spirals, it was transferred to a known volume for measurement of pressure and yield. Purity of the sulfur dioxide was verified by measurement of its vapor pressure at Dry Ice temperature.

Sample data are listed in Table I. It will be seen that while the yield is somewhat erratic, it is not greatly sensitive to variations in the experimental conditions. Accordingly, it is recommended that barium sulfate be mixed with at least its own weight of red phosphorus, and that the flow meter be dispensed with.

TABLE I

Wt. $BaSO_4$, mg.	Wt. P/wt. $BaSO_4$	Flow l./sec. $\times 10^2$	Yield, %
586	1.63	6.2	97
585	1.63	6.2	87
590	1.63	3.5	90
586	1.63	3.5	86
585	1.63	13.4	92
194	1.63	6.2	90
193	1.63	6.2	87
630	0.81	6.2	90
585	0.40	6.2	70
580	0.40	6.2	74

Sulfur dioxide, prepared by this method from radioactive barium sulfate, was examined for sulfur trioxide impurity by means of an apparatus which consisted essentially of two small flasks connected to each other, through a stopcock, by means of ground joints, with another stopcock and ground joint to permit connection to a vacuum line for evacuation and introduction of sulfur dioxide. Prior to evacuation, dilute hydrochloric acid was placed in one of the flasks and sodium hydroxide solution in the other. The liquids were frozen, the apparatus evacuated, and the stopcock connecting the two flasks was then closed. The sulfur dioxide was distilled onto the hydrochloric acid solution by means of liquid air, and the other stopcock closed. The apparatus was then removed from the vacuum line and the liquids allowed to melt. The stopcock connecting the flasks was opened and then, by cooling of the sodium hydroxide solution with a Dry Ice-bath, the solution of sulfur dioxide was vacuum distilled almost to dryness. The apparatus was taken apart, bromine water was added to the sulfite solution, sodium sulfate carrier added to both flasks, and the contents of the two flasks precipitated as barium sulfate. Radioactivities of the precipitates were determined in a manner which did not differ greatly from a method used previously for radiocarbon.[5] The results showed that the sulfur dioxide contained less than 0.1% of sulfur trioxide. The procedure, permitting rigorous exclusion of oxygen was preferable for our purposes to more standard titrimetric methods for analysis of sulfurous acid solutions. These are usually somewhat inaccurate due to air oxidation of sulfurous acid.

The radiosulfur was obtained carrier free (in potassium chloride) from the Atomic Energy Commission.

CORVALLIS, OREGON RECEIVED JUNE 29, 1949

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[5] P. E. Yankwich, G. K. Rollefson and T. H. Norris, *J. Chem. Phys.*, **14**, 131 (1946).

The Density of Solutions of Alkali Metals in Liquid Ammonia

BY WARREN C. JOHNSON, ALBERT W. MEYER AND ROBERT D. MARTENS

Recent interest in the apparent molar volume of sodium in liquid ammonia[1,2] has prompted the writers to submit some data pertaining to lithium, sodium, and potassium solutions which were acquired a number of years ago, with the thought that they might be of assistance in the formulation of better theoretical concepts for these unusual solutions.

The procedure used for the determination of the density of solutions was essentially the same as that described by Kraus, Carney and Johnson[3] and Johnson and Meyer.[4]

The data for lithium solutions are given in Table I.

TABLE I

THE DENSITY OF SOLUTIONS OF LITHIUM IN LIQUID AMMONIA AT −33.2°

Li, g.	NH_3, g.	Mole fraction Li	Density
0.2291	16.476	0.0331	0.639
.5545	22.452	.0571	.611
.5053	16.030	.0713	.597
.9170	16.813	.1180	.554
.9170	12.199	.1557	.523
1.0697	13.621	.1616	.518
0.9170	9.241	.1958	.498
1.0697	8.895	.2105[a]	.490

[a] Saturated solution, as determined by Johnson and Piskur, *J. Phys. Chem.*, **37**, 93 (1933).

An interpolation between Jaffe's two values for the saturated solution at −33° gives a value of 0.486 for the density[5]: this is in good agreement with our value of 0.490. The plot of mole fraction of lithium *versus* density gives a smooth curve and at zero mole fraction it intercepts the density axis at the density of pure liquid ammonia at −33.2°.[6]

The difference in volume, ΔV, per mole of solute, between the volume of the solution and the sum of the volume of its components, when plotted against the dilution (moles of ammonia per mole of lithium) gives a curve very similar to those obtained from comparable plots for sodium and potassium solutions.[3,4] The curve passes through a maximum at a ΔV value of about 46 cc. This volume change is greater than that for either so-

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[1] Ogg, THIS JOURNAL, **68**, 155 (1946); *J. Chem. Phys.*, **14**, 114, 295, 399 (1946); *Phys. Rev.*, **69**, 668 (1946).

[2] Stosick and Hunt, THIS JOURNAL, **70**, 2826 (1948).

[3] Kraus, Carney and Johnson, *ibid.*, **49**, 2206 (1927).

[4] Johnson and Meyer, *ibid.*, **54**, 3621 (1932).

[5] Jaffe, *Z. Physik*, **93**, 741 (1935).

[6] Cragoe and Harper, *Bur. Standards Sci. Papers*, **420**, 313 (1921).

dium or potassium. Coulter[7] has reported some density measurements for lithium solutions, which are in quite good agreement with the above data. He gives a value of 0.4920 for the density of the saturated solution at −35°, and a ΔV value of 41.4 cc. for the most dilute solution studied.

It is believed the density data given in the present study are reliable to about 0.5%. The density of pure ammonia is well known.[6] For the density of metallic lithium, the value of 0.53 at 20°, given by Richards and Brink,[8] was used. The error in the ΔV calculation caused by the difference in the density of lithium between 20 and −33° is not serious. On the other hand, an error of 0.5% in the density of the lithium solutions causes an uncertainty as great as 10% in the ΔV value in dilute solutions.

In the present investigation the temperature and concentration range was such as to avoid the appearance of a two liquid phase system.

Sodium and Potassium Solutions

Recently Stosick and Hunt[2] have repeated some of the experiments of Ogg[1] on the determination of the density of solutions of sodium in liquid ammonia at low temperatures, and the subsequent calculation of the apparent molar volume of sodium. They were unable to confirm the unusually large apparent molar volumes reported by Ogg.[1] In this study a question arose regarding the density–temperature coefficient of sodium solutions and lacking data of this type, they assumed the solutions to have the same coefficient of expansion as ammonia.

A number of years ago we made some measurements on the density of saturated solutions of sodium and potassium in liquid ammonia at temperatures ranging from about −32 to −51°, and found the density in each case to be essentially a linear function of the temperature over this relatively small temperature range.

The data are given in Table II.

TABLE II

DENSITY OF SATURATED SOLUTIONS OF SODIUM AND POTASSIUM IN LIQUID AMMONIA AT DIFFERENT TEMPERATURES

Sodium solutions				Potassium solutions	
Temp., °C.	Den.	Temp., °C.	Den.	Temp., °C.	Den.
−31.6	0.576	−45.0	0.584	−32.2	0.628
−33.0	.578	−46.1	.585	−33.3	.625
−33.3	.578	−47.0	.585	−39.0	.627
−40.7	.581	−47.8	.586	−40.5	.629
−41.6	.582	−48.5	.586	−41.0	.629
−43.0	.583	−50.0	.587	−43.0	.634
−44.5	.584	−51.0	.587	−46.4	.636
				−49.6	.638

Due to difficulties in temperature control, by reducing the pressure of ammonia vapor above the liquid and then allowing time for equilibrium to be established, the data are probably not reliable to better than 1%. However, they show the trend of the change in density with temperature, and are sufficiently accurate for general purposes. The change in density with the temperature in each case is approximately 0.1% per degree. The density increases with decreasing temperature, as is to be expected. There is no abrupt change in the density–temperature plot revealing the appearance of a two liquid phase system or an unusually large change in volume. Since the solutions in this study were saturated with metal and, as a consequence, are not comparable to those employed by Ogg and by Stosick and Hunt, who worked with solutions at a concentration of about 0.003 *M*, it is not possible to make any direct comparisons. It is sufficient to say that our experience with these solutions is such that we have never observed the large volume changes that have been reported.

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[7] Coulter, *The Northwest Science*, **16**, 80 (1942).

[8] Richards and Brink, THIS JOURNAL, **29**, 117 (1907).

A Catalytic Synthesis of Triphenylmethyl Mercaptan

BY NORMAN KHARASCH AND HOMER R. WILLIAMS

Vorländer and Mittag[1] reported 60–90% yields of triphenylmethyl mercaptan *via* the reaction of triphenylmethyl chloride with sodium hydrosulfide in ethanol. In many repetitions of this procedure, we obtained only 50–60% of the product; and frequently much lower yields resulted. Blicke[2] made similar observations. In an attempt to reduce the competitive alcoholysis which occurs in this reaction, Gleason[3] substituted isopropyl alcohol for ethanol, and was able to obtain 70–75% conversion to the mercaptan.

We have now found that 75–80% yields of pure triphenylmethyl mercaptan may be readily obtained by the direct interaction of triphenylmethyl chloride with hydrogen sulfide, in dry dioxane as a reaction medium. For this purpose, activated alumina is an essential and very effective catalyst.

Experimental

Commercial dioxane was refluxed with 4% of its weight of sodium for four hours. To 400 ml. of this solvent there was added 100 g. of activated alumina (Alcoa F-20) and 100 g. of triphenylmethyl chloride. Dry hydrogen sulfide was then passed into the mixture, through a 6–8 mm. inlet tube which dipped below the surface of the alumina, at such a rate as to agitate the suspended alumina gently and to keep the solution saturated with the gas. After fifteen hours, the alumina was collected on the suction filter plate and washed with two 50-ml. portions of dioxane. The combined washings and filtrate were then poured into two liters of ice-water, and the mixture was stirred until a granular product precipitated. This was collected by suction filtration, dried between sheets of filter paper, and dissolved in 500 ml. of boiling isopropyl alcohol. On slow cooling of the solution, pale-yellow crystals of tri-

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[1] D. Vorländer and E. Mittag, *Ber.*, **46**, 3450 (1913).

[2] F. F. Blicke, THIS JOURNAL, **45**, 1967 (1923).

[3] G. I. Gleason, private communication, May 14, 1948.