CCXCVII.—*The Solubility of Sodium Thiocyanate in Water and in Organic Solvents.*

By Owen Lewis Hughes and Thomas Hobson Mead.

This investigation deals with the determination of the solubility of sodium thiocyanate in water, acetone, ethyl alcohol, methyl alcohol, and nitromethane, for which no data are at present available. The method, due to Hartley and Thomas (J., 1906, **89**, 1013), consists in heating the solid thiocyanate with the solvent in a sealed tube until one or two small crystals remain; two temperatures are then noted such that at one the sharpness of the crystal edges indicates that they are growing, and at the other their roundness shows that they are dissolving. Since these two temperatures never differed by more than 0·5°, their mean may be taken as the temperature of saturation. This method is very convenient for volatile organic solvents, and is particularly suited to the case of sodium thiocyanate, which is both hygroscopic and extremely soluble.

Sodium thiocyanate was prepared by heating A. R. ammonium thiocyanate with an equimolecular proportion of caustic soda in aqueous solution until no more ammonia was evolved. The solution was then evaporated until sodium thiocyanate crystallised. The product was crystallised once from ethyl alcohol, once from acetone, and finally from ethyl alcohol, the centrifuge being used to remove the last traces of mother-liquor.

Owing to the extreme deliquescence of sodium thiocyanate, the following method of introducing the salt into the tubes was adopted. The tube was weighed with a rubber cap and transferred to an oven at 130°. The thiocyanate was kept in the same oven, and introduced into the tube while still hot. The tube was then quickly constricted in a flame, allowed to cool in a desiccator, and weighed with the cap on. The solvent was then introduced by means of a roughly calibrated pipette, the constriction sealed up, and the tube and cap weighed again.

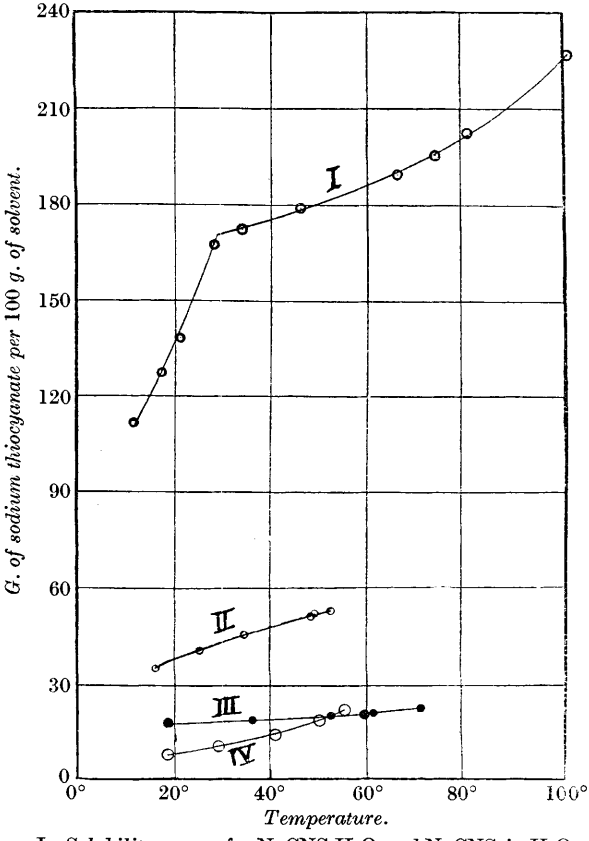
The thermometer, graduated in 0·2°, was standardised at the melting point of ice, the transition point of the system $Na_2SO_4,10H_2O \rightleftharpoons Na_2SO_4 + 10H_2O$, and in steam. In each case there was a correction of − 0·2°.

In the tables, s denotes grams of sodium thiocyanate (NaCNS) dissolved by 100 g. of solvent.

Water.—Conductivity water was used. There is a sharp break in the curve at about 30°. This transition point was also determined by the thermometric method, and two independent experi-

ments with different samples gave transition temperatures of 30·5° and 30·3°. The composition of the hydrated salt was found to correspond to the monohydrate (Found : H_2O, 20·0, 20·6. Calc. for $NaCNS,H_2O$: H_2O, 20·4%).

FIG. 1.



I. *Solubility curves for* $NaCNS,H_2O$ *and* NaCNS *in* H_2O.
II. *Solubility curve for* NaCNS *in* MeOH.
III. ,, ,, ,, NaCNS *in* EtOH.
IV. ,, ,, ,, $NaCNS,C_3H_6O$ *in acetone*.

NaCNS, g.	H_2O, g.	*s.*	Equil. temp.	NaCNS, g.	H_2O, g.	*s.*	Equil. temp.
0·3870	0·3436	112·7	10·7°	0·6866	0·3856	178·0	46·1°
0·7354	0·5768	127·5	17·3	0·8364	0·4414	189·5	65·8
0·4484	0·3224	139·3	21·3	0·9310	0·4744	196·2	73·8
0·4720	0·8790	167·5	29·2	0·9346	0·4626	202·0	81·8
0·8258	0·4790	172·4	33·8	0·9050	0·4012	225·6	101·4

Methyl Alcohol.—Conductivity methyl alcohol was used (Hartley and Raikes, J., 1925, **127**, 524). For the tube which came to

equilibrium below room temperature, a device described by Hammick and Mullaly (J., 1921, **119**, 1802) was employed, a pocket being blown in the side of the tube by means of which some crystals could be kept out of the solution until the tube was put into the bath.

NaCNS, g.	MeOH, g.	*s.*	Equil. temp.	NaCNS, g.	MeOH, g.	*s.*	Equil. temp.
0·2510	0·7166	35·00	15·8°	0·3500	0·6866	50·98	48·0°
0·1859	0·4643	40·04	24·7	0·2208	0·4285	51·5	48·9
0·2290	0·5072	45·14	34·6	0·6505	1·2151	53·54	52·3

Ethyl Alcohol.—Conductivity alcohol was used (Woolcock and Hartley, *Phil. Mag.*, 1928, **5**, 1133).

NaCNS, g.	EtOH, g.	*s.*	Equil. temp.	NaCNS, g.	EtOH, g.	*s.*	Equil. temp.
0·1382	0·7521	18·37	18·8°	0·1475	0·6645	22·20	59·6°
0·2580	1·3544	19·05	35·8	0·1382	0·6124	22·60	61·8
0·1820	0·9410	19·34	39·6	0·1165	0·4770	24·43	70·9
0·1438	0·6832	21·05	52·8				

Acetone.—Poulenc's best acetone was dried over anhydrous potassium carbonate, fractionated twice, and finally distilled in a current of pure dry air: this purification was carried out by Mr. Ross Kane for conductivity measurements, and he will publish details shortly. It was suspected that the sodium thiocyanate formed a compound with acetone, so crystals from this solvent were centrifuged, weighed, heated to about 130°, and weighed again. As the results were discordant, a specimen of the compound was kept for a day over anhydrous sodium thiocyanate in a desiccator to remove any excess of acetone. The analysis corresponds to an equimolecular *compound* (Found: C_3H_6O, 45·3, 45·8. NaCNS,C_3H_6O requires C_3H_6O, 45·0%).

NaCNS, g.	C_3H_6O, g.	*s.*	Equil. temp.	NaCNS, g.	C_3H_6O, g.	*s.*	Equil. temp.
0·1040	1·5192	6·85	18·8°	0·2608	1·4016	18·61	51·0°
0·1965	2·0691	9·50	29·2	0·1996	0·9332	21·40	56·0
0·3812	2·7066	14·08	41·9				

Nitromethane.—Solubility measurements by the sealed tube method proved impossible, since the concentration of the saturated solution was only about 0·02*M*.

The solubilities in the various solvents have been plotted in the accompanying diagram.

The authors desire to thank Sir Harold Hartley, F.R.S., for his advice during the course of this investigation.

PHYSICAL CHEMISTRY LABORATORY,
BALLIOL COLLEGE AND TRINITY COLLEGE,
OXFORD.

[*Received, August 20th*, 1929.]