LXV.—*A Comparison of Some of the Physical Properties of the Alkali Cyanates and Azides.*

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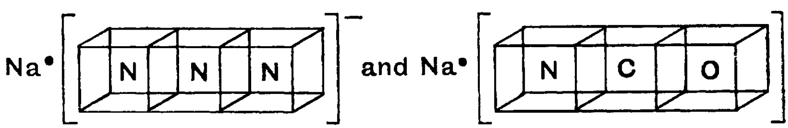
ACCORDING to modern ideas of the structure of atoms, the chemical and physical properties of elements depend on the number and arrangement of the outer electrons of the atom of the element.

The cyanate and azide ions have the same number of external electrons in their alkali salts, and it is possible that these electrons are arranged in the same way. According to the older views of valency, however, it was more common to find a ring structure assigned to azides and a straight-chain structure to cyanates. The constitutional formulæ were thus represented as

$$\mathrm{Na{-}N}\!<\!\begin{array}{c}\mathrm{N}\\ \|\\ \mathrm{N}\end{array} \text{ and } \mathrm{Na{-}O{-}C{\equiv}N}.$$

The appearance of these formulæ does not suggest any close resemblance between the physical properties of the compounds. The formulæ suggested by the octet theory for these compounds are



and their great similarity suggests a close resemblance of the physical properties of these two salts. As far as previously published data go, the evidence favours the formulæ of the octet theory, and it was the object of this investigation to supplement the data, which were rather meagre.

Preparation of Salts.—The following salts were prepared and purified according to the recognised text-book methods : Potassium cyanate, potassium azide; sodium cyanate, sodium azide.

Investigation of Physical Properties.—1. *Densities of solutions.* Since comparative, rather than absolute, values for the data for the various physical properties were aimed at, great care was taken to carry out all measurements for the cyanates and azides under uniform conditions.

A pyknometer of about 17 c.c. capacity was used for the determination of the densities of the solutions that were made up. Cyanates are decomposed by water, but the rate of decomposition is greatly reduced in presence of alcohol. The solvent employed for the various dilutions was accordingly a mixture of about equal volumes of alcohol and water. All measurements were carried out after the pyknometer containing the solutions had been immersed in a thermostat at 16° for 20 minutes. The results are in Table I.

2. *The refractive indices of* the various solutions were determined by the Abbé refractometer at the same temperature at which their densities had been observed. The results are also in Table I.

TABLE I.

Strength of soln.	Density.		Refractive index.		Density.		Refractive index.	
	KN_3 soln.	KCNO soln.	KN_3 soln.	KCNO soln.	NaN_3 soln.	NaCNO soln.	NaN_3 soln.	NaCNO soln.
N	—	—	—	—	0·979	0·978	1·371	1·374
N/2	0·956	0·956	1·362	1·362	0·954	0·954	1·362	1·364
N/4	0·948	0·948	1·360	1·360	0·946	0·946	1·359	1·360
N/8	0·941	0·941	1·359	1·359	0·941	0·941	1·351	1·352
N/16	0·938	0·938	1·357	1·358	—	—	—	—

3. *The densities of the crystalline salts* were determined by immersing a weighed quantity, about 5 g., in benzene contained in an ordinary specific gravity bottle. Previous experiment had shown that the solubility of these salts in benzene at room temperature is less than 0·1 g. in 100 c.c. Too great reliance cannot be placed on the value obtained for sodium cyanate, owing to the instability of this salt; although different determinations gave consistent values, there was always a detectable quantity of carbonate formed during the measurements. The mean values obtained were as follows:

TABLE II.

	KN_3.	KCNO.	NaN_3.	NaCNO.
Density at 20°	2·056	2·056	1·846	1·937

4. *Determination of solubilities.* The solubilities of these salts in alcohol ($d^{17°}$ 0·799) were determined at 0° and at the boiling point of the saturated solution. Definite volumes of the solutions were withdrawn by means of a pipette, and the solutions weighed. The cyanates were estimated volumetrically by the method suggested by Masson (*Chem. News*, 1906, **90**, 5, 17), the azides by the method suggested by Raschig (*Chem. Ztg.*, 1908, 1203).

Solubilities were also measured in 20% water and 80% alcohol at 0° and at the boiling point of the saturated solution, and as well as in benzene at the boiling point.

TABLE III.

Solvent.	Weight dissolved in 100 g. of solvent.			
	KN_3.	KCNO.	NaN_3.	NaCNO.
Alcohol at 0°	0·16	0·16	0·22	0·22
Alcohol at b. p.	0·54	0·53	0·46	0·52
80% Alcohol, 20% Water at 0°	1·8	1·9	—	—
,, ,, at b. p.	5·9	6·2	—	—
Benzene at b. p.	0·15	0·18	0·10	0·13

5. *Conductivity of solutions.* A preliminary attempt to determine the hydrion concentration of a solution of an alkali azide by the electrometric method showed that the salt is decomposed by water in presence of platinum black. This decomposition is very rapid when hydrogen is present occluded in the platinum. Nitrogen and ammonia are liberated, and the solution becomes progressively more alkaline. Apparently the reaction is as follows: $3KN_3 + 3H_2O = 3KOH + 4N_2 + NH_3$.

Since cyanates are also decomposed by water, the solvent used in the conductivity measurements was methyl alcohol ($d^{20°}$ 0·789).

The following results were obtained.

TABLE IV.

Strength of solution.	Equivalent conductivity at 25°.			
	NaN_3.	NaCNO.	KN_3.	KCNO.
$N/10$	58·7	58·3	62·8	60·3
$N/20$	69·0	68·0	68·0	68·6
$N/40$	78·8	75·6	77·2	77·6
$N/80$	90·4	88·0	88·8	88·8

The investigations of Carrara (*Gazzetta*, 1896, **26**, i, 134) have shown that the ionic conductivities of sodium and potassium are approximately equal in methyl alcohol.

Discussion of Results.

It will be seen from the above tables that all the physical properties investigated have shown the great resemblance between sodium azide and sodium cyanate on the one hand and potassium azide and potassium cyanate on the other. This, taken in conjunction with the similarity of crystal structure noted by Langmuir (*J. Amer. Chem. Soc.*, 1919, **41**, 1543), is strong evidence that the arrangement of electrons and atoms in the cyanate and azide ions is the same.

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