

**Chemistry.** — “*The conductive power of hydrazine and of substances dissolved therein.*” By Prof. ERNST COHEN and Prof. C. A. LOBRY DE BRUYN. (Communicated by Prof. C. A. LOBRY DE BRUYN).

(Communicated in the meeting of February 28, 1903).

The investigation of the conductive power of non-aqueous solutions has of late years been known to have an increasing significance and particularly so on account of the important result that the laws and rules applying to aqueous solutions do not appear to apply in the case of other solvents. Apart from methyl and ethyl alcohol (the constitution of which does not differ much from the type water) sulphur dioxide, ammonia ( $\text{NH}_3$ ), formic acid, hydrocyanic acid, pyridine, some nitriles, hydrogen peroxide and others have been studied as such<sup>1)</sup>.

The physical properties of free hydrazine<sup>2)</sup>  $\text{N}_2\text{H}_4$ , although still incompletely known, might lead us to suppose that this liquid would manifest a strong ionising power. In the first place, like water, the lower alcohols and acids, it possesses an abnormally high boiling point. This is obvious if this point (about  $113^\circ$  at 760 m.m.) is compared with that of ammonia ( $-34^\circ$ ), difference of  $147^\circ$ , and if one considers that the difference between the boiling points of  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$  is decidedly less ( $80^\circ$ ); this fact as well as the high critical temperature of (at least)  $380^\circ$  point to an association of the  $\text{N}_2\text{H}_4$  molecules. The solubility of several alkali salts in hydrazine has also been shown to be very considerable although less than in water. Another existing observation points to the fact that hydrazine may, like ammonia take the place of water of crystallisation<sup>3)</sup>. And finally, the dielectric constant of hydrazine, which Prof. P. DRUDE (Giessen) had the kindness to determine at our request, has turned out to be rather high, namely, 53 at  $22^\circ$ . It is now a known fact that there exists a certain although sometimes remote parallelism between the dissociating power of a liquid on the one hand and the association of its molecules, the solvent power and the dielectric constant on the other hand. As according to the experiments of FRANKLIN and KRAUS and of Cady liquefied ammonia is an ionising solvent, this might also be expected in the case of hydrazine. From the experiments<sup>4)</sup> presently to be described it will be seen that such is the case.

<sup>1)</sup> Compare JONES, Am. Ch. J. 25. 232. KAHLBERG, J. Phys. Chem. 5. 339. WALDEN and CENTNERSZWER, Z. phys. Ch. 39. 514, 557 e. by J. TRAUBE, Chem. Zt. 26. 1071. (1902).

<sup>2)</sup> LOBRY DE BRUYN, Recueil des Travaux Chimiques des Pays-Bas. 15. 174.

<sup>3)</sup> Ibid. 179.

<sup>4)</sup> Some preliminary determinations were already made in 1896. l. c. 179.

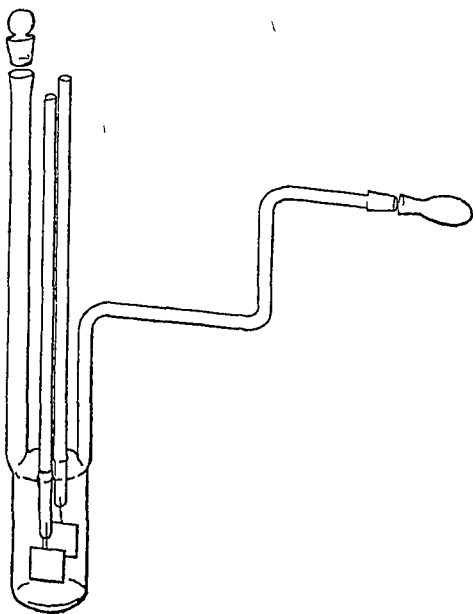
Let us first observe that the dielectric constant of hydrazine is only surpassed by those of five other liquids and is decidedly larger than that of  $\text{NH}_3$ . We have namely:

hydrocyanic acid	95	acetonitrile	40
hydrogen peroxide	93	nitrobenzene	36.5
water	82	methylalcohol	32.5
formic acid	57	ammonia	22 (at $-34^\circ$ )
nitromethane	56.5	pyridin	20
hydrazine	53		

The peculiar properties of hydrazine (its very hygroscopic nature and liability to oxidation by atmospheric oxygen) demand great precautions in its preparation. It took place, according to the method already described<sup>1)</sup>, by treatment of the so-called hydrate with barium oxide and distillation in an atmosphere of hydrogen.

The heating with barium oxide and subsequent distillation were thrice repeated and the base was finally collected in six different fractions in pipette-shaped tubes in the manner previously described. During the last distillation the base had been only in contact with purified, dry hydrogen.

Apart from the properties of hydrazine mentioned, the high cost of the material was a factor which in our experiments had to be taken into account. A special apparatus (see illustration) was, therefore constructed which admitted of working with a small quantity of the base



(about 5.5 c.c.) and through which pure, dry nitrogen<sup>2)</sup> could be passed, whilst through the exit tube for the gas the weighed portions of the different salts could be introduced.

On account of the somewhat limited quantity of the base at disposal we could not, as is customary in the determination of the conductive power of solutions, start with the largest concentration and successively dilute this by adding the solvent, but the reverse was to be done.

<sup>1)</sup> l. c. p. 175.

<sup>2)</sup> We take the opportunity to call attention to the fact that platinised electrodes

Weighed quantities of a salt were, therefore, successively dissolved; on account of the unavoidable errors in weighing it was difficult to experiment with very dilute solutions of accurately known composition, but by evaporating a measured quantity of a very dilute aqueous solution in a pipette which was then rinsed with the hydrazine we have reached for KCl a concentration of  $V = \pm 900$ .

In view of the above we wish to remark generally that our results cannot lay claim to very great accuracy, although they quite suffice even from a quantitative point of view, to prove that free hydrazine has a strong ionising power comparable with that of water.

We have worked with solutions of  $H_2O$ , KCl, KBr, and KJ and made a few experiments with a solution of Na and  $H_3N$  in  $N_2$ ,  $H_4$ .

In the first experiment the six different fractions of the hydrazine had not been kept separate; as we had previously found <sup>1)</sup> that the meltingpoints of the second and fourth fractions were the same we thought we might conclude that at least the middle fractions were similar. It then appeared, however, that the conductive power of the bases taken from different tubes often showed appreciable differences.

For this reason a second preparation was made and the hydrazine of each fraction (each time collected in several tubes) was examined separately as to its conductive power. From the following figures it appears that the conductive power gradually decreases and is smallest for the last fraction.

fraction n <sup>o</sup> . 2	$\kappa$ at 25° = 18.1.10 <sup>-5</sup>
3	12.8 "
4	11.2 "
5	10.0 "
6	6.5 "

We do not know what impurity (in any case very small) is the cause of this; possibly we are dealing here with a minute quantity of ammonia which is present in largest amount in the first fractions

The smallest conductive power observed by us in any fraction prepared previously was 4.10<sup>-5</sup>.

Our experiments have been mostly conducted with fraction N<sup>o</sup>. 6 of the above-mentioned quantity.

dried in the air may occlude such an appreciable amount of oxygen that this must make its influence felt when working with readily oxidisable liquids. Such appeared to be the case when filling our apparatus with hydrogen when a spontaneous deposit of visible drops of water was formed.

<sup>2)</sup> Prepared from air and phosphorus.

<sup>1)</sup> l. c. p. 177.

The apparatus was put into a glass vessel containing paraffin oil which was placed in an Ostwald thermostat; the temperature was 25°.

Hydrazine and water ( $t = 25^\circ$ )				
5 <sup>e</sup> fraction.	$G = 5.185.$		6 <sup>e</sup> fraction.	$G = 4.249.$
N.	$\kappa$		N	$\kappa$
0	$10.0 \cdot 10^{-5}$		0	$6.04 \cdot 10^{-5}$
0.93	9.79 »		41.1	4.71 »
7.94	8.95 »		49.5	4.5 »
21.15	7.68 »		58.4	4.36 »
33.8	7.22 »		69.5	4.55 »
65.6	6.04 »		81.6	4.9 »
82.4	6.09 »		124.7	7.3 »
101.8	7.85 »			
156	10.51 »			
255.5	17.51 »			

## Potassiumchloride.

$t = 25^\circ$				
G	g	V	$\kappa = 6,2 \cdot 10^{-5}$ $N_2H_4$	$\Lambda^1$
5.369	0,0272	14.7	$7.0 \cdot 10^{-3}$	102.9
»	0,0157	25.4	4.2 »	103.7
»	0,0080	49.7	2.2 »	109.3
[ $\pm 5.4$	0,00045	$\pm 900$	$1.2 \cdot 10^{-4}$	$\pm 107^2$ ]

## Potassiumbromide.

$t = 25^\circ$				
G	g	V	$\kappa = 6,5 \cdot 10^{-5}$ $N_2H_4$	$\Lambda$
5.350	0,0617	10.3	$10.05 \cdot 10^{-3}$	103.8
»	0,0329	19.3	5.66 »	109.2
»	0,0214	29.9	3.77 »	112.7
»	0,0105	60.7	1.965 »	118.9

<sup>1</sup>)  $\Lambda_\infty$  could not be determined, so that the degree of dissociation of the salts is not known. The  $\Lambda$ 's, however, agree in magnitude with those of the aqueous solutions of the same salts.

<sup>2</sup>) This value, obtained in the manner described on p. 553, is as a matter of fact uncertain. It proves that a very minute quantity of a dissolved substance may increase the conductive power considerably.

## Potassiumiodide.

G	g	V	$t = 25^\circ$	
			$N_2H_4$	$\kappa = 5,6.10^{-5}$
			$\kappa$	$\Lambda$
5 600	0,072	12 9	$8 19 10^{-3}$	105 6
»	0,0493	18 8	5.79 »	108 8
»	0,0280	33 2	3.40 »	112.8
»	0,0129	72	1.64 »	118

G = weight of hydrazine in grams.

$\Lambda$  = aequivalent conductive power.

g = weight of the salt in grams.

V = number of Liters, in which is dissolved one mol. of the substance.

$\kappa$  = specific conductive power

$\kappa$  for the water used =  $0,28.10^{-5}$

Without committing a grave error the sp. gr. of hydrazine at  $25^\circ$  may be taken as 1.00.

It is already known that sodium dissolves in hydrazine with evolution of hydrogen<sup>1)</sup>. Pure hydrazine ( $\kappa=9,1.10^{-5}$ ) was introduced into the apparatus and two particles of sodium (weighing about 10 milligrams) were added.

The metal slowly dissolved with evolution of hydrogen and after solution was complete the specific conductive power appeared to have increased to  $131.10^{-5}$ .

It seemed very peculiar that a powerful evolution of gas still went on after the sodium had dissolved, showing a decomposition of the hydrazine with formation of ammonia. This decomposition ceased as soon as the liquid was poured out of the apparatus; apparently it only takes place by contact with the platinum black present on the electrodes and is, therefore, quite comparable to the spontaneous decomposition of an alkaline solution of hydrogen peroxide exposed to the same influence.

Finally a few experiments were made with a solution of ammonia in hydrazine. The solubility of that gas at the ordinary temperature did not seem to be large; about 4.3 per cent of  $NH_3$  is present in the saturated solution. After a few bubbles of ammonia had been absorbed in the hydrazine (with  $\kappa = 5.2.10^{-5}$ ) the conductive power appeared to be but slightly increased ( $\kappa = 6.9.10^{-5}$ ); this was also still the case after the liquid had been saturated with ammonia (about

<sup>1)</sup> l. c. p. 183. Dr. J. W. Duro has found that an atom of hydrogen is replaced here; the  $NaH, N_2$  formed is a substance which on being exposed to the air causes a violent spontaneous explosion.

220 mgr. of  $H_3N$  in 4.920 gr. of  $N_2H_4$ ,  $v = 0.38$ ,  $\kappa = 9.10^{-5}$ . It is known that on dissolving ammonia in water the conductive power is but very slightly increased.

From the foregoing we may draw the conclusion that, with regard to its ionising power, hydrazine is comparable to water.

As regards mixtures of hydrazine and water it may be observed that on addition of water the conductive power at first decreases reaching a minimum with a mixture of 60 mols. of  $H_2O$  to 100 mols.  $N_2H_4$  (about 25 per cent of  $H_2O$  and 75 per cent of  $N_2H_4$ ) then increasing again. This minimum, therefore, does not correspond with the composition  $N_2H_4 + H_2O$ , or the so-called hydrate.

*Utrecht—Amsterdam, January 1903.*

**Chemistry.** — “*The velocity of transformation of tribromophenol-bromine into tetrabromophenol.*” By Mr. A. H. J. BELZER <sup>1)</sup>. (4<sup>th</sup> Communication on intramolecular rearrangement, presented by Prof. C. A. LOBRY DE BRUYN).

(Communicated in the meeting of February 28, 1903).

BENEDIKT <sup>2)</sup> found in 1879 that tribromophenol brought into contact with bromine water is capable of exchanging a fourth hydrogen atom for bromine with formation of a tetrabromo-derivative. The study of this substance led him to the conclusion that one Br-atom occupies a peculiar position in the molecule; it is, in fact, the cause of a certain number of reactions in which that Br-atom is readily displaced. As moreover the new substance seemed to have lost the character of a phenol as shown by its insolubility in alkalis, BENEDIKT gave it the formula  $C_6H_2Br_3 \cdot OBr$  and the name of tribromophenolbromine. BENEDIKT also noticed that, when melted under sulphuric acid, it passes into the already known isomeric tetrabromophenol, a true phenol which no longer contains a loosely bound Br-atom.

In his first publication BENEDIKT looked upon this transformation into tetrabromophenol not as an intramolecular displacement of atoms but as a process taking place between two mols of tribromophenolbromine; in a later communication however he does so, without stating any reasons.

When a few years ago, JOH. THIELE <sup>3)</sup> found that BENEDIKT'S

<sup>1)</sup> Proc. 31 May, 28 June and 25 Oct. 1902.

<sup>2)</sup> Annalen 199. 127, Monatshefte 1. 361.

<sup>3)</sup> Ber. 33. 673 (1900).