Anal. Calcd. for $C_{13}H_{15}ON_3$: N, 18.33; OC_2H_5, 19.66. Found: N, 18.14; OC_2H_5, 19.50.

On evaporating on a steam-bath with concentrated hydrochloric acid and making alkaline with ammonia, this compound gave 2-anilino-4-oxy-5-methoxypyrimidine, m. p. 254–255° from alcohol. This same compound was obtained for comparison by heating 2-ethylmercapto-4-oxy-5-methylpyrimidine with aniline on a steam-bath until all the ethylmercaptan was evolved. Benzene was added and the solid removed by filtering. This was recrystallized from alcohol, m. p. 254–255°.

Anal. Calcd. for $C_{11}H_{11}ON_3$: N, 20.88. Found: N, 20.70.

2 - Ethylsulfonyl - 4 - amino - 5 - methylpyrimidine.—Two grams of 2-ethylsulfonyl-4-chloro-5-methylpyrimidine was heated with 25 cc. of ethanol, saturated with dry ammonia at 0°, for two hours at 100°. The alcohol was then evaporated and the residue extracted with hot ethyl acetate. The ethyl acetate solution was concentrated to a small volume and cooled. There was obtained 0.9 g. of crystals, m. p. 128–130°. A further quantity was obtained from the filtrate (0.13 g.). This was recrystallized from ethyl acetate, m. p. 135.5–136.5°.

Anal. Calcd. for $C_7H_{11}O_2N_3S$: N, 20.88; S, 15.94. Found: N, 20.90; S, 16.18.

On hydrolysis[2] with hydrochloric acid this sulfone evolved sulfur dioxide. The aqueous solution on evaporation gave 5-methylcytosine hydrochloride.[8] This was recrystallized from an alcohol-concentrated hydrochloric acid solution by addition of ether, m. p. 288–290° (dec.).

Anal. Calcd. for $C_5H_7O_3N_3 \cdot HCl$: N, 26.00; Cl, 21.95. Found: N, 25.80; Cl, 22.21.

Summary

In this paper is described the behavior of several 2-ethylsulfonylpyrimidines when allowed to interact with sodium alcoholate, alkali, ammonia and aniline. The ethylsulfonyl group of the pyrimidine reacts in all these changes in a similar manner as a halogen atom being easily replaced by alkoxyl, hydroxyl and amino groups.

[8] Wheeler and Johnson, *Am. Chem. J.*, **31**, 598 (1904).

NEW HAVEN, CONNECTICUT

RECEIVED DECEMBER 26, 1935

Calculation of the Solubility of a Mixture of Hydrogen and Nitrogen in Water at 25° in the Pressure Range of 50 to 1000 Atmospheres

BY JACOB KIELLAND[1]

Introduction

R. Wiebe and V. L. Gaddy[2] have recently published experimental data concerning the solubility of a 76.42:23.58 hydrogen–nitrogen mixture in water at 25°, and at high pressure. It was found that the solubility of the mixture could be calculated to within a few per cent. from the values of the pure constituents, by multiplying the mole fraction of each separate gas by its own solubility at a pressure equal to the total pressure of the mixture, and then adding these values together.

However, on examining the solubility of each one of the constituents it will be found that there is a certain amount of difference between the values observed and those calculated. As far as the nitrogen is concerned, there is a deviation of about 13% at 800 to 1000 atm., Wiebe and Gaddy's own analyses of the composition of the gas in the water phase being employed (see Table I).

Discussion

The difference between the calculated and observed solubilities—assuming that there is no systematical error in measurement—may be explained by the existence of deviations from the fugacity rule[3] of Lewis and Randall, which is the basis of method of calculation, and states

$$\bar{f}_i = \frac{\partial f_i}{\partial n_i} = N_i f_i$$

or, in other words, that the activity coefficient of a gas is the same at constant pressure, irrespective of whether the gas occurs alone or in mixtures. According to A. R. Merz and C. W. Whittaker,[4] however, this rule does not apply to hydrogen–nitrogen mixtures at the pressures in question in the present case. From the work carried out by them, the values for γ_i/γ_i^0 or $\bar{f}_i/N_i f_i^0$, given in Table II, columns 2 and 3, have been taken.

In the water phase, where the action of the water molecules on the activity coefficients must be assumed to be of greater importance than the interaction of the separate gases, the latter process will not be taken into consideration. The results obtained prove this assumption to be perfectly justified.

It must be pointed out that the solubility correction for deviations from the Lewis and Randall

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[2] Wiebe and Gaddy, THIS JOURNAL, **57**, 1487 (1935).

[3] *Cf.* Newton and Dodge, *Ind. Eng. Chem.*, **27**, 578 (1935).

[4] Merz and Whittaker, THIS JOURNAL, **50**, 1522 (1928).

TABLE I

THE SOLUBILITY OF A HYDROGEN–NITROGEN MIXTURE IN WATER AT 25° (CC. OF GAS AT S. T. P. PER G. OF WATER) ACCORDING TO MEASUREMENTS AND CALCULATIONS BY WIEBE AND GADDY

Pressure, atm.	Observed,			Calculated,			Obsd. − Calcd. in %		
	H_2	N_2	Total	H_2	N_2	Total	H_2	N_2	Total
50	0.6694	0.1655	0.8349	0.663	0.159	0.822	0.9	3.9	1.6
100	1.328	.315	1.643	1.321	.298	1.619	0.5	5.4	1.5
200	2.652	.557	3.209	2.591	.532	3.123	2.3	4.5	2.7
400	5.118	.950	6.068	5.021	.893	5.914	1.9	6.0	2.5
600	7.482	1.327	8.809	7.321	1.188	8.509	2.1	10.4	3.4
800	9.665	1.662	11.327	9.522	1.446	10.968	1.5	13.0	3.2
1000	11.778	1.946	13.724	11.616	1.686	13.302	1.4	13.4	3.1

rule, which reach 13% in the case of the gas mixture containing 76% of hydrogen, would reach nearly 20% for either of these gases when it is present in small proportions in the gas mixture.

Since this paper was prepared, a publication of I. R. Krichevsky and J. S. Kasarnovsky appeared [THIS JOURNAL, **57**, 2168 (1935)] concerning the solubilities of either nitrogen or hydrogen in water, which was shown to follow the formula $\ln f_2/N_2 = \ln K_{\text{Henry}} + (\bar{v}_2P/RT)$. They pointed out that this formula may also be used in the case of gas mixtures; this means that the partial molal volume of either gas in aqueous solution is assumed to be independent of the other gas. The validity of this assumption, which is identical with the one made by the author, is confirmed by the present work.

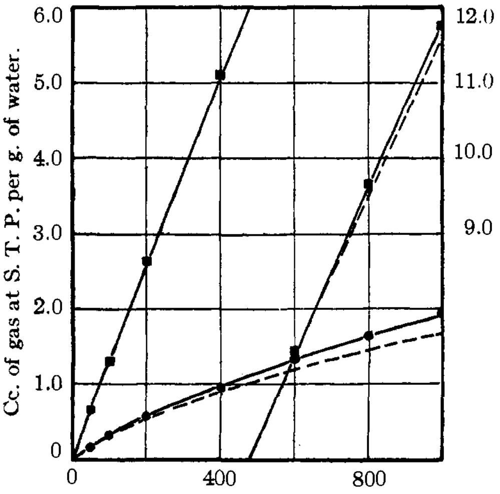
Results

When equilibrium is established the fugacity or activity will be equally great in both phases, wherefore it is necessary to multiply the solubilities calculated by Wiebe and Gaddy by the corresponding values of γ_i/γ_i^0. This has been done in Table II, columns 4 and 5. In columns 7, 8 and 9 are shown the deviations from the experimental data thus obtained, and in Fig. 1, the results are illustrated graphically.

TABLE II

SOLUBILITY OF A HYDROGEN–NITROGEN MIXTURE IN WATER AT 25° (CC. OF GAS AT S. T. P. PER G OF WATER)—CALCULATED BY THE AUTHOR

Pressure, atm.	γ_i/γ_i^0		Calcd. soly.			Obsd. − Calcd. in %		
	H_2	N_2	H_2	N_2	Total	H_2	N_2	Total
50	1.00	1.01	0.663	0.161	0.824	0.9	2.7	1.3
100	1.00	1.03	1.321	.307	1.628	0.5	2.5	0.9
200	1.00	1.06	2.591	.563	3.154	2.3	−1.1	1.7
400	1.005	1.10	5.046	.983	6.029	1.4	−3.5	0.6
600	1.01	1.12	7.394	1.332	8.726	1.2	+0.4	0.9
800	1.01	1.12	9.617	1.625	11.24	0.5	+2.2	0.8
1000	1.01	1.12	11.78	1.89	13.67	−0.0	2.9	0.4



Pressure of gas mixture in atmospheres.

Fig. 1.—Solubility in water at 25° of a 76.4:23.6 hydrogen–nitrogen mixture: ■ and ●, observed by Wiebe and Gaddy for hydrogen and nitrogen respectively; – – –, calculated by Wiebe and Gaddy; ———, calculated by the present author. (The right-hand ordinate scale refers to hydrogen at 500 to 1000 atm.)

On the basis of this, it should be possible to calculate both the total and the partial solubility to within a few per cent. of any mixture of hydrogen and nitrogen.

Summary

It was found how both the total and the partial solubility in water of hydrogen–nitrogen mixtures at pressures of from 50 to 1000 atmospheres could be calculated to within a few per cent.

OSLO, NORWAY

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