squares fit. The relative error in P_0/Z_0 from this source after an average of 12 expansions is 0.0024%. The relative error in the compressibility factors at intermediate pressures is then approximately $0.0024 - j\epsilon$ for the jth expansion, because this error in any individual Z value is caused only by the effect of the N_0 error on the subsequent expansions. Therefore, the error in compressibility factor from this source at initial pressure is 0.168%.

The maximum uncertainty in the extrapolation in the curve $P_j \Pi_{i=1}^{j} N_i$ vs. P_j to get the cell constant is 0.02%. When all these possible errors are considered, the Z values determined are probably accurate to ±0.19%.

Acknowledgment

The assistance of H. Kalra in processing some of the data is recognized.

Nomenclature

a = coefficient in equation for elastic distortion of steel
B, C, D = virial coefficients
n = number of moles
N = Burnett cell constant
P = absolute pressure
R = gas constant
T = absolute temperature
V = molal volume
Z = compressibility factor

Subscripts and Superscripts

0 = value as P approaches zero
1, 2 = number of expansion in Burnett experiment or designation of volume chambers in Burnett cell
i, j = any expansion in Burnett experiment
M = value for a mixture

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Equilibrium-Phase Properties of Nitrogen-Hydrogen Sulfide System

George J. Besserer[1] **and Donald B. Robinson**[2]
Department of Chemical Engineering, The University of Alberta, Edmonton, Alta., Canada

Vapor and liquid equilibrium-phase compositions and refractive indices were determined for the nitrogen-hydrogen sulfide system at 1.9°, 40.1°, 80.4°, 119.7°, and 160°F from the vapor pressure of hydrogen sulfide to a pressure of 3000 psia. The equilibrium ratios were calculated for each component at each temperature from the phase composition data. The equilibrium-phase densities were calculated from the measured phase composition and refractive index by use of the Lorentz-Lorenz molar refractivity relationship.

In recent years there has been an increasing interest in the volumetric and phase behavior of binary systems, particularly those containing one of the nonhydrocarbon components frequently found in petroleum or natural gas reservoirs. Information on binary systems is required for evaluating the parameters used in improved correlations for predicting the behavior of multicomponent systems and for evaluating the coefficients in equations of state. Although the behavior of many binary systems containing nitrogen or hydrogen sulfide as one of the components is reported in the literature, the authors were unable to find reference to any previous work on the phase behavior of the nitrogen-hydrogen sulfide system itself. The information presented in this paper is based on a recent study of the coexisting phase properties of the nitrogen-hydrogen sulfide system at temperatures between 0° and 160°F and at pressures up to 3000 psia. The work is part of an overall study of this system which has included heat capacity (*3*) and density (*8*) measurements.

Experimental Method

The experimental equipment and procedures have been described in detail in earlier papers by Besserer and Robinson (*1*, *2*). Experiments were carried out at each of five temperatures which were nominally 0°, 40°, 80°, 120°, and 160°F. At temperatures below ambient, the temperature of the cell contents was maintained by circulating a refrigerated fluid through the cooling coil in the aluminum shroud at each end of the cell. At each temperature, measurements of equilibrium-phase compositions and refractive indices were made at a series of pressures from the vapor pressure of hydrogen sulfide to pressures in the vicinity of the critical region or to 3000 psia, whichever was lower. The temperature was measured with a calibrated pair of iron constantan thermocouples with the reference junction in an ice bath and is believed known to ±0.1°F. The pressure was measured with a 3000-psia calibrated stainless-steel bourdon tube Heise gauge so that pressures are believed known to ±3 psi.

Materials and Analysis

The nitrogen used in this work was obtained from a local supplier and was stated to have a purity of 99.993 mol %. A sample of this material was analyzed on a silica gel column, and no impurity peaks were detected. The

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[1] Present address, Hudson's Bay Oil and Gas Co. Ltd., Calgary, Alta., Canada.
[2] To whom correspondence should be addressed.

Table I. Experimental Equilibrium-Phase Properties of Nitrogen–Hydrogen Sulfide System

Press, psia	Composition[a]		Refractive index[b]		Molar volume[c]		Equilibrium constant	
	Liquid	Vapor	Liquid	Vapor	Liquid	Vapor	Nitrogen	Hydrogen sulfide
160.0°F								
1033	0.0148	0.148	1.28558	1.04731	0.864	4.56	10.00	0.864
1254	0.0290	0.242	1.27886	1.06005	0.877	3.42	8.33	0.778
1503	0.0448	0.281	1.27275	1.07012	0.887	2.86	6.28	0.749
1750	0.0636	0.321	1.26440	1.08109	0.904	2.42	5.04	0.726
2000	0.0849	0.342	1.25598	1.08989	0.920	2.15	4.03	0.719
2250	0.111	0.357	1.24306	1.10519	0.952	1.83	3.22	0.723
2500[d]	0.146	0.330	1.22253	1.13206	0.013	1.49	2.26	0.785
2570[d]	0.161	0.331	1.21196	1.13970	1.051	1.41	2.05	0.798
P	x	y	n_L	n_V	V_L	V_V	K_{N_2}	K_{H_2S}
119.7°F								
503	0.0000	0.0000	1.33047	1.02569	0.762	9.13	...	1.000
590	0.0040	0.108	1.32981	1.02805	0.762	7.88	26.9	0.896
791	0.0129	0.265	1.32560	1.03355	0.767	6.00	20.5	0.745
1007	0.0220	0.364	1.32245	1.03968	0.770	4.76	16.5	0.651
1240	0.0325	0.429	1.31840	1.04644	0.775	3.89	13.2	0.590
1487	0.0451	0.478	1.31452	1.05400	0.778	3.23	10.6	0.547
1738	0.0571	0.516	1.30987	1.06160	0.783	2.76	9.04	0.513
2028	0.0702	0.525	1.30551	1.07106	0.788	2.38	7.46	0.510
2277	0.0825	0.538	1.30008	1.07886	0.795	2.13	6.52	0.504
2500	0.0979	0.539	1.29571	1.08695	0.799	1.93	5.51	0.511
2750	0.113	0.543	1.29074	1.09542	0.805	1.76	4.82	0.515
3000	0.126	0.533	1.28453	1.10599	0.814	1.60	4.22	0.535
80.4°F								
300	0.000	0.000	1.36095	1.01472	0.704	15.9	...	1.000
510	0.0071	0.332	1.35815	1.02053	0.706	9.35	46.8	0.673
745	0.0153	0.488	1.35581	1.02636	0.707	6.54	31.9	0.520
1015	0.0239	0.576	1.35305	1.03359	0.709	4.81	24.1	0.435
1265	0.0317	0.628	1.35058	1.04006	0.710	3.87	19.8	0.385
1497	0.0401	0.653	1.34824	1.04634	0.711	3.55	16.3	0.361
1749	0.0495	0.674	1.34562	1.05339	0.712	2.80	13.6	0.343
1994	0.0570	0.684	1.34356	1.06010	0.713	2.47	12.0	0.335
2248	0.0663	0.691	1.34089	1.06702	0.714	2.20	10.4	0.331
2508	0.0762	0.695	1.33846	1.07425	0.715	1.99	9.13	0.330
2751	0.0844	0.694	1.33631	1.08095	0.716	1.83	8.22	0.334
3000	0.0957	0.693	1.33389	1.08765	0.716	1.69	7.24	0.340
40.1°F								
169	0.000	0.000	1.38967	1.01025	0.657	22.8	...	1.000
251	0.0035	0.271	1.38629	1.01035	0.661	19.3	77.3	0.732
495	0.0102	0.582	1.38431	1.01631	0.662	9.82	57.1	0.422
765	0.0186	0.698	1.38276	1.02313	0.661	6.29	37.5	0.308
990	0.0241	0.743	1.38132	1.02897	0.661	4.84	30.8	0.264
1250	0.0314	0.769	1.37955	1.03552	0.661	3.85	24.5	0.238
1501	0.0377	0.791	1.37760	1.04214	0.662	3.19	21.0	0.217
1755	0.0416	0.798	1.37642	1.04866	0.663	2.75	19.2	0.211
2000	0.0468	0.806	1.37516	1.05531	0.663	2.40	17.2	0.204
2250	0.0540	0.810	1.37393	1.06171	0.662	2.15	15.0	0.201
2500	0.0586	0.806	1.37282	1.06777	0.662	1.96	13.8	0.206
2753	0.0642	0.811	1.37181	1.07526	0.661	1.76	12.6	0.202
3000	0.0685	0.809	1.37107	1.08014	0.661	1.66	11.8	0.205
1.9°F								
257	0.0049	0.625	1.40851	1.00894	0.629	17.3	128.8	0.377
498	0.0084	0.776	1.40676	1.01490	0.630	9.09	92.4	0.226
773	0.0145	0.839	1.40556	1.02210	0.630	5.78	57.9	0.163
1009	0.0176	0.866	1.40457	1.02816	0.630	4.41	49.2	0.136
1255	0.0230	0.873	1.40408	1.03486	0.629	3.55	37.9	0.130
1516	0.0268	0.881	1.40260	1.04182	0.629	2.94	32.9	0.122
1766	0.0312	0.887	1.40257	1.04848	0.628	2.52	28.4	0.117
2008	0.0348	0.887	1.40222	1.05993	0.627	2.04	25.5	0.117
2259	0.0385	0.892	1.40192	1.06159	0.626	1.98	23.2	0.113
2508	0.0390	0.891	1.40138	1.06757	0.627	1.81	22.9	0.113
2758	0.0430	0.886	1.40119	1.07356	0.626	1.67	20.6	0.120
3003	0.0448	0.890	1.40089	1.07293	0.625	1.55	19.9	0.116

[a] Mole fraction nitrogen. [b] Relative to vacuum at 6328 Å. [c] Ft^3/lb mol calculated from refractive index and composition data. [d] Near critical zone, analysis may be less accurate.

hydrogen sulfide was CP grade obtained from Matheson, Inc., and had a purity of 99.8+ mol %. This material was distilled once, and the condensed liquid phase was used. This minimized contamination from carbon dioxide and mercaptans.

The phase compositions were determined with a Hewlett-Packard Model 700 gas chromatograph equipped with a thermal conductivity cell detector. The column used was made from a 3-ft by ⅛-in. diam stainless-steel tube packed with poropak QS. It was maintained at 60°C. The chromatograph was calibrated using pure components, and the response was linear at 1-cc sample loop pressures up to 0.3 atm. The response factor for converting area fraction to mole fraction was 1.125 for hydrogen sulfide, compared to 1.000 for nitrogen.

Samples of the equilibrium liquid and vapor phases were expanded to a pressure of about 150 mm of mercury through a micrometering valve into an evacuated line connected to the gas chromatograph gas sampling valve. The pressure in the line was measured with a differential pressure transducer. Two samples of each phase were taken, and triplicate chromatographs were run on each sample. For each point, the six analyses were generally repeatable to within ±0.2 mol %, and the accuracy was judged to be ±0.3 mol %.

Results and Discussion

The experimental measurements of the equilibrium-phase compositions and refractive indices, together with the calculated phase densities and vapor-liquid equilibrium ratios for both components, are given in Table I. The vapor and liquid-phase compositions are shown as a function of pressure at each of the five temperatures 1.9°, 40.1°, 80.4°, 119.7°, and 160.0°F in Figures 1 and 2. Figure 3 is a representation of the volumetric behavior of the equilibrium liquid phase. From Table I, the volume of the saturated vapor phase goes through a maximum at constant pressure as the temperature changes from 160° to 1.9°F. This is because the effect of increasing nitrogen concentration on the vapor density is greater than the effect of temperature as one goes, for example, from 160°F and 2000 psia to 80.4°F and 2000 psia. The calculated equilibrium ratios are shown in Figure 4 which illustrates how the volatility of nitrogen in the liquid increases rapidly as temperature decreases.

The equilibrium-phase densities were calculated from the experimental phase compositions and refractive indices by use of the Lorentz-Lorenz molar refractivity relationship as explained in earlier papers (*1*, *2*):

$$R_{\mathrm{LL}} = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{\rho}$$

The refractivity of the mixtures was assumed to be additive on a molar basis. Keilich (*4*), in a theoretical study of molar refractivities of dense mixtures, has shown that R_{LL} is strictly additive only in the case of perfect gases. The nonadditive terms were functions of the polarizabilities, molecular symmetry, and dipole moments of the molecules. However, even though the existence of nonadditive terms appears to be well founded in theory, experimentally, these terms are exceedingly small. For example, Smyth et al. (*9*) studied the refractive index and density of 15 binary liquid mixtures. Their study included binary systems containing a wide variety of substances such as ethyl and butyl alcohols, ethyl and butyl bromides, iodides, and chlorides, heptane, and carbon tetrachloride. In every case, the maximum deviation from the molal additivity rule was less than 0.1%. Since the materials used in this study included compounds having dipole moments more than double the dipole moment of hydro-

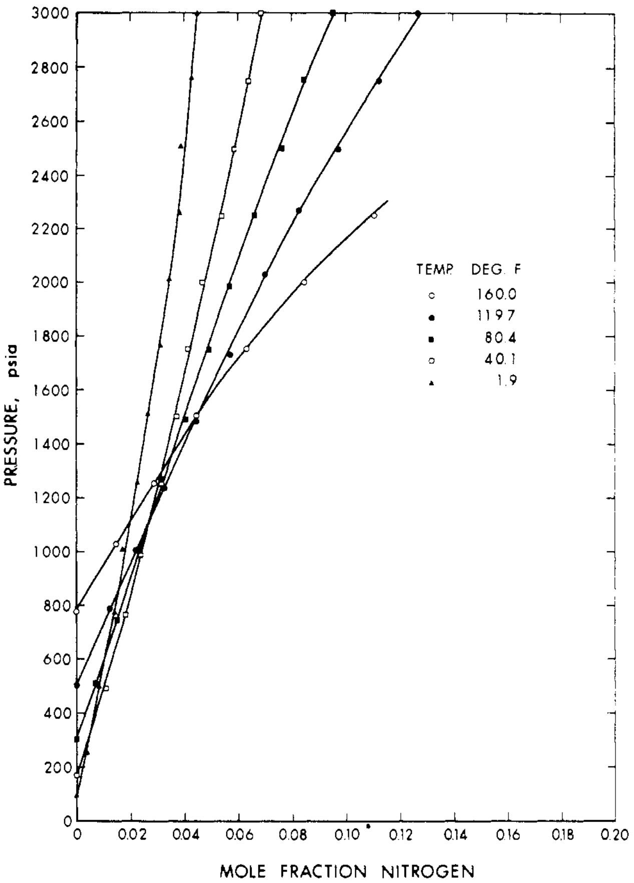

Figure 1. Equilibrium liquid-phase composition for hydrogen sulfide–nitrogen system

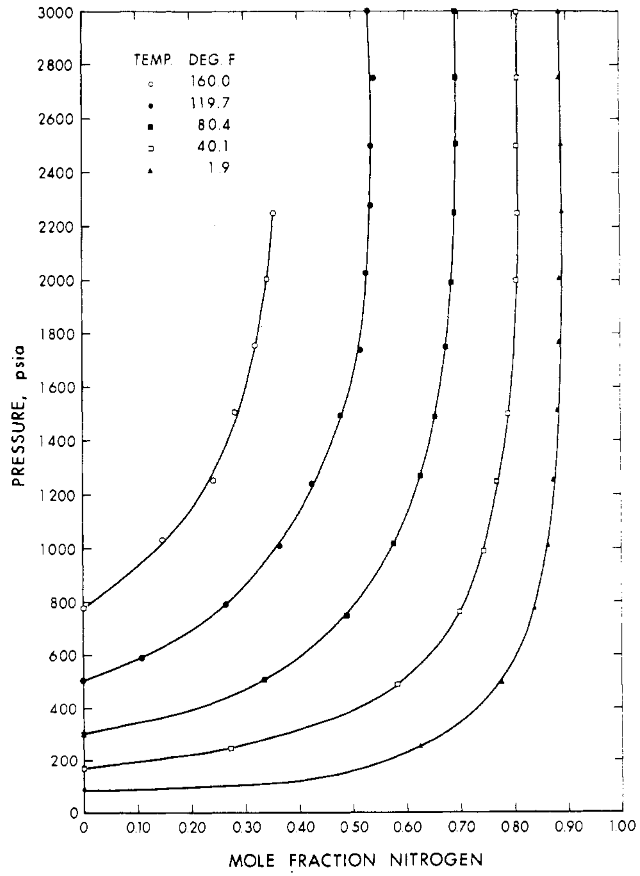

Figure 2. Equilibrium vapor-phase composition for hydrogen sulfide–nitrogen system

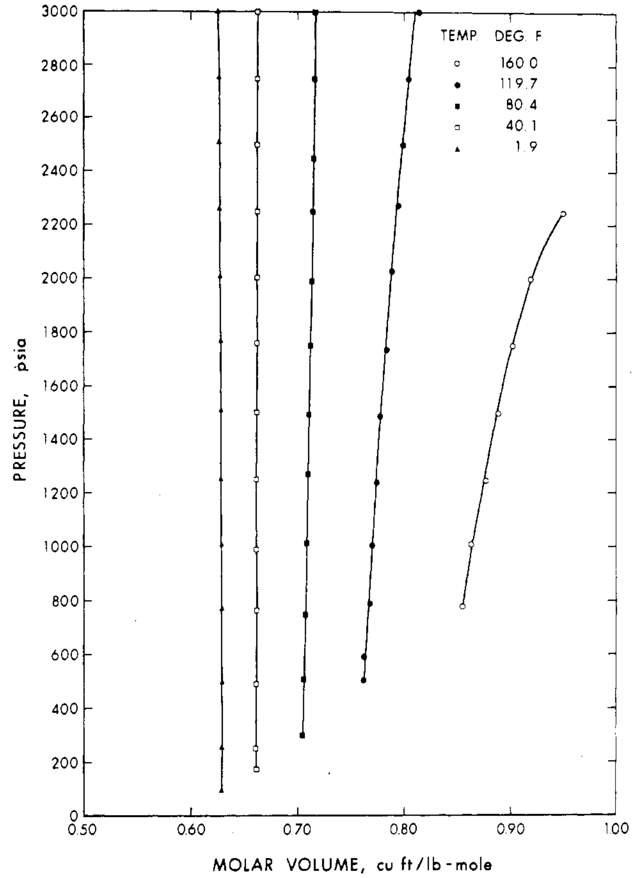

Figure 3. Equilibrium liquid-phase densities for hydrogen sulfide-nitrogen system

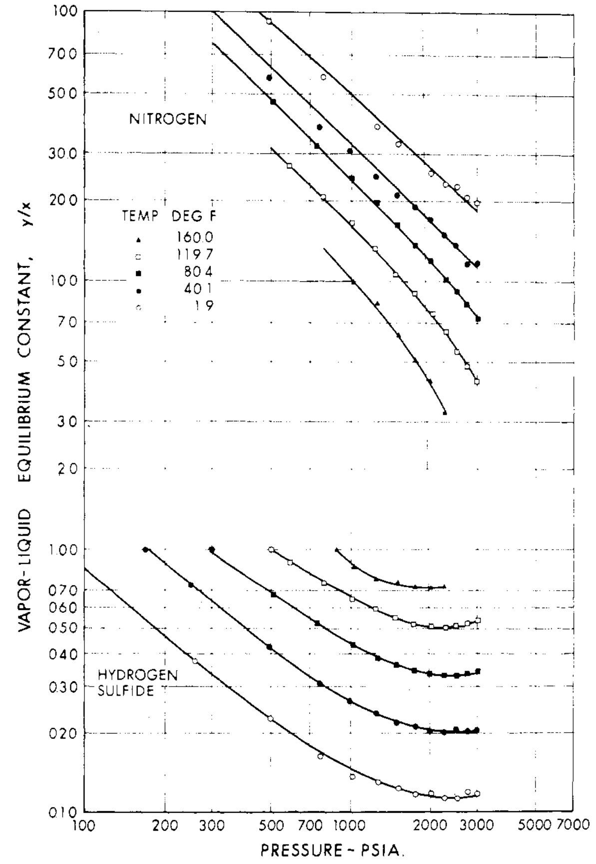

Figure 4. Equilibrium ratios for hydrogen sulfide and nitrogen in hydrogen sulfide-nitrogen system

Table II. Pure Component Lorentz-Lorenz Refractivities in cc/g mol at 6328 Å

	Temp, °F				
Component	1.9	40.1	80.4	119.7	160.0
Nitrogen	4.44	4.44	4.44	4.44	4.44
Hydrogen sulfide	9.68	9.66	9.65	9.60	9.55

gen sulfide and some having dipole moments considerably in excess of that of water, it was concluded that the assumption of the additivity of the Lorentz-Lorenz refractivities was entirely justified.

The refractivities of hydrogen sulfide were obtained from refractive indices measured experimentally in this work and from densities calculated from the Benedict-Webb-Rubin equation of state. The coefficients in the equation would reproduce the densities of hydrogen sulfide to within an rms error of ±0.9% over a range of temperatures between 40° and 280°F and at pressures to 10,000 psia. The refractivities for nitrogen were obtained from the work of Michels et al. (7) because these values were considered to be the best available. Their work showed the refractivities to be independent of pressure in the range of interest. They were assumed to be independent of temperature since they were reported at only 25°C. This assumption is not unreasonable because the refractivities of several other substances such as carbon dioxide, ethylene, and isobutane are a very weak function of temperature (*2, 5, 6*) and are usually within about ±0.6% over a range of 150°F. The values of the pure component refractivities which were used in this work are given in Table II.

Conclusions

The work reported herein has served to provide a set of experimental data on the phase behavior of a binary system containing components commonly encountered in the production and processing of natural gases and related systems. The volatility of nitrogen decreased rather rapidly with increasing temperature. This is shown by the vapor-liquid equilibrium ratios in Figure 4 and is typical of the behavior of nitrogen in other liquid solutions. The calculated molar volumes are subject to the errors in the experimental measurements and to the assumptions made with respect to the calculation of the molar refractivities but are considered to be reliable within about ±1.5%.

This study represents the conclusion of a program which was designed to make experimental measurements of the heat capacity, density, and phase behavior of nitrogen-hydrogen sulfide binary mixtures at temperatures near ambient and above. The phase behavior work is continuing to lower temperatures.

Acknowledgment

The authors acknowledge the work of Hans Rempis who took much of the experimental data and the contribution of Harish Kalra who assisted with the refractivity determinations.

Nomenclature

K_{H_2S} = equilibrium ratio for hydrogen sulfide
K_{N_2} = equilibrium ratio for nitrogen
M = molecular weight
V = refractive weight
n_L = refractive index of liquid
n_V = refractive index of vapor
P = pressure, psia

R_{LL} = Lorentz-Lorenz molar refractivity
x = mole fraction of component in liquid phase
y = mole fraction of component in vapor phase
V_L = molar volume of liquid, ft^3/lb mol
V_V = molar volume of vapor, ft^3/lb mol
ρ = density

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Solubility of Mixtures of Carbon Dioxide and Hydrogen Sulfide in 5.0*N* Monoethanolamine Solution

Jong Il Lee Frederick D. Otto, and Alan E. Mather[1]
Department of Chemical Engineering, The University of Alberta, Edmonton, Alta., Canada

The solubility of mixtures of carbon dioxide and hydrogen sulfide in 5.0*N* monoethanolamine solution was determined at temperatures of 40° and 100°C. Partial pressures of carbon dioxide ranged from about 0.1 to 810 psia and of hydrogen sulfide from 0.1 to 510 psia. The results were combined with data for the pure components, and smoothed values are presented.

Although a number of studies of the solubility of CO_2 and H_2S individually in aqueous monoethanolamine (MEA) solutions have been made, only a few workers have investigated the solubility of mixtures of CO_2 and H_2S in MEA solutions. All the studies of mixtures were made at partial pressures of the acid gases below 2 atm and for the 2.5*N* MEA solution. A literature review was made of the solubility of the individual acid gases in MEA solutions as part of a previous paper (*5*).

Three papers have been published on the solubility of mixtures of CO_2 and H_2S in MEA solutions. Leibush and Shneerson (*6*) measured the equilibrium solubilities for a 2.5*N* MEA solution at 25°C. Partial pressures of the acid gases were below 75 mm Hg. Muhlbauer and Monaghan (*7*) determined the solubility of mixtures of CO_2 and H_2S in a 2.5*N* MEA solution at 25° and 100°C, at partial pressures of the acid gases of less than 1000 mm Hg. Jones et al. (*1*) studied the solubility of mixtures of H_2S and CO_2 in a 2.5*N* MEA solution at temperatures between 60° and 120°C at partial pressures of CO_2 and H_2S up to 3000 and 1000 mm Hg, respectively.

Experimental

The MEA solution was made up to 5.0*N* from commercially available MEA and distilled water and charged to a windowed equilibrium cell. Carbon dioxide and hydrogen sulfide were added to amounts determined by observation of the total pressure on a bourdon gauge. The vapor phase was circulated by means of a magnetic pump and bubbled through the liquid. After equilibrium was reached, samples of the vapor and liquid were withdrawn for analysis. The apparatus and the analytical procedure have been described in previous papers (*2-4*).

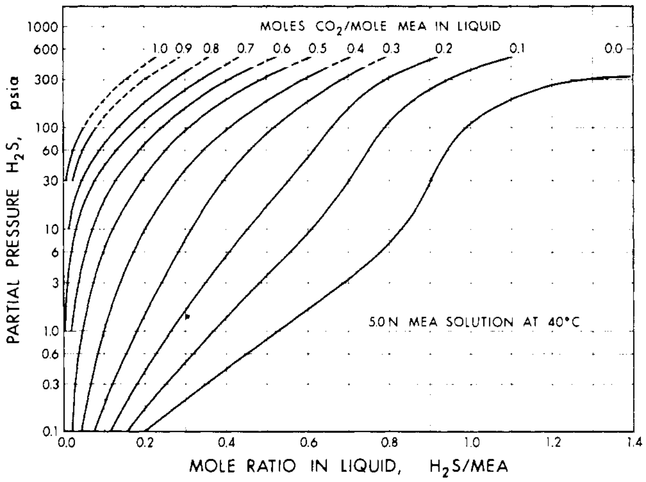

Figure 1. Effect of CO_2 on partial pressure of H_2S in 5.0*N* MEA solution at 40°C

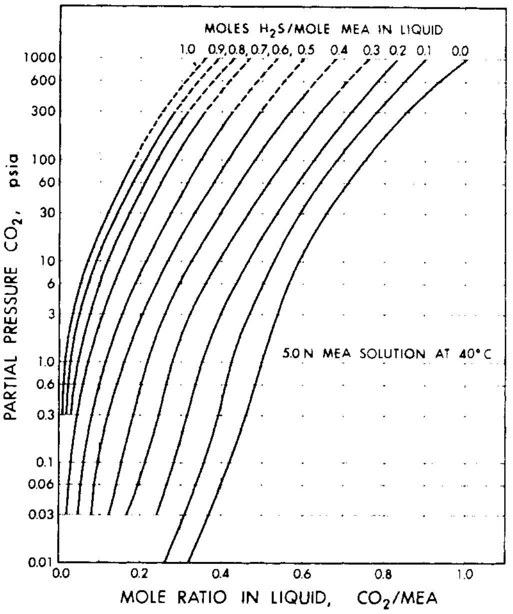

Figure 2. Effect of H_2S on partial pressure of CO_2 in 5.0*N* MEA solution at 40°C

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[1] To whom correspondence should be addressed.