which show a slight, but easily discernible, rise in slope at the point where the solid ammonia finally disappears, the curve hereafter becoming practically a straight line. This portion of the phase curve represents the solubility of ammonia in the metal.

The upper flat step in the warming curve for dilute solutions represents the melting point of solid ammonia at a temperature which remains constant because of the appearance of two liquid phases of fixed concentrations. This phase separation is well known for sodium[1] and calcium[2]; our results confirm it for potassium with an upper consolute point at $\sim -74°$ C., but show that it is very unlikely for lithium. Kraus[4] has stated that the deviations of the vapour pressure of the solutions from Raoult's law (shown diagrammatically in Fig. 2) arise as a result
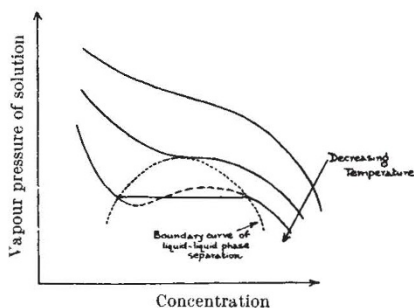

Concentration

Fig. 2

of the phase separation, and not as a result of aggregation of the solute. It is clear, however[5], that the phenomenon of separation into two liquid phases in equilibrium is to be regarded as a direct consequence of the deviations from Raoult's law. Bowden has pointed out: "this is reminiscent of the van der Waals $p—v$ curve . . ." It appears to us that, in fact, a first quantitative approximation may be derived by using the van der Waals' modification of Boyle's law in Van't Hoff's law of osmotic pressure, deriving the constants in the equation from known data at the upper consolute point. The existence of associative forces would be expected to lead to aggregation of the solute molecules, and this is shown even at the boiling point by an apparent rise in molecular weight for increasing concentrations above a low value. If this association were great enough, it could explain the rise in vapour pressure in the intermediate region which would occur in absence of liquid-liquid phase-separation, and which does, in fact, produce the separation into a more concentrated and a more dilute phase. The rapid fall near the eutectic concentration can be attributed to almost complete binding of the ammonia.

It would appear that similar phenomena should occur with the other alkali and alkaline earth metals. A more detailed discussion of this work will be published elsewhere.

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[1] Ruff and Zedner, Ber. deutsch. chem. Ges., 41, 1948 (1908).
[2] Kraus, J. Amer. Chem. Soc., 30, 653 (1908).
[3] Birch, J. Chem. Soc., 593 (1946).
[4] Franklin and Kraus, Amer. Chem. J., 20, 850 (1898).
[5] See, for example Bowden, "The Phase Rule and Phase Reactions", 131 (Macmillan, London, 1945).

Isomorphic Form of Urea Picrate

UREA picrate is described by Smolka[1] as having m.p. 142° C. and formula $CH_4ON_2,C_6H_3O_7N_3$ (form A). A new isomorphous form with m.p. 275° C. and the same formula (form B) is here described.

Preparation. Form A is prepared by mixing solutions of urea and picric acid. Although various solvents—water, acetone and methyl, ethyl and n-propyl alcohols—have been tried, in every case form A was precipitated. 4 : 1, 1 : 1, and 1 : 4 molar ratios of urea and picric acid were also tried. Again form A was always precipitated.

Form B may be prepared in two ways : (a) Repeated recrystallization. After several recrystallizations from alcohol, the melting point of form A is raised to 170° C. or higher. One or two further recrystallizations then raise the melting point to about 255° or 260° C. (b) Chromatography. If an alcoholic solution of form A is passed down a sand column and then concentrated, the resulting crystals usually melt well above 200° C. A further recrystallization is usually sufficient to raise the m.p. to 255°–260° C. In these preparations of form B, two points are noteworthy. Once the melting point is raised above c. 170° C., little difficulty is experienced in raising it to 255–260° C. Several further recrystallizations are necessary to raise it to 275° C.

Crystallography. Crystals of both forms were examined by Dr. C. O. Hutton, of the Geology Department here. He reports that while form A is monoclinic or possibly triclinic, form B is orthorhombic.

Analysis. Analytical figures obtained were as follow :

		C. 29·1% ; H, 2·58% ; Urea N, 9·7, 9·7, 9·9, 10·1%
Found		
Calc. for		
$CH_4ON_2,C_6H_3O_7N_3$	29·1	2·42	9·7
$CH_4ON_2,2C_6H_3O_7N_3$	30·1	1·93	5·4

Kjeldahl analyses for total nitrogen even on the same sample gave results ranging from 21 to 24 per cent. While the carbon and hydrogen values agree closely with those calculated for $CH_4ON_2,C_6H_3O_7N_3$, since the figures for the two formulæ are so close, urea nitrogen was estimated by the urease method.

The unreliability of the melting points of picrates is notorious. The case of urea picrate is just another example. It is felt that to prevent others being led astray, this abnormality should be reported.

I have to thank Mr. C. L. Carter, senior lecturer in chemistry at the University of Otago, for the microdetermination of carbon and hydrogen.

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Smolka, Monatsch., 6, 915 (1885) ; Brit. Chem. Abs., 50, 453 (1886).

Neo-pentyl Alcohol and Steric Hindrance

Whitmore and Rothrock[1] showed that the hydroxyl group in neo-pentyl alcohol has remarkable resistance against replacement by a halogen atom through the agency of thionyl chloride and phosphorus tribromide. Dostrovsky, Hughes and Ingold[2] attribute this to steric hindrance to 'end-on' approach to the α-carbon atom. Whitmore and Rothrock, however, leave the impression that neo-pentyl alcohol does not interact at all with these reagents, and indeed state : "The inactivity of neopentyl alcohol to heat and reagents