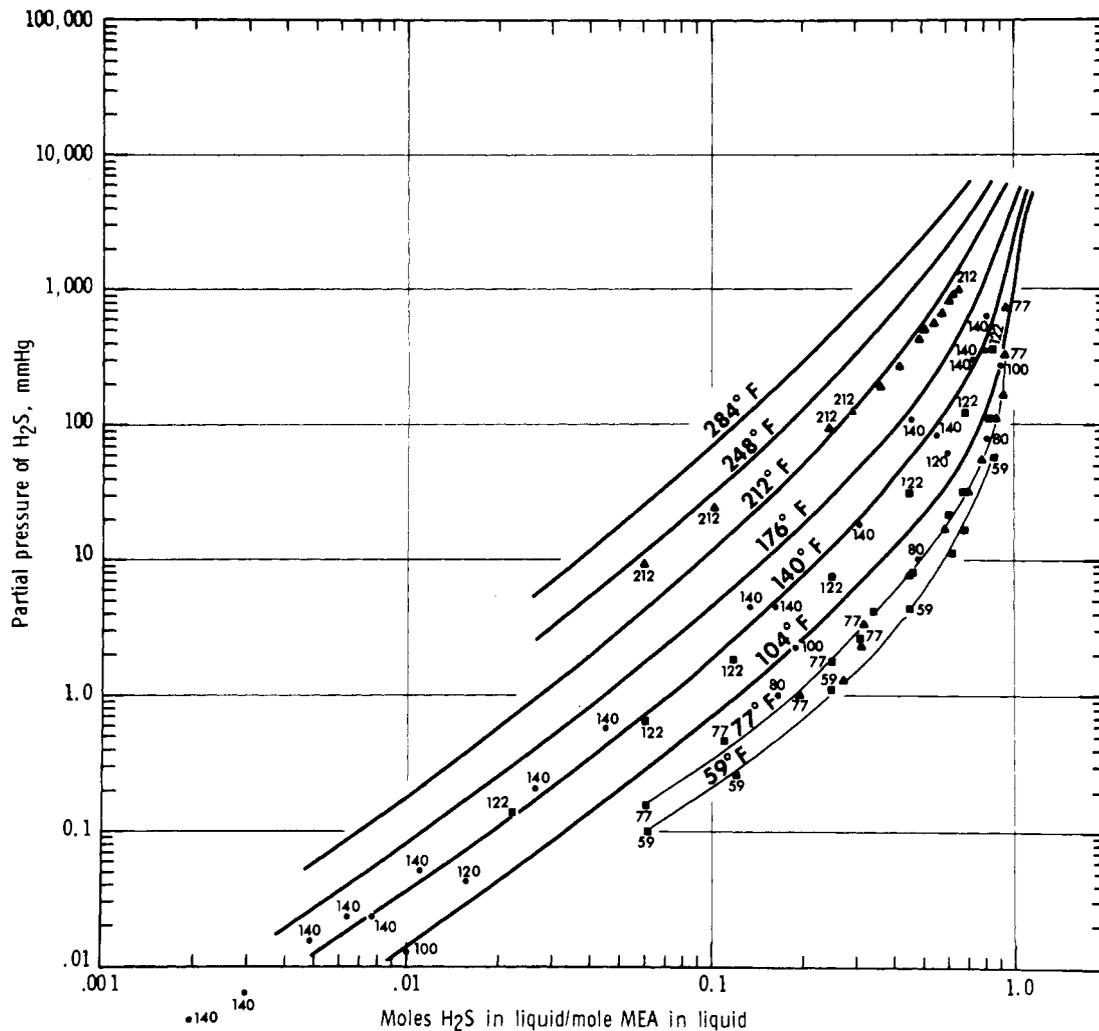
Figure 6. Solubility of H_2S in 15 wt % MEA–H_2S mixtures. Data from other sources compared to isotherms of this study and Jones et al. (7)

Girdler (2, 3)
Muhlbauer and Monaghan (19)
Leibush and Schneerson (15)

● °F @ 80°, 100°, 120°, 140°F
▲ °F @ 77°, 212°F
■ °F @ 59°, 77°, 122°F

Table VII. Solubility of H_2S, CO_2, and Their Mixtures in 30 Wt % MEA

Temp, °F	Liquid compn, mol/mol amine H_2S	CO_2	Vapor compn, partial press, mm Hg H_2S	CO_2	Temp, °F	Liquid compn, mol/mol amine H_2S	CO_2	Vapor compn, partial press, mm Hg H_2S	CO_2
	H_2S only					CO_2 only			
80	0.081		0.57		200		0.404		170.
	0.231		3.9				0.452		430.
	0.311		6.9				0.501		888.
	0.406		13.				0.567		3400.
100	0.0083		0.01			H_2S and CO_2 mixtures			
	0.048		0.62		100	0.0128	0.119	0.04	. . .
	0.199		5.6			0.197	0.331	65.	. . .
	0.616		80.			0.277	0.405	620.	175.
200	0.0089		0.27		150	0.0128	0.113	0.13	. . .
	0.0509		9.6			0.205	0.324	160.	. . .
	0.207		107.			0.291	0.403	1300.	620.
	0.570		1250.		200	0.0130	0.116	3.2	. . .
						0.196	0.304	470.	. . .
						0.280	0.392	2170.	1720.
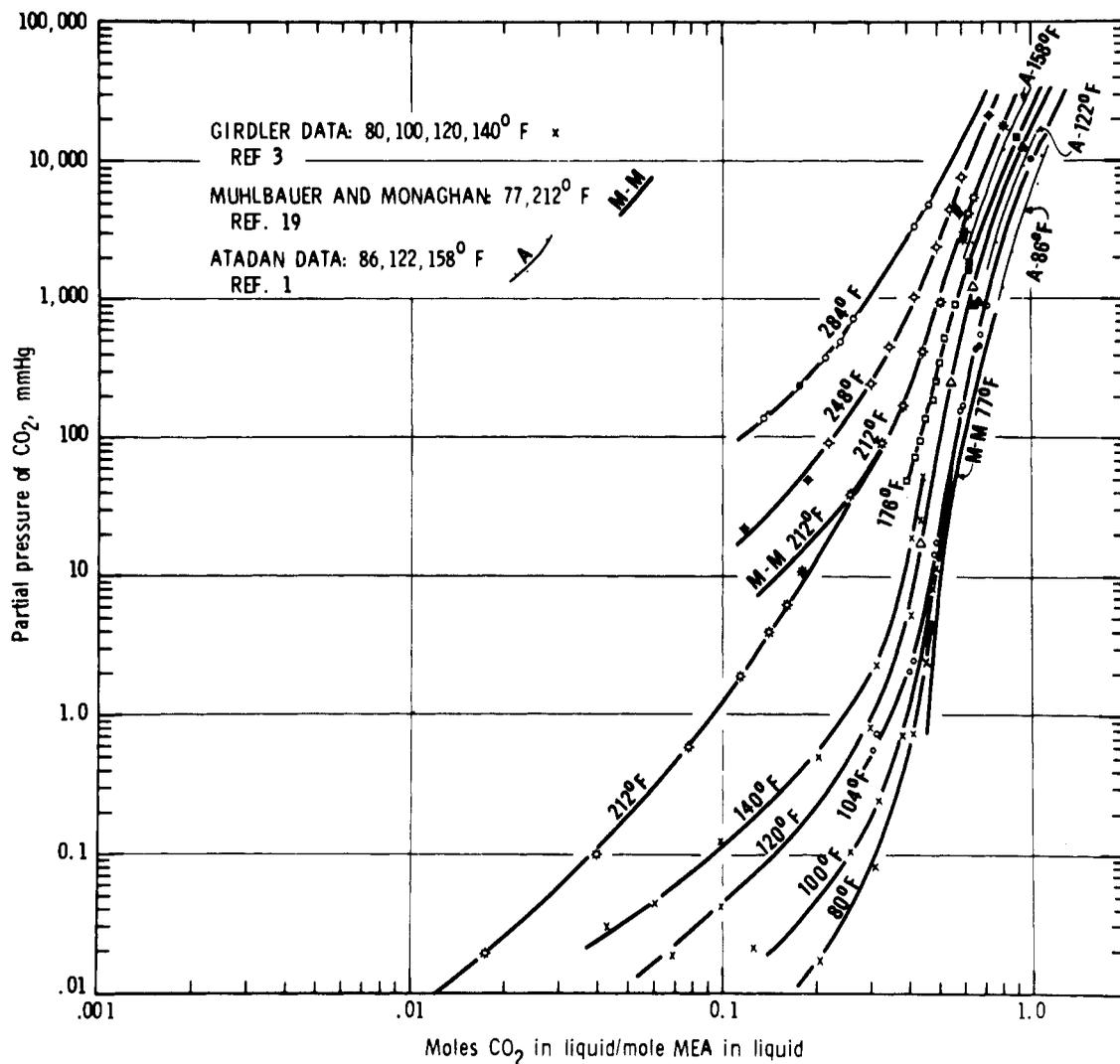
Figure 7. Solubility of CO₂ in 15 wt % MEA-CO₂ mixtures

GIRDLER DATA: 80,100,120,140° F ×
REF. 3

MUHLBAUER AND MONAGHAN: 77,212° F M-M
REF. 19

ATADAN DATA: 86,122,158° F A
REF. 1

Moles CO_2 in liquid/mole MEA in liquid

Partial pressure of CO_2, mmHg

Data of this study		Jones et al. (7)	
●	104°F	O	104°F
▲	140°F	△	140°F
■	176°F	□	176°F
✳	212°F	✳	212°F
◆	248°F	◇	248°F
▰	284°F	▱	284°F

Table VIII. Solubility of H_2S, CO_2, and Their Mixtures in 50 Wt % DEA

Temp, °F	Liquid compn, mol/mol amine		Vapor compn, partial press, mm Hg	
	H_2S	CO_2	H_2S	CO_2
	H_2S only			
100	0.0111		0.09	
	0.0522		2.9	
	0.212		24.	
	0.553		190.	
140[a]	0.0053		0.07	
	0.124		33.	
	0.587		650.	
200	0.011		3.4	
	0.055		31.	
	0.211		290.	
	0.566		2070.	
	CO_2 only			
77[a]		0.458		45.
		0.602		420.
100		0.400		69.

Temp, °F	Liquid compn, mol/mol amine		Vapor compn, partial press, mm Hg	
	H_2S	CO_2	H_2S	CO_2
	CO_2 only			
100		0.585		590.
		0.739		3500.
		0.745		3300.
200		0.186		210.
		0.222		270.
		0.311		610.
		0.411		1630.
	H_2S and CO_2 mixtures			
100	0.0026	0.111	0.12	...
	0.260	0.438	520.	450.
150	0.0030	0.114	0.85	...
200	0.0028	0.116	2.6	64.
	0.233	0.390	1800.	4200.

[a]Values at 140° and 77°F were for 54.5 wt % DEA.

(19). The Muhlbauer and Monaghan data show higher hydrogen sulfide and carbon dioxide partial pressures, especially at low acid gas concentrations. Other mixed acid gas–amine system data are available, but, again, direct comparisons cannot be made because of differing amine concentrations and temperatures.

Conclusions

The data obtained in this study extend the range of definition of H_2S and CO_2 solubility in MEA and DEA solutions. The data are accurate and in good agreement with data from other sources.

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Hydrocarbon Gas Solubility in Sweetening Solutions: Methane and Ethane in Aqueous Monoethanolamine and Diethanolamine

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The solubility of methane and ethane in monoethanolamine and diethanolamine solutions is measured. The experimental procedures used to collect the data are presented along with selected data and graphs showing effects of temperature, amine concentration, and acid gas content. The solubilities of these hydrocarbons in the amine solutions are about the same as their solubility in an equal weight or volume of water. However, the type and concentration of amine, temperature, and presence of hydrogen sulfide and carbon dioxide affect the methane and ethane solubility.

Aqueous solutions of monoethanolamine (MEA) or diethanolamine (DEA) are used as absorbants in natural gas sweetening systems to selectively remove hydrogen sulfide and carbon dioxide from the plant feed gas. In the process some hydrocarbon gas also is absorbed in the amine solution. Knowledge of the amounts of hydrocarbon gas in the amine stream is necessary for design of the sweetening system and associated Claus sulfur recovery unit.

Previous work. Published data on hydrocarbon solubility in amine solutions are limited to two curves plotted in Kohl and

Riesenfeld (5) for methane solubility at 80° and 160°F in 25.3 wt % MEA having 0.47 mole of acid gas per mole MEA. The data of this study are in general agreement with the Kohl data.

Published data for hydrocarbon gas solubility in water are more plentiful. These data are given in Culberson and McKetta (2), Davis and McKetta (3), and Kobayashi and Katz (4). A review and presentation of these data are given in the API Technical Data Book (7). Solubilities for hydrocarbon mixtures are given in a publication by Amirijafari and Campbell (1).

Experimental

Amine solutions were prepared from distilled water and commercial grade MEA and DEA. Both amines checked better than 99% pure by acid titration. Hydrocarbon gases used were 99 mol % minimum. The gas compositions were checked by mass spectrometer analyses.

The equilibrium cell used for the gas solubility determinations is described in a previous publication by Lawson and Garst (6). The cell was evacuated, and 500–600 g of solution was drawn into the cell. The cell was pressured with hydrocarbon gas and rocked at test temperature for at least 16 hr.

Liquid-phase samples were taken in a 10-ml sample container and weighed. Sample container tare weight established the weight of liquid sample. The volume of gas dissolved was measured volumetrically by water displacement from a sec-

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