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

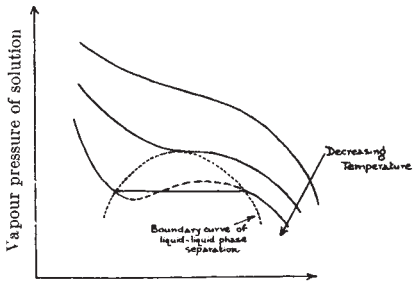

Fig. 2

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:

Found	C, 29·1% ;	H, 2·58% ;	Urea N, 9·7, 9·7, 9·9, 10·1%
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 micro-determination of carbon and hydrogen.

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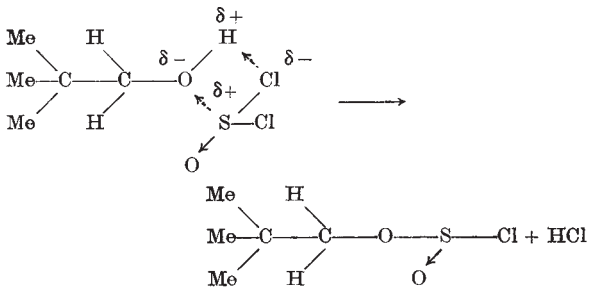
Smolka, *Monatsch.*, **6**, 915 (1885); *Brit. Chem. Abs.*, **50**, 453 (1886).

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

has been demonstrated"; but the work of Gerrard[3] enabled us to predict probability of easy 'broadside' approach.

neo-Pentyl alcohol and thionyl chloride quite readily gave us the chlorosulphinate, ROSOCl, and in the presence of pyridine, the sulphite, R_2SO_3, in excellent yields. Phosphorus trichloride, and tribromide in the absence of pyridine, produced the halogenophosphites, for example, ROPCl_2, while in the presence of pyridine, an *ester* of phosphorous acid was readily obtained. Phosphorus oxychloride in the presence of pyridine gave an *ester* of phosphoric acid. We conclude that *neo*-pentyl alcohol very readily responds to 'broadside' four-centre attack; for example:



We find that the hydroxyl group in αα-dimethyl-*neo*-pentyl alcohol, a tertiary alcohol, is replaceable by halogen through the interaction with these reagents, in accordance with the theory of substitution developed by Ingold and Hughes.

Details of these experiments are being prepared for publication.

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[1] Whitmore and Rothrock, *J. Amer. Chem. Soc.*, **54**, 3431 (1932).
[2] Dostrovsky, Hughes and Ingold, *J. Chem. Soc.*, 173 (1946).
[3] Gerrard, *J. Chem. Soc.*, 688 (1936); 99 (1939); 218 (1940); 85 (1944).

Precipitating Effect of Cationic Detergents on Soluble Starch

Cationic detergents, the bactericidal property of which was discovered by Domagk (1938), have a precipitating effect on certain proteins (Kuhn–Bielig, 1940). Since this precipitation occurs at high *p*H values, it is evident that it is due to salt-like bonds between the positively charged groups of the detergent and negative groups of the proteins. It is not surprising, therefore, that similar precipitates were observed when solutions of polysaccharidic acids, such as agar-agar, heparin, or gum arabic, were added to those of 'Desogen' (Geigy), that is, methyl-phenyl-dodecyl-trimethyl-ammonium methosulphate. In the course of these experiments it was observed, however, that polysaccharides *devoid of acidic groups* were also precipitated by 'Desogen'. Thus soluble starch (Merck, Schuchardt), dissolved in distilled water or in salt solution at different *p*H values, gave distinct precipitates. Two minima of turbidity were observed, one at a *p*H of 14 and another close to *p*H 7 (see table).

Each of the test tubes used in this experiment contained 160 mgm. of soluble starch, 40 mgm. of 'Desogen' and 20 ml. of 0·1 *M* borate buffer solution. The intensity of the turbidities was measured nephelometrically. Then the precipitate brought about at a *p*H of 9·2 was centrifuged, dried and weighed. The quantity of the other precipitates was calculated by comparison of this value with the nephelometric values.

*p*H values:	0(=*N* HCl)	1	2·3	6·5	8·2	9·2	11	14(=0·1 *N* NaOH)
Precipitates (mgm.):	36·6	23	4·6	5·5	34	50	52	8·8

When starch and 'Desogen' were dissolved in distilled water, the amount of precipitate was negligibly small; a distinct precipitate was observed in isotonic and hypertonic solutions of sodium chloride.

The amount of precipitate depends on the relative concentration of both components. Maximal precipitates were obtained with mixtures containing 20 mgm. of 'Desogen' with 80 mgm. of soluble starch in 10 ml. of the buffer solution. The turbidity and the precipitates began to disappear when the solutions were heated to 30–40°, and the solutions became entirely transparent at 70°; on cooling, the precipitate appeared again. Moreover, we observed that the colour reaction of soluble starch given by iodine was inhibited by 'Desogen'. The blue colour was changed to a reddish-violet or to a pale yellow, depending on the amount of 'Desogen' added to the starch solution.

The details of these and other experiments will be published elsewhere.

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Muscle-Relaxing Ethers of Glycerol

The discovery of the useful applications of curare in medicine and surgery has directed attention to other substances which are capable of producing muscular relaxation in man. In 1910, Gilbert and Descomps[1] administered the α-phenyl ether of glycerol to guinea pigs and observed: "Au bout d'un laps de temps variant, suivant la dose injectée, de trois minutes à dix minutes, on voit apparaître un certain degré de parésie des membres, parfois précédée de quelques rares et courtes contractures passagères. Cette paralysie incomplète est toujours transitoire, et sa durée oscille en général entre quinze et trente minutes; une seule fois, elle persista une heure." Launoy[2] studied the action of the same compound and observed a "résolution musculaire" and the antagonism of the drug to strychnine. Muscle-relaxing properties were later and independently observed in several glycerol ethers[3], and one of these, the α-*o*-tolyl ether ('Myanesin'), was found to be effective in man[4]. The present note indicates some of the relationships which have been observed between the molecular structure of glycerol ethers and their muscle-relaxing power. For the purpose of discussion it is useful to consider the molecular median paralysing dose ($P.D._{50}$/mol. wt.) in mgm. per kgm., that is, the mole-fraction of the glycerol ether which is required to paralyse 50 per cent of white mice to which it has been administered subcutaneously.

The presence of the grouping —O—CH_2—CROH—CR_2OH appears to be necessary for muscle-relaxing activity. Most of the β- and γ-alkyl derivatives of the α-ethers that we have tested are relatively inactive, as also are a few *O*-glucosides of active glycerol ethers. Some esters show activity of a low order, but this may be due to hydrolysis following injection. The