olefin. Measurements of gas density made by a magnetic gas-density balance showed that three separations were not sufficient, as 1 to 5% of the olefin one carbon atom lower in the series was present.

Owing to the presence of relatively large amounts of ethyl mercaptan in the C_6 fraction, it was necessary to find a satisfactory method for separating C_2H_5SH and C_6H_{12}. Condensation on a bright surface of metallic sodium was found fairly satisfactory. Experiments made with pure C_2H_5SH showed that at temperatures between 0° and −10° hydrogen and sodium mercaptate were the main products, only a few per cent. of diethyl sulfide being obtained. The analytical data are given in Table III.

TABLE III

ANALYSIS OF REACTION PRODUCTS, PER CENT.

Compound	2-hour experiments	3-hour experiments
Propylene	34.4	39.2
Butylenes	31.4	29.1
Pentenes	29.0	14.4
Hexenes	2.8	14.4
Higher olefins	2.4	2.9
Ratio of propylene to butylene	1.1	1.35

The increase in the C_3H_6/C_4H_8 ratio in the third hour seem to confirm the evidence presented in the first paper[3] concerning the primary product of the reaction. The question is, however, not answered, for even in the two-hour sample corresponding to polymerization of only about 1% of the total ethylene present the fractions of C_3H_6 and C_5H_{10} are of the same order as that of C_4H_8.

Summary

Several methods of preparation of "pure" ethylene were tried in an unsuccessful effort to obtain reproducible rates of polymerization. It was found that the addition of small amounts (about 0.1 per cent.) of ethyl mercaptan to ethylene prepared by fractionation of "anaesthesia grade" tank ethylene, decreased the rate of polymerization about tenfold; and the $C_2H_4 + C_2H_5SH$ mixture polymerized at rates which were reproducible to within about 5%. These rates were in good agreement with the lowest rates obtained in the absence of the mercaptan. The addition of mercaptan did not eliminate the induction period observed in ethylene to which no mercaptan had been added; but did cut down markedly the duration of this induction period. The latter appears to be due to the rate of formation of some intermediate compound which survives freezing to −180° and subsequent revaporization into the reaction chamber at 393°. The polymerization of ethylene is probably not a simple bimolecular reaction. The evidence as to the nature of the primary product is not conclusive but indicates that butylene precedes propylene. The activation energy is 43,500 cal.

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[CONTRIBUTION FROM FERTILIZER INVESTIGATIONS, BUREAU OF CHEMISTRY AND SOILS]

The Partial Molal Volumes of Ammonia and Hydrogen in Liquid Ammonia-Hydrogen Mixtures under Pressure at 100°

BY R. WIEBE AND T. H. TREMEARNE

Ångström[1] measured the change of volume of water and various other organic liquids when hydrogen and other gases were dissolved in them. From his measurements he calculated

$$\Delta V/\Delta V_g = \delta \qquad (1)$$

wherein ΔV_g denotes the volume of gas at standard temperature and pressure dissolved, and ΔV the attending increase in the volume of solvent at constant temperature and pressure. He found that under atmospheric pressure, δ remained constant with varying V_g, Horiuti[2] extended the work of Ångström and confirmed the constancy of δ with concentration in the low pressure region, with sulfur dioxide in various organic liquids an exception.

Upon multiplying both sides of Eq. (1) by V_0, the volume of a mole of the dissolved gas at standard temperature and pressure we obtain $\Delta V/(\Delta V_g/V_0) = \Delta V/\Delta n_2 = V_0\delta$, which leads at once to the relation

$$(\mathrm{d}V/\mathrm{d}n_2)_{P,T} \equiv \bar{v}_2 = V_0 \qquad (2)$$

first stated explicitly by Horiuti[2] (p. 136).

Ångström and Horiuti both worked at low concentrations. At the relatively high concentra-

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[1] Ångström, *Wied. Ann.*, **15**, 297 (1882); *ibid.*, **33**, 223 (1888).

[2] Horiuti, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), No. 341, **17**, 125-256 (1931).

tions used in the present work it is found that for hydrogen in liquid ammonia, $\bar{v}_2$, and hence δ also, is positive and increases with the concentration of hydrogen except at the lowest pressure. Then because[3] $N_1(\mathrm{d}\bar{v}_1/\mathrm{d}N_1)_{\mathrm{P,T}} = -N_2(\mathrm{d}\bar{v}_2/\mathrm{d}N_2)_{\mathrm{P,T}}$, it follows that the partial molal volume $\bar{v}_1$ of ammonia decreases as the concentration of hydrogen increases.

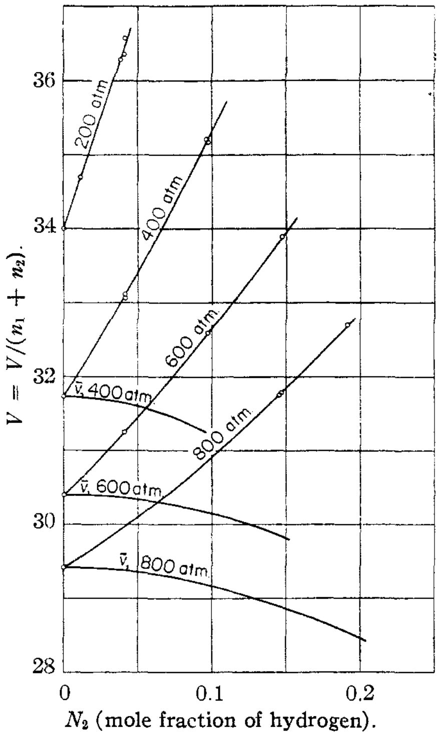

Fig. 1.—Molal volume of liquid ammonia hydrogen mixtures and partial molal volumes of liquid ammonia.

Apparatus and Procedure

The apparatus was identical with one used previously[4] except for a section of tubing fitted with a valve at each end and connected with the lower part of the high pressure bomb. At frequent intervals the volume of this section of tubing was measured by filling it with hydrogen at 100 and 200 atmospheres. In each experiment a sample of the equilibrium mixture from the bomb was turned into this calibrated section, and cut off. The amount of each constituent contained therein could then be determined, following methods previously outlined.

This device permits samples to be made up at concentrations intermediate between pure solvent (liquid ammonia) and saturation. The mixture in the calibrated tube—taken, for example, from a 400 atmosphere equilibrium mixture—can be raised quickly to a higher pressure, say 600 atmospheres, by increasing the pressure of the gas above the solution in the bomb to this figure. This new pressure is transmitted instantly to the contents of the tube, which then unsaturated can be cut off and analyzed as before.

The mixture in the bomb is itself unsaturated when it is suddenly subjected to a new pressure, whereupon diffusion begins at once, attended by a downward creep in pressure. The pressure reading is taken at the moment of cut-off. Diffusion to the bottom of the bomb is slow and there is sufficient opportunity to make one or two analyses before the composition of the samples is affected.

Results

The data are given in Table I and the figure. The molal volumes for pure liquid ammonia were calculated from the results of Keyes.[5] The first

TABLE I

AVERAGE VALUES CALCULATED FROM NUMBER OF RUNS GIVEN

Number of runs	Mole fraction of ammonia N_1	$v = V/(n_1 + n_2)$
	100 atm.	
	1.0000	35.456
6	0.9888	37.189
	200 atm.	
	1.0000	34.017
2	0.9888	34.695
7	.9612	36.276
2	.9589	36.343
4	.9584	36.577
	400 atm.	
	1.0000	31.739
1	0.9588	33.118
1	.9582	33.071
5	.9094	34.963
3	.9036	35.211
1	.9026	35.244
3	.9024	35.172
	600 atm.	
	1.0000	30.399
1	0.9591	31.147
1	.9025	32.597
3	.8527	33.891
	800 atm.	
	1.0000	29.419
1	0.8529	31.779
3	.8083	32.701

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(3) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York City, 1923, p. 43.

(4) R. Wiebe and T. H. Tremearne, THIS JOURNAL, **55**, 975 (1933).

(5) Frederick G. Keyes, *ibid.*, **53**, 965 (1931).

column of Table I gives the number of individual runs from which the data were computed. The partial molal volumes were calculated from the relations[3] (p. 38)

$$\bar{v}_1 = v - N_2\,(\mathrm{d}v/\mathrm{d}N_2)$$
$$\bar{v}_2 = v + N_1\,(\mathrm{d}v/\mathrm{d}N_2)$$

$v = V/(n_1 + n_2)$ being the molal volume of the mixture and N_1 the mole fraction of ammonia, both of which are given in Table I. The derivative $\mathrm{d}v/\mathrm{d}N_2$ was obtained from suitable equations representing the molal volume *vs.* N_2 curves in the figure. Table II and the figure show the partial molal volumes.

TABLE II

N_1	$\bar{v}_1$	$\bar{v}_2$
	100 atm.	
1.0000	35.46	190.2
0.99	35.46	190.2
.9888	35.46	190.2
	200 atm.	
1.0000	34.02	95.16
0.99	34.02	94.20
.9888	34.03	93.88
.96	34.10	90.92
.9586	34.11	90.77
	400 atm.	
1.0000	31.74	62.13
0.99	31.73	63.23
.96	31.65	66.45
.9585	31.64	66.65
.91	31.29	71.60
.9029	31.22	72.62
	600 atm.	
1.0000	30.40	50.66
0.99	30.40	51.13
.96	30.36	52.50
.9591	30.36	52.54
.91	30.21	54.68
.9025	30.18	55.00
.86	29.94	56.75
.8527	29.89	57.04
	800 atm.	
1.0000	29.42	41.91
0.99	29.42	42.39
.96	29.38	43.80
.91	29.22	46.06
.86	28.95	48.20
.8529	28.42	48.49
.8083	28.53	50.28

We wish to point out briefly the thermodynamic significance of the work. At equilibrium where

$$\mathrm{d}\bar{F}_1 = \mathrm{d}\bar{F}_1' \qquad (3)$$

$\bar{F}_1$ and $\bar{F}_1'$ being the partial molal free energies of constituent 1 in the liquid and gas phases respectively, we have at constant temperature[3] (p. 216)

$$(\mathrm{d}\bar{F}/\mathrm{d}P)_{N_1}\,\mathrm{d}P + (\mathrm{d}\bar{F}_1/\mathrm{d}N_1)_P\,\mathrm{d}N_1 = (\mathrm{d}\bar{F}_1'/\mathrm{d}P)_{N_1'}\,\mathrm{d}P + (\mathrm{d}\bar{F}_1'/\mathrm{d}N_1')_P\,\mathrm{d}N_1'$$

Transposing and noting that

$$(\mathrm{d}\bar{F}_1/\mathrm{d}P)_{N_1} = \bar{v} \text{ and } (\mathrm{d}\bar{F}_1'/\mathrm{d}P)_{N_1'} = \bar{v}_1'$$

we obtain at constant temperature

$$(\mathrm{d}N_1/\mathrm{d}P)_{\text{sat.}} = (\bar{v}' - \bar{v}_1 + (\mathrm{d}\bar{F}'/\mathrm{d}N')_P\,(\mathrm{d}N'/\mathrm{d}P)_{\text{sat.}})/(\mathrm{d}\bar{F}_1/\mathrm{d}N_1)_P$$

The values of $(\mathrm{d}N_1/\mathrm{d}P)_{\text{sat.}}$ are readily calculated from previous work[6] and are given in Table III. The value of $\bar{v}_1$ is known from the present work. Further work on the gas phase at this Laboratory will supply directly $\bar{v}_1'(\mathrm{d}\bar{F}_1'/\mathrm{d}N_1')_P$ and $(\mathrm{d}N_1'/\mathrm{d}P)_{\text{sat.}}$. The solubility $(\mathrm{d}N_1/\mathrm{d}P)_{\text{sat.}}$ could be calculated indirectly provided we knew the value of $(\mathrm{d}\bar{F}_1/\mathrm{d}N_1)_P$ at one isobar.

TABLE III

Total pressure, in atm.	Mole fraction of ammonia N_1	$\mathrm{d}N_1/\mathrm{d}P$
75	0.9956	0.00031
100	.9882	30
150	.9731	30
200	.9585	29
300	.9302	28
400	.9035	27
500	.8783	25
600	.8546	23
700	.8329	22
800	.8118	21
900	.7917	20
1000	.7723	19

This scheme has already been used for liquid-solid system under pressure by Adams and Gibson.[7]

Summary

The volumes of ammonia-hydrogen mixtures in the liquid phase have been measured.

The partial molal volumes of both constituents were calculated.

The thermodynamic significance of the data has been discussed and the desirability of further measurements pointed out.

WASHINGTON, D. C. RECEIVED SEPTEMBER 30, 1935

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[6] R. Wiebe and T. H. Tremearne, THIS JOURNAL, **56**, 2357 (1934).

[7] L. H. Adams, *ibid.*, **53**, 3769 (1931); *ibid.*, **54**, 2229 (1932); L. H. Adams and R. E. Gibson, *ibid.*, **54**, 4520 (1932).