Beech and Glasstone[5] came to the same conclusion in regard to the relative efficiency of these alcohols in bringing about miscibility of ethyl acetate and water although a simple study of their binodal curves alone does not indicate the relation.

Methyl alcohol has the highest values for internal pressure, dielectric constant and dipole moment, and isopropyl alcohol has the lowest values for these constants among these alcohols. Since water has very high values and toluene very low values we may consider that the above solubility studies support the idea that liquids of high internal pressure and polarity tend to "squeeze out" relatively non-polar liquids.

A comparison of the tie lines is also interesting. The alcohols dissolve chiefly in the water layer, especially when they are present in relatively small proportions. As the amounts of the alcohols increase, increasing proportions are found in the toluene layer. The proportion of ethyl alcohol in the toluene layer increases more rapidly with increasing proportions of alcohol than is noted with methyl alcohol, but the proportion of isopropyl alcohol increases most rapidly of all. This increase in the case of isopropyl alcohol continues to such an extent that a horizontal tie line finally results, after which more alcohol is found in the toluene layer than in the water layer.

Inasmuch as the alcohols have values of internal pressure, etc., nearer to the values for toluene than to the values for water, we might expect more alcohol to be found in the toluene layer. The isopropyl alcohol, however, is most like toluene, and the relatively greater tendency which it has to enter the toluene is what would be expected.

Summary

The solubility relationships for the ternary system toluene, isopropyl alcohol and water have been determined at 25.0°.

The refractive indices of these saturated solutions have been determined and used to study the distribution of isopropyl alcohol between toluene and water at 25.0°.

This system has been briefly compared with similar systems containing methyl and ethyl alcohols in place of isopropyl alcohol.

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[5] D. G. Beech and S. Glasstone, *J. Chem. Soc.*, 67 (1938).

[CONTRIBUTION FROM COLUMBIA UNIVERSITY]

The Vapor Pressures, Heats of Vaporization and Melting Points of N^{14} and N^{15} Ammonias

BY HARRY G. THODE*

It has been observed previously[1,2] that the nitrogen isotopes are concentrated to a slight extent by the distillation of liquid ammonia, indicating that the N^{14} ammonia has the higher vapor pressure. However, the vapor pressure difference between N^{14} and N^{15} ammonia can now be measured directly since high concentrations of N^{15} have been obtained.[3] In this paper a simple apparatus is described for measuring the vapor pressure difference between two isotopic samples of liquid ammonia. With this apparatus the vapor pressure difference, and the difference in melting points between ordinary NH_3 and 70.6% $N^{15}H_3$, have been measured and the results reported.

Experimental

The ammonia used in this investigation was prepared by the action of a saturated solution of potassium hydroxide on C. P. ammonium chloride. The gas was subjected to preliminary drying by passing it through a vertical glass column containing potassium hydroxide pellets. The ammonia was then condensed over sodium in one of a series of distillation bulbs. About 1 g. of NH_3 was treated in this way. Following each distillation the sample was cooled to the temperature of liquid nitrogen and the apparatus was then evacuated to 10^{-4} mm. or better. The 70.6% $N^{15}H_3$ samples were treated in a similar manner, except that the original samples had to be recrystallized from ethyl alcohol to remove traces of amines which concentrated along with the N^{15} in the chemical separation process. The samples were considered pure when further purification produced no change, within experimental error, in the vapor pressure difference between the two samples.

The apparatus is shown diagrammatically in Fig. 1. It consists of an 8-mm. glass tube C, divided into two com-

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[1] M. K. Wahl, J. R. Huffman and J. Hipple, *J. Chem. Phys.*, **3**, 434 (1935).

[2] H. C. Urey and A. H. W. Aten, Jr., *Phys. Rev.*, **50**, 575 (1936).

[3] H. G. Thode and H. C. Urey, *J. Chem. Phys.*, **7**, 34 (1939).

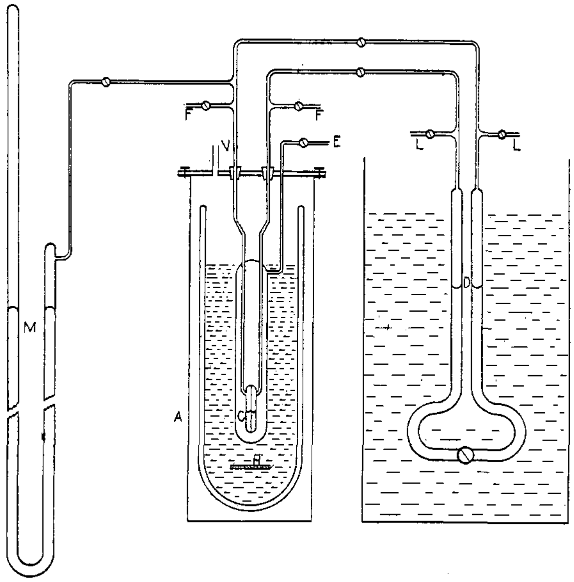

Fig. 1.

partments by a platinum partition, with each compartment partially filled with coiled platinum wire. The platinum partition and the coiled platinum serve to equalize the temperature between the two samples of ammonia whose vapor pressures are to be compared. The sample cells and the lead tubes are enclosed in a glass jacket which can be evacuated at E, and the whole apparatus is immersed in a liquid ammonia cryostat. The temperature of the cryostat is varied by regulating the pressure under which the liquid ammonia boils, with a vacuum pump and pressure regulator at V. A small heater H serves to stir the ammonia bath. The temperature of the cryostat could be controlled to 0.1°. Both the dewar flask and the steel container of the cryostat have windows through which the samples can be observed. However, during measurements the windows and lead tubes are covered with aluminum foil to keep out radiation. The two compartments at C can be connected by lead tubes to the arms of a differential oil (Apiezon) manometer D, thermostated at 27.2°, and one compartment can also be connected to a mercury manometer M. The two samples of ammonia, about half a gram of each, are condensed into the two compartments of C. The cryostat is regulated to the desired temperature and the glass jacket enclosing the two samples is evacuated. The differential manometer is then connected to the two samples and after twenty minutes readings are made with a cathetometer. The absolute vapor pressure of ordinary ammonia is measured on the mercury manometer before and after each reading of the vapor pressure difference on the differential oil manometer. From the absolute vapor pressure of ordinary ammonia the absolute temperature is deduced, using the vapor pressure data of Overstreet and Giauque for liquid ammonia.[4] With the above apparatus the measured vapor pressure difference between two samples of ordinary ammonia was found to be less than ±0.0005 cm. at 239°K. This corresponds to a difference in temperature between the two samples of ±0.00013°.

The Vapor Pressure Difference.—The vapor pressure data for the liquids can be represented by the equation

$$\log_{10}(P_1/P_2) = (0.9593/T) - 0.003252 \qquad (1)$$

where P_1 is the vapor pressure of ordinary NH_3 (0.38% N^{15}), P_2 that of 70.6% $N^{15}H_3$, and T is the absolute temperature. The assumption is made that the differences in the vapor pressures of the two samples follow an equation of the type

$$\log_{10}(P_1/P_2) = (A/T) + B$$

and equation 1 is obtained by the application of least squares to the data in Table I. The ratio P_1/P_2 is obtained from the difference $(P_1 - P_2)$.

TABLE I

P_1, cm.	Temp., °K.	$P_1 - P_2$, cm. oil	$P_1 - P_2$, cm.	$(P_1 - P_2)$ (calcd.) − $(P_1 - P_2)$ (obsd.)	P_1/P_2, calcd.
5.488	197.7	0.320	0.0202	−0.00002	1.00369
9.060	204.4	.475	.0299	+ .00001	1.00332
12.593	208.8	.583	.0368	+ .00200	1.00310
21.570	217.2	.916	.0578	+ .00020	1.00268
41.030	228.2	1.462	.0922	− .00220	1.00219
41.550	228.4	1.478	.0933	− .00280	1.00218
59.560	234.9	1.797	.1134	+ .00060	1.00192
75.340	239.5	2.095	.1322	− .00170	1.00173

Table I includes the vapor pressure P_1 as determined on the mercury manometer, the temperature corresponding to the pressure P_1, and the vapor pressure difference $(P_1 - P_2)$ in cm. of oil as measured on the differential oil manometer. The table also includes the difference between calculated and observed $(P_1 - P_2)$, and the calculated ratios P_1/P_2.

Although the absolute temperature as deduced from the observed absolute vapor pressure of the ordinary ammonia is given to the nearest 0.1°, the difference in temperature between the two samples, as pointed out above, was probably less than 0.0002° at 239°K. Each arm of the oil manometer was read to the nearest 0.001 cm. with a probable error of ±0.003 cm. The mean difference between calculated and observed values of the vapor pressure difference $(P_1 - P_2)$ is ± 2%.

If the simple assumption is made that the vapor pressure of an isotopic mixture is a linear function of the mole fractions, we get the equation

$$\log_{10} \frac{P_{N^{14}H_3}}{P_{N^{15}H_3}} = \frac{1.3665}{T} - 0.004632 \qquad (2)$$

The Difference in Heats of Vaporization.—If the vapor pressures of each of the samples of am-

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[4] Roy Overstreet and W. F. Giauque, THIS JOURNAL, **59**, 254 (1937).

monia follow an equation of the form

$$\log_{10} P_n = \frac{\Delta H_n}{2.303RT} + C$$

then

$$\log_{10} P_1/P_2 = (\Delta H_2 - \Delta H_1)/2.303RT + C' \quad (3)$$

The subscripts 1 and 2 refer to ordinary ammonia and 70.6% N^{15} ammonia, respectively. The difference in the heats of vaporization of the two isotopic samples of ammonia can be calculated from the experimental data by comparing equation 3 with equation 1

$$\Delta H_2 - \Delta H_1 = 4.39 \text{ cal.} \quad (4)$$

where ΔH_1 is given in the literature[4] as 5581 ± 9 cal. By simple extrapolation, the heat of vaporization of pure N^{15} ammonia is calculated to be 6.25 cal. higher than the heat of vaporization of N^{14} ammonia.

The normal boiling point difference for the two forms of ammonia can be calculated from equation 1 by successive approximations, when T = 239.720°K., P_2 = 759.99 mm. or the n. b. p. difference. is 0.040°K., giving 0.055° for the pure N^{15} form.

The Difference in Melting Points.—A sample of ordinary ammonia was condensed into one cell of the apparatus and frozen with a liquid nitrogen bath. The jacket around the samples was then evacuated and the liquid nitrogen bath removed. A cooled dewar was placed around the apparatus to prevent the sample from warming up too fast. The vapor pressure of the sample was followed and a time–vapor pressure curve plotted. It was found that the sharp break in this curve, which occurs at the melting point, could be reproduced from experiment to experiment with great accuracy. The same procedure was followed for a sample of 70.6% $N^{15}H_3$; the results obtained are given in Table II.

TABLE II

V. P. at triple point in cm.

Sample 1, Ordinary NH_3 (0.38%N^{15})	Sample 2, 70.6% $N^{15}H_3$
4.560	4.574
4.562	4.572
4.561	4.576
Av. 4.561	4.574

From these data, and from the vapor pressure difference equation, the melting point difference between the two samples can be deduced. With the two samples at the same temperature, the triple point of ordinary ammonia (195.36°K., 4.558 cm.),[3] the vapor pressure of sample 1 will be 0.0173 cm. higher than the vapor pressure of sample 2 (from equation 1). However, from Table II it is seen that sample 2 has a higher vapor pressure at its melting point than sample 1 has at its melting point (0.013 cm.). Therefore sample 2 must melt at a higher temperature than sample 1, and the two effects must be additive. From the relation between temperature and pressure for liquid ammonia given by Overstreet and Giauque,[4] we find that dP/dT equals 0.365 cm./deg. at the triple point of N^{14} ammonia. Thus we calculate the melting point difference between ordinary and 70.6% N^{15} ammonia to be

$$(0.0173 + 0.013)/0.365 = 0.083°\text{K.}$$

If we make the simple assumption that the difference in triple points for isotopic mixtures is proportional to the mole fraction of one constituent, we find that N^{15} ammonia melts at a temperature 0.118° higher than N^{14} ammonia. The experimental error in this result may be as high as 10%.

The author is indebted to Professor H. C. Urey for making this experiment possible and for helpful suggestions.

Summary

The vapor pressure difference between 70.6% $N^{15}H_3$ and ordinary ammonia has been measured for the liquids over a range of temperatures by means of a differential oil manometer. The vapor pressure data for the liquids can be represented by the equation: $\log_{10} (P_1/P_2) = 0.9593/T - 0.00325$, where P_1 is the vapor pressure of ordinary ammonia and P_2 that of the 70.6% material. The vapor pressure of ordinary ammonia is 0.371 and 0.174% higher than the heavy ammonia sample at 195°K. (triple point of ammonia) and 239.68°K. (n. b. p.), respectively. The heavier sample of ammonia has a heat of vaporization 4.39 cal. per mole higher than that of ordinary ammonia. The triple points of the two samples differ by 0.081°, that of the 70.6% material being higher.

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