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Equilibria between Hydrogen Sulfide and Aqueous Solutions of Monoethanolamine at 25°, 45° and 60°

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The ethanolamines have become of importance industrially in removing acidic impurities from gases. Various reports have been made on the processes and some of the equilibria involved,[1-7] but to date the only data published for hydrogen sulfide and monoethanolamine are by Bottoms.[8] He used the commercial grade of monoethanolamine which is largely a mixture of mono-, di- and triethanolamines in varying proportions. J. W. Mason[9] has determined the equilibrium for hydrogen sulfide and diethanolamine solutions, but his work has not been published. In choosing a suitable solution for scrubbing gases a knowledge of the equilibria involved is essential. In this investigation data have been obtained on the equilibria between hydrogen sulfide and aqueous solutions of monoethanolamine over a range of concentrations from 0.5 to 4.0 normal and for partial pressures of hydrogen sulfide ranging from 25 to 700 mm., at 25, 45 and 60°.

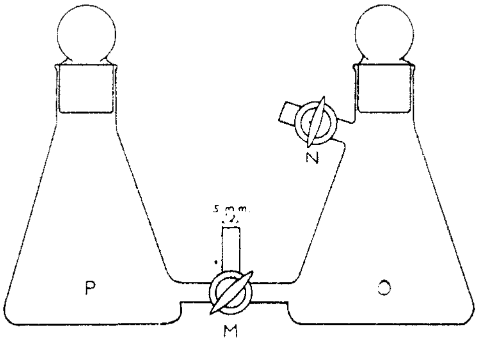

Fig. 1.—Gas sampling pipet.

Experimental

Materials.—The gases used were from commercial cylinders. The hydrogen sulfide on analysis was found to require no further purification. The nitrogen was passed through ascarite to remove carbon dioxide. The monoethanolamine was a product of the Carbide and Carbon Chemicals Corporation for technical use. It was purified by distillation; the boiling point of the product was 170.1° and the refractive index at 25° was 1.4539. These values are in agreement with those reported by Reitmeier.[10] Iodine, potassium iodide, and sodium thiosulfate were of analyzed reagent quality and were used without further purification. The sodium thiosulfate solutions were standardized against potassium dichromate and then were used as a secondary standard for the iodine solutions. The iodate content of the potassium iodide was found to be negligible.

Apparatus.—Two types of apparatus were used. For the determinations at 25°, hydrogen sulfide was run through the amine solutions in two modified Bichowsky-Storch type absorbers[11] connected in parallel. The modification consisted of a ground glass joint at the base of the absorber through which liquid samples could be taken Before entering the absorbers the gas was presaturated by allowing it to pass through an amine solution of the same concentration and at the same temperature as that in the absorbers. The gas sampling pipet was introduced into the system between the presaturator and the absorbers. This pipet is illustrated in Fig. 1; P and O are 125-cc. glass stoppered erlenmeyer flasks; N is an ordinary stopcock and M a three-way stopcock. This apparatus was first filled with nitrogen and the gas containing the hydrogen sulfide was passed through M into O and out through N. Flask P was later filled with iodine solution to use in analyzing the gas sample.

The liquid sampling pipet, A, Fig. 3, had a capacity of about 10 cc. and was constructed to fit the ground-glass joint at the bottom of each absorber so that the liquid would be forced by gravity to fill the pipet. The pipet was first weighed and filled with gas of the same hydrogen sulfide content as that passing through the absorbers. Connection was then made by the ground glass joint at the bottom of the absorber. Cocks I and K remained closed, and H opened to allow the space between them to be washed out with the equilibrium solution before filling A with the sample.

While gas circulated through the solution, simultaneous gas and liquid samples were taken. The liquid sample was analyzed for hydrogen sulfide content only; a second liquid sample was taken before the partial pressure of the gas was changed, and this was analyzed for amine content.

To change the partial pressure of the hydrogen sulfide, the gas was allowed to mix with a stream of nitrogen before entering the presaturator. The velocity of flow of hydrogen sulfide and nitrogen was controlled by separate flowmeters, stopcocks, and pressure heads.

The apparatus from the presaturator to the outlet from the absorbers was kept in a constant temperature air-bath (±0.05°). Before beginning each run the system was washed out with pure nitrogen to avoid oxidation of hydrogen sulfide. About eight hours was allowed for equilibrium to be established for each determination.

The second type of apparatus was designed for determinations at 45 and 60° since the water vapor loss in the first was too great at these temperatures. It is illustrated in Fig. 2. The two bulbs, A and A', are of about 500-cc. capacity. The liquid sampling pipet may be attached to the ground-glass joint C, while F' and G' fit the ground joints F and G of the gas sampling pipet E; B, J and R are ordinary stopcocks; and D is a three-way cock which is connected to a vacuum pump and a nitrogen tank. The bulbs are mounted on a suitable wooden frame. A shaft is connected at X perpendicular to the plane of the paper.

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(1) Mason and Dodge, *Trans. Am. Inst. Chem. Engrs.*, **32**, 27 (1936).

(2) Wood and Storrs, *Natl. Petroleum News*, **30**, R276 (1938).

(3) Powell, *Ind. Eng. Chem.*, **31**, 789 (1939).

(4) Wood and Storrs, *Am. Petroleum Inst.* (Proc.), Midyear meeting, Section III, **19**, 34 (1938).

(5) Reed and Wood, *Trans. Am. Inst. Chem. Engrs.*, **37**, 363 (1941).

(6) Storrs, *Ind. Eng. Chem.*, *News Ed.*, **17**, 627 (1939).

(7) Storrs and Reed, *Trans. Am. Inst. Mech. Engrs.*, **64**, 299 (1942).

(8) Bottoms, *Ind. Eng. Chem.*, **23**, 501 (1931).

(9) J. W. Mason, unpublished communication to the Girdler Corp., Louisville, Kentucky.

(10) Reitmeier, Sivertz and Tartar, THIS JOURNAL, **62**, 1943 (1940).

(11) Bichowsky and Storch, *ibid.*, **37**, 2695 (1915).

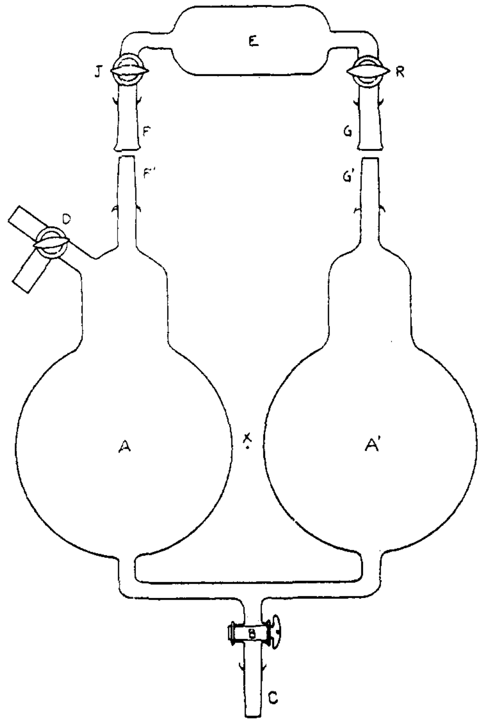

Fig. 2.—Apparatus for equilibrium between gaseous and liquid phases.

It leads through the wall of the air-bath to an eccentric so that the whole apparatus is rotated about an axis perpendicular to X through an angle of about 25° at the rate of about half a revolution per minute. This allows gas to be pumped back and forth through the pipet E until equilibrium is established. The time required in this method was decreased to about three or four hours.

For the runs at 45 and 60° the equilibrium mixtures were prepared in the Bichowsky-Storch type absorbers at room temperature. The solution was then transferred to the equilibrium bulbs and the pipet E, filled with hydrogen sulfide, was connected. After the apparatus had come to temperature, the excess pressure was released by opening cock D to the air. When equilibrium was reached, simultaneous gas and liquid samples were taken; a second liquid sample was taken for amine analysis before the partial pressure was changed.

To decrease the partial pressure of the hydrogen sulfide the gas pipet E was again connected and the system evacuated through D. Nitrogen was then added through D to replace the hydrogen sulfide.

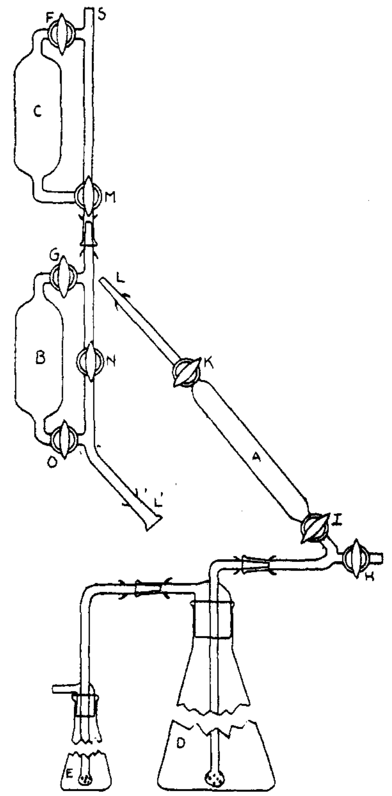

Fig. 3.—Apparatus for the analysis of the liquid phase.

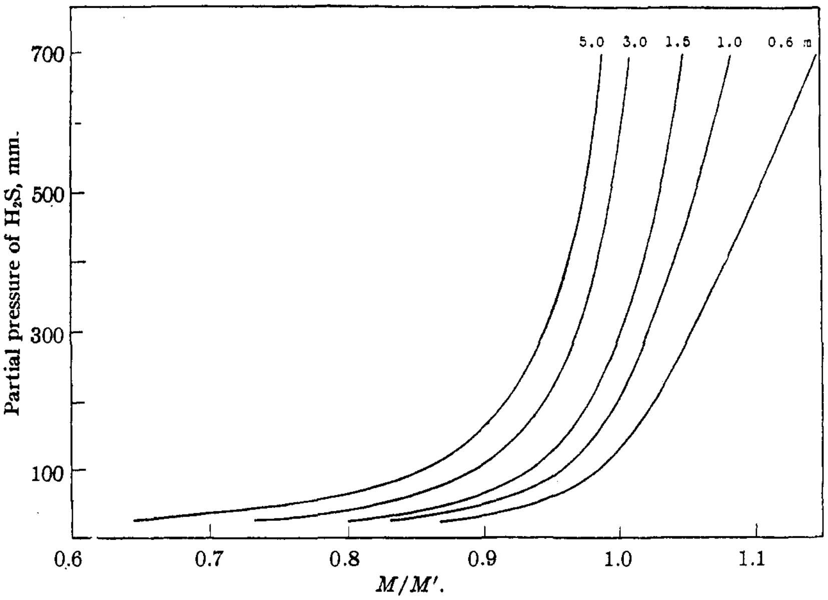

Fig. 4.—Equilibrium pressures of hydrogen sulfide from aqueous solutions of monoethanolamine at 25°.

Analysis of Samples.—The samples were analyzed for hydrogen sulfide content by transferring the sample without loss to standard iodine solution and titrating the excess iodine with standard sodium thiosulfate solution. In the case of the gas samples this was accomplished by connecting the flask containing the iodine solution directly to the gas pipet and allowing the solution to run into the pipet. In calculating the partial pressure of hydrogen sulfide, its molar volume was taken to be 22.159 liters under standard conditions.

For the analysis of the liquid sample the apparatus shown in Fig. 3. was used. The pipet A was connected to a 500-cc. erlenmeyer flask D fitted with a ground glass stopper which led to a similar 25-cc. erlenmeyer. The large flask contained enough iodine dissolved in aqueous potassium iodide to react completely with the hydrogen sulfide in the sample, and also enough hydrochloric acid to react with the amine. Sodium lauryl sulfate solution was added to cause the sulfur to precipitate in finely divided form, without appreciable adsorption of iodine.

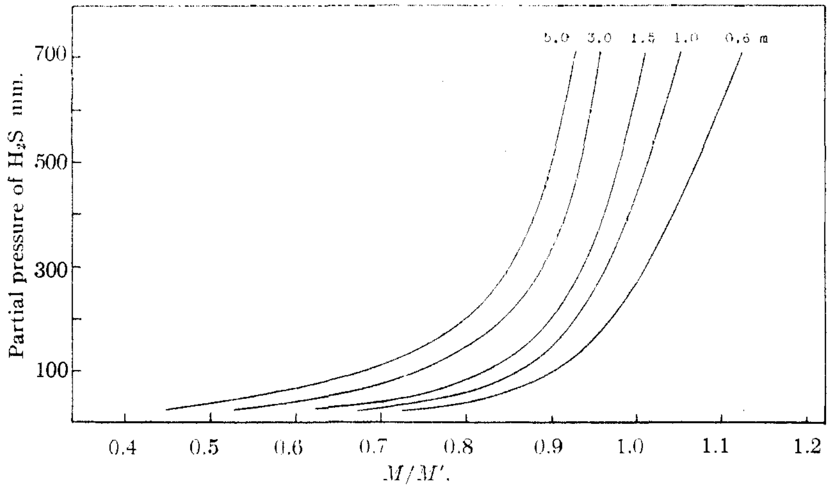

Fig. 5.—Equilibrium pressures of hydrogen sulfide from aqueous solutions of monoethanolamine at 45°.

The small flask and a 25-cc. pipet B connected to the other end of the sampling pipet A contained 0.05 N iodine solution for purposes of reacting with the last traces of hydrogen sulfide. A second 25-cc. pipet C connected to the pipet containing the iodine solution was filled with distilled water to wash the two pipets. The opening of the last pipet was connected to a nitrogen tank. The whole set-up was mounted on a suitable frame and was well shaken throughout the addition of the sample to the iodine.

Analysis of the sample for amine content was accomplished by titrating directly with standard hydrochloric acid to a methyl orange end-point or by first diluting the sample and then titrating aliquot samples.

The determination of amine concentration is believed to be accurate to 0.3% except where the sulfide concentration is appreciable in which case the error is slightly greater. The hydrogen sulfide concentration may be determined to an accuracy of 0.5% as may also the partial pressure of hydrogen sulfide. Doubtful values obtained with the first apparatus were checked with the second.

Results

Calculations were carried out to obtain the partial pressure of hydrogen sulfide, the molality of the amine solution both before and after reacting with hydrogen sulfide, and the ratio of moles of hydrogen sulfide per mole of amine. For purposes of converting the data to other units the densities of the solutions were also determined.

Since the experimentally determined values of molality of amine in general differed somewhat from the nominal value, it was necessary to convert the data to common values of amine molality. This was accomplished by the following procedure: first, the values of the ratio of moles hydrogen sulfide per mole amine, M/M′, were plotted against the partial pressures of hydrogen sulfide for each nominal amine molality. Smooth curves were drawn through these experimental points, care being taken to obtain a reasonable family of curves and still have the points fall on the curves within the experimental error. From these curves, values of M/M′ were read off at constant partial pressures and these values plotted against the corresponding values of molality of amine found experimentally. Where the point chosen fell, between two experimental points, a weighted average of the two amine molalities on either side was used. Smooth curves of M/M′ against experimental molality of amine were again drawn through this second set of points for constant partial pressure and temperature. From these graphs, values of M/M′ were read off for each partial pressure at constant amine molality. By interpolation, values were also obtained for intermediate amine molalities. These corrected data are presented in Table I and Figs. 4, 5 and 6.[12]

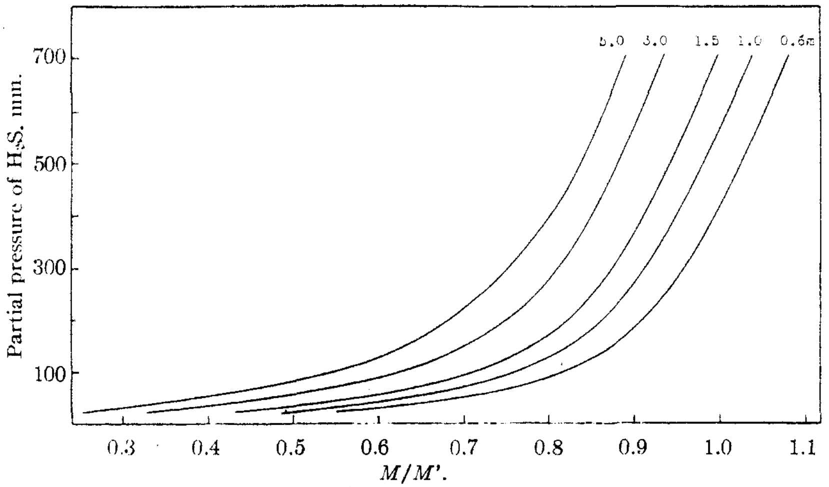

Fig. 6.—Equilibrium pressures of hydrogen sulfide from aqueous solutions of monoethanolamine at 60°.

[12] The actual experimental data may be found in "The Solubility of Hydrogen Sulfide in Aqueous Solutions of Monoethanolamine," Evamaria Riegger, Ph.D. Thesis, University of Washington Library, Seattle 5, Washington. The number of experimental points are as follows: At 25°, 20 points at 0.552 *m*, 19 points at 1.057 *m*, 18 points at 2.317 *m*, 13 points at 3.569 *m*, 14 points at 5.218 *m*. At 45°, 9 points at 0.549 *m*, 6 points at 2.2953 *m*, 7 points at 5.156 *m*. At 60°, 7 points at 0.551 *m*, 7 points at 2.303 *m*, 6 points at 5.162 *m*.

TABLE I

MOLES OF HYDROGEN SULFIDE PER MOLE OF AMINE FOR MONOETHANOLAMINE SOLUTIONS CORRECTED TO IDENTICAL VALUES OF AMINE MOLALITY

Partial pressure of H_2S, mm.	Molality of amine						
	0.6	1.0	1.5	2.0	3.0	4.0	5.0
	Temperature 25°						
700	1.148	1.086	1.050	1.033	1.011	0.998	0.991
600	1.126	1.072	1.041	1.025	1.004	.991	.984
500	1.101	1.058	1.032	1.016	0.996	.980	.974
400	1.080	1.042	1.020	1.006	.985	.971	.963
300	1.053	1.022	1.002	0.990	.970	.955	.945
200	1.027	0.998	0.979	.966	.946	.931	.918
100	0.986	.956	.934	.919	.893	.870	.852
50	.934	.902	.876	.856	.819	.784	.758
25	.866	.833	.802	.777	.730	.687	.643
	Temperature 45°						
700	1.124	1.051	1.011	0.988	0.958	0.940	0.927
600	1.097	1.033	0.996	.975	.948	.928	.914
500	1.070	1.012	.980	.960	.934	.913	.899
400	1.045	0.993	.961	.943	.918	.897	.880
300	1.011	.967	.939	.921	.891	.869	.850
200	0.971	.929	.900	.880	.846	.819	.800
100	.908	.864	.826	.795	.748	.714	.684
50	.826	.782	.742	.706	.648	.601	.564
25	.731	.686	.631	.601	.533	.487	.453
	Temperature 60°						
700	1.083	1.040	0.998	0.968	0.934	0.909	0.891
600	1.056	1.011	.970	.944	.910	.884	.865
500	1.027	0.984	.945	.916	.880	.858	.837
400	0.995	.952	.912	.885	.848	.821	.801
300	.960	.916	.876	.847	.810	.778	.753
200	.908	.863	.822	.793	.751	.714	.683
100	.811	.757	.708	.674	.624	.581	.547
50	.694	.634	.576	.532	.474	.425	.386
25	.551	.490	.433	.388	.331	.291	.285

In the solutions there exists an equilibrium between hydrogen sulfide, hydrosulfide ion, monoethanolamine, monoethanolammonium ion, hydrogen ion, hydroxide ion and water. The concentration of sulfide ion is small enough to be negligible. Through the use of the ionization constants at 25° of hydrogen sulfide, 1.15×10^{-7},[13] monoethanolamine, 3.19×10^{-5},[14] and water 1.01×10^{-14}, we can calculate the concentration of undissociated hydrogen sulfide in the various solutions. Upon carrying out this calculation for the 0.6 *m* monoethanolamine solutions at partial pressures of hydrogen sulfide of 200, 400 and 600 mm., using a value of 0.77 for the mean ionic activity coefficient, the points fall quite close to the partial pressure–concentration line for hydrogen sulfide in water alone.[15] These results are shown in Fig. 7.

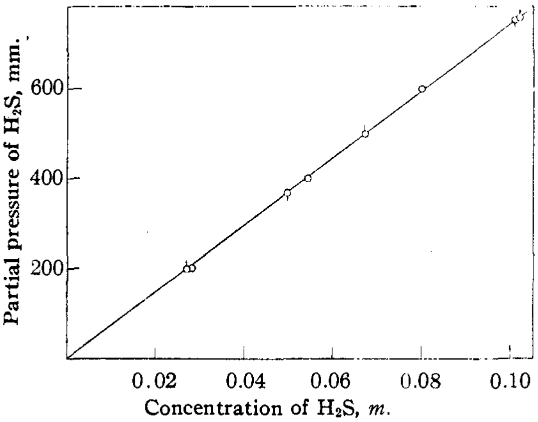

Fig. 7.—Partial pressures of hydrogen sulfide *vs.* concentration of undissociated hydrogen sulfide at 25°: O, this research, 0.6 *m* monoethanolamine solution; O, "I. C. T.," water alone; O, Wright and Maass, water alone.

Similar calculations at higher concentrations or at higher temperatures were not made because of increased uncertainties in activity coefficients and ionization constants.

Summary

1. Apparatus has been designed for accurate measurements on the equilibria between hydrogen sulfide and ethanolamine solutions.

2. The equilibria at 25, 45 and 60° have been determined between hydrogen sulfide at partial pressures 25 to 700 mm. and aqueous solutions of monoethanolamine of concentrations ranging from 0.5 to 4.0 *N*. The experimental data have been corrected to common values of amine molality and presented in tabulated and graphical form.

3. The relationship between partial pressure and concentration of undissociated hydrogen sulfide in 0.6 *m* monoethanolamine solution at 25° has been shown to obey Henry's law.

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(13) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, N. Y., 1923, p. 543

(14) Sivertz, Reitmeier and Tartar, THIS JOURNAL, **62**, 1379 (1940).

(15) "International Critical Tables," Vol. 3, p. 259; Wright and Maass, *Can. J. Research*, **6**, 94 (1932).