TABLE I

Carbonyl compound, ketone	Physical appearance of 2,4-dinitrophenylhydrazone	Ultraviolet absorption, maxima	M.p., °C.	Dumas Nitrogen, % Calcd.	Obsd.
n-Hexyl phenyl	Red monoclinic prisms showing all pinacoid views	378	135.0	15.13	15.07
	Orange monoclinic plates	378	135.0	15.13	14.63
n-Heptyl phenyl	Orange monoclinic plates lying on 010; very thin	379	103.0–103.5	14.58	14.38
n-Tridecyl phenyl	Orange plates; very thin; either monoclinic or triclinic	382	100.0–100.1	11.96	11.90
n-Pentadecyl phenyl	Orange monoclinic plates lying on 010	375	98.0–99.0	11.28	11.10
n-Heptadecyl phenyl	Orange monoclinic tablets lying on 100 and 010	380	98.0–99.0	10.68	10.79

more than seven carbon atoms result in the formation of oils and solid solutions. In order to learn more about the effect of large alkyl side chains on the formation of 2,4-dinitrophenylhydrazones, derivatives of several alkyl phenyl ketones were prepared by Brady's[1] method. None of the above mentioned difficulties was observed. It is believed that the two forms of hexyl phenyl ketone 2,4-dinitrophenylhydrazone are polymorphs. Both exhibit the same melting point and the same ultraviolet absorption maxima. There is no resultant melting point depression when the two are mixed. The results of the work are summarized in Table I.

The *n*-hexyl phenyl ketone 2,4-dinitrophenylhydrazone was previously reported as one form melting at 135.0°[2]; the *n*-tridecyl phenyl ketone derivative was reported as melting at 98.0 to 98.5°.[2]

[1] O. L. Brady, *J. Chem. Soc.*, 756 (1931).

[2] T. Y. Ju, G. Shen and C. E. Wood, *J. Inst. Petroleum*, **26**, 514 (1940).

DEPARTMENT OF CHEMISTRY
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The Heat of Solution of Lithium in Ammonia at −33°

BY LOWELL V. COULTER AND LOUIS MONCHICK

A common heat of reduction of ammonium ion in liquid ammonia by dilute solutions of sodium, potassium and cesium[1] has indicated an identical state for the reducing agent, "the solvated electron," in moderately dilute solutions of these metals. For this reaction represented by the equation

$$\frac{1}{2}e_2^-(\text{am}) + \text{NH}_4^+(\text{am}) = \text{NH}_3(\text{l}) + \frac{1}{2}\text{H}_2(\text{g}) \quad (1)$$

$\Delta H = -40.4 \pm 1$ kcal. per equivalent which has been calculated from the experimentally measured heats of solution of these metals in pure ammonia[2] and the heats of reaction of the solid metals with ammonium ion in liquid ammonia.[1] For this reaction in lithium solutions, however, $\Delta H = -42.5$ kcal. based, in part, on 8.0 kcal.[2] for the exothermic heat of solution of lithium in pure ammonia. Indication of typical alkali metal behavior has been obtained for lithium solutions, however, by Coulter and Maybury[1] who have obtained $\Delta H = -40.9$ kcal. for equation 1 based on a single redetermination of the heat of solution of lithium in pure ammonia.

In view of the significance of this thermochemical value for the proper understanding of lithium metal solutions relative to the other alkali metals we have remeasured the heat of solution of lithium in liquid ammonia over the concentration range 150 to 600 moles of ammonia per gram atom of metal.

The calorimetric procedure employed in this research has already been described.[1] To ensure the complete elimination of water from the calorimeter solvent, anhydrous ammonia was distilled directly into the calorimeter from an ammonia solution of sodium metal.

The lithium used for the measurements was obtained from the Metalloy Corporation and was specified to have a low sodium content as indicated by the following typical analysis furnished by the supplier: Na, 0.005%; K, 0.005%; Ca, 0.02%; N, 0.06%. Analysis, in this research, by the collection of evolved gas upon solution in water indicated 101.2% lithium. Titration for total alkalinity gave a purity of 99.6%. Samples were prepared by cutting cylinders of the metal from ingots under oil followed by anhydrous benzene rinses and storage of the samples in evacuated fragile sample bulbs.

The results of the measurements are presented in Table I.

TABLE I

Sample wt., g.	Moles NH_3/Li	Obsd. heat effect, cal.	$-\Delta H$, kcal.
0.3038	154	425.0	9.71
.1811	277	251.6	9.64
.1059	461	148.2	9.71
.1001	525	136.0	9.43
.0782	599	110.3	9.78
Mean			9.65 ± 0.2

For the concentration range 150 to 600 moles of ammonia per gram atom of lithium the mean value, 9.65 kcal., is in good agreement with the single value, 9.55 kcal., at a dilution ratio of 99 previously reported from this Laboratory.[1]

As a consequence, the earlier tentative value for the ΔH of equation 1 remains essentially unchanged at −40.8 kcal. for lithium solutions thereby confirming the earlier conclusion that lithium forms a typical alkali metal solution with ammonia in the moderately dilute region.

Experiments now in progress indicate that an energy absorption process, presumably the uncoupling of electron spins, is associated with the dilution of potassium solutions having a concentration ratio of ~100 moles NH_3/K. In accordance with

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[1] L. V. Coulter and R. H. Maybury, THIS JOURNAL, **71**, 3394 (1949).

[2] C. A. Kraus and F. C. Schmidt, *ibid.*, **56**, 2298 (1934), and F. C. Schmidt, F. J. Studer and J. Sottysiak, *ibid.*, **60**, 2780 (1938).

these measurements as well as the general properties of the metal solutions we have written the "solvated electron" in equation 1 in a paired state instead of in an unpaired state as previously written for the moderately dilute region.[1]

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The Compressibility of Trimethylamine

BY H. O. DAY[1] WITH W. A. FELSING

Recently the authors determined[2] the critical constants of pure trimethylamine by the method of determining numerous isotherms very near, above and below, the critical temperature. Since these determinations involved the use of the dead-weight piston gage[3] of this Laboratory, it was decided to extend the measurements to include compressibility determinations for the temperature range +80 to 275°, since no such data could be located in the literature.

Apparatus and Material.—The dead-weight piston gage, its accessories and its operation, have been described previously.[3] Thermostat temperatures were measured with a platinum resistance thermometer, calibrated by the National Bureau of Standards, and these temperatures were held constant by means of this same resistance thermometer system in conjunction with a photoelectric cell relay.

The trimethylamine was prepared from highly purified trimethylamine hydrochloride, dried, stored, and transferred as described by Day and Felsing.[2] The purity was estimated to be 99.9 mole per cent.

The Experimental Data.—The compressibility data[4] at nine temperatures are presented graphically in Fig. 1; the accuracy of these data is from 0.1 to 0.2% over the entire range of temperature.

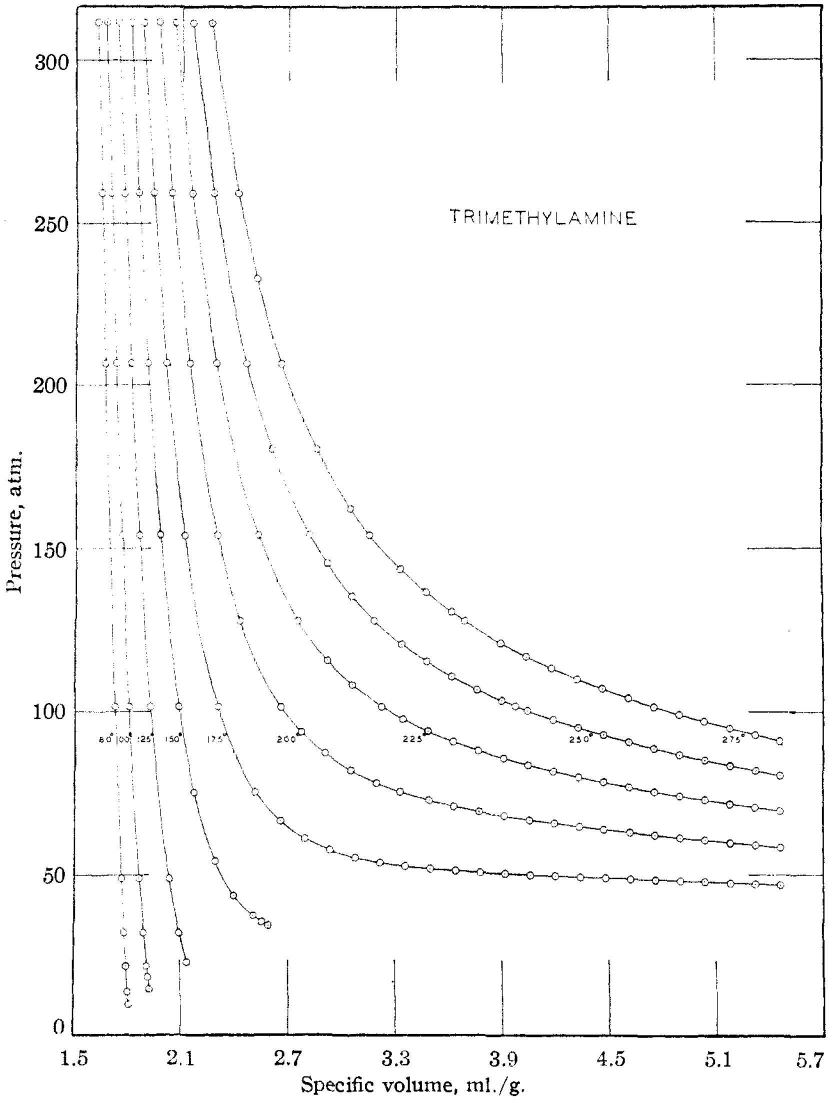

Fig. 1.

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(1) Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tenn.

(2) Day with Felsing, THIS JOURNAL, **72**, 1698 (1950).

(3) Kelso with Felsing, *ibid.*, **62**, 3132 (1940); *Ind. Eng. Chem.*, **34**, 161 (1942).

(4) For tables supplementary to this article, order Document 3333 from American Documentation Institute, 1719 N. Street, N. W., Washington, D. C., remitting $1.00 for microfilm (images one inch high on standard 35 mm. motion picture film) or $1.00 for photocopies (6 × 8 inches) readable without optical aid.