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Mathematisk-fysiske Meddelelser. **XIV,** 3.

STUDIES ON HALOGEN-CYANIDES II.

THE DISTRIBUTION OF IODINE CYANIDE AND CYANOGEN BROMIDE BETWEEN BENZENE AND WATER, AND BETWEEN BENZENE AND SOME AQUEOUS SALT SOLUTIONS. THE SYNTHESIS AND THE MOLECULAR WEIGHT OF IODINE CYANIDE

BY

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1936

Printed in Denmark.
Bianco Lunos Bogtrykkeri A/S.

1. Introduction.

In an investigation of the equilibrium:

$$ICN + I^- + H^+ \rightleftarrows I_2 + HCN,$$

KOVACH[1] attempted to calculate the equilibrium constant. But the value which was obtained from the conductivity measurements and the potentiometric estimations cannot be correct, such as it was realized already by KOVACH, since the value of the iodine-iodide ion potential, calculated by means of the equilibrium constant, is not in agreement with the accepted value.

This disagreement may be due to, either that the activity of iodine cyanide is strongly effected by salts in general, or that iodine cyanide reacts with iodide ions and cyanide ions to form complex compounds, or to both of these effects.

The following research was started to investigate the salting out effect on iodine cyanide and cyanogen bromide, and to investigate if these substances actually are able to unite with halogen ions to form complex ions, similar to the tri-iodide ion, I_3^-.

When this investigation was in progress YOST & STONE[2] published a paper dealing with the complexformation of iodine cyanide with iodide and cyanide ions.

[1] Z. phys. Chem. **80** (1912) 107.
[2] Jour. Amer. Chem. Soc. **55** (1933) 1889.

From the distribution of iodine cyanide between carbon tetrachloride and aqueous solutions of potassium iodide and potassium cyanide, these authors have estimated two quantities, which should be the complexity constants of the ions $ICNI^-$ and $ICNCN^-$. In the calculation they have assumed, that the activity of the iodine cyanide, for the same concentration of iodine cyanide, is the same in water and in an aqueous salt solution. This, however, is not permissible, since a considerable salting out effect is observed, such as it will be seen in the following. If the authors had used sodium iodide and sodium cyanide, in place of the potassium salts, the computed complexity constants would have been different, but equally wrong.

In the following investigation of the distribution of iodine cyanide and cyanogen bromide between benzene and aqueous salt solutions the effect of iodide ions has not been dealt with, as it appeared to require special precautions. Even a minute quantity of carbon dioxide in the solutions produces a formation of free iodine, which changes the distribution ratio (estimated by thiosulphate titrations) considerably. In solutions of potassium cyanide the hydroxyl ions produce a slow hydrolysis of iodine cyanide and a rapid hydrolysis of cyanogen bromide, probably accompanied by other reactions, and the cyanide solutions, therefore, have not been dealt with in this paper.

2. The Synthesis of Cyanogen Bromide and Iodine Cyanide.

The cyanogen bromide was prepared as mentioned in a previous paper[1] and was perfectly pure.

[1] Det Kgl. Danske Vid. Selskab. Math.-fys. Medd. XII, 17 (1934).

According to SERULLAS[1] and SEUBERT & POLLARD[2] iodine cyanide may be prepared from mercuric cyanide and iodine, either by sublimation of the stoechiometric mixture, or by adding the iodine in the form of an ethereal solution to the mercuric cyanide, evaporate to dryness, and extract the iodine cyanide, which is formed, by means of ether[3].

None of these methods, however, are practical for the production of larger quantities of iodine cyanide, and it is difficult to obtain a perfect separation from free iodine and the mercuric salts.

Another method, therefore, was applied, similar to SCHOLL's cyanogen bromide synthesis, and a similar method has been employed by YOST & STONE (l. c.).

21.1 grams of pure sodium cyanide (98—99 %) were dissolved in 80 ccs. of water in a bottle with a wide neck. The solution was placed in ice and stirred by means of a glass rod fitted to an electric stirrer. To the ice-cold solution 100 grams of iodine were added in small portions (2—3 grams at the time), and the next portion first added when the previous had reacted. When all the iodine is added, the solution, which still contains a slight excess of cyanide ions, is extracted trice with ether in a separatory funnel. The first time with 90 ccs., then with 70 ccs. and finally with about 50 ccs. of ether.

The ethereal solution is now evaporated at ordinary temperature in a hood with good ventilation, until all ether has disappeared. The crystalline mass is dissolved in alcohol, just enough to effect a complete dissolution. After a filtra-

[1] Ann. Chim. Phys. (2) **27** (1824) 188.
[2] B. **23** (1890) 1062.
[3] Linnemann: Lieb. Ann. **120** (1861) 36.

tion water is added to the alcoholic solution, until a slight precipitation occurs, which does not disappear on stirring. After 24 hours the major part of the iodine cyanide has crystallized out. It is filtered by suction, washed with water, and dried over calcium chloride (which has been treated with carbon dioxide to remove any alkaline components). The yield is about 45 to 47 grams of a slightly brownish substance (theory 60.3 grams).

To effect a further purification the iodine cyanide is sublimed. This has been done in two ways. The first method is to place the brownish iodine cyanide in the bottom of an ordinary filter pump suction flask, cover it with a piece of filter paper, and in the neck of the flask fix a wide test tube filled with carbon dioxide snow and ether. On evacuation of the flask the iodine cyanide sublimes and deposites on the test tube in needleshaped crystals. The sublimation may also be effected by placing the impure iodine cyanide in the bottom of a wide glass tubing, cover it with a piece of filter paper, close the tube with a rubber stopper fitted with a glass stopcock, evacuate and place the tube on the top of a radiator for heating the room.

The products obtained by these sublimations are perfectly pure, i. e. they give the theoretical quantity of iodine on addition to a solution of potassium iodide acidifyed with acetic acid.

For instance 0.9212 gram of iodine cyanide was dissolved with water in a measuring flask, and the volume made up to 500.2 ccs. The solution thus is 0.01204 molar. 10.01 ccs. of this solution were added to a solution of 2 grams of potassium iodide in 25 ccs. of 5 % acetic acid, and the liberated iodine titrated with a 0.01017 N. solution of sodium thiosulphate. In 6 estimations the consumption of iodine

was: 23.72, 23.71, 23.69, 23.71, 23.69, 23.69 ccs., or on the average 23.70 ccs. From this result the molarity of the iodine cyanide solution is calculated to 0.01204, which is in complete agreement with the result above.

3. The Analytical Estimation of Cyanogen Bromide and Iodine Cyanide.

Cyanogen bromide and iodine cyanide have in the following been estimated, as already mentioned, by an iodometric titration with thiosulphate. It should only be mentioned that special precautions are necessary when 0.01 N. solutions of sodium thiosulphate are standardized, such as it has been stated in a previous paper.[1]

4. The Molecular Weight of Iodine Cyanide in Aqueous Solutions and in Benzene.

To be certain that no polymerization occurs in benzene solutions of iodine cyanide, the molecular weight was determined by the freezing point method. The applied benzene was of a pure brand for molecular weight estimations. It was dried over metallic sodium and distilled. After this it had the correct freezing point.

In a series of estimations it was found, within an experimental error of about 2—3 %, that the molecular weight of iodine cyanide is the same in benzene and aqueous solutions and equal to the theoretical value.

The molecular weight of cyanogen bromide has been investigated in a previous paper[2] and has the theoretical value both in water and benzene.

[1] Max Møller: Z. analyt. Chem. **99** (1934) 353.
[2] l. c.

5. The Distribution of Iodine Cyanide and Cyanogen Bromide between Water and Benzene at 25°. The Estimation of d_0.

The experiments were made by weighing out a certain quantity of the halogen cyanide in a small phial with glass stopper, dissolving the content in water saturated with benzene at 25° and making the solution up to the desired volume. This solution was then titrated by the usual iodometric method. Then a certain volume of the halogen cyanide solution (50 or 100 ccs.) was taken out by means of a pipette and runned to the equal volume of benzene (saturated with water at 25°) in a glass stoppered bottle. After securing the stopper with a rubber cap, the bottle was rotated in a water thermostate at 25° ± 0.02°. The equilibrium is attained in less than half an hour. Samples of the benzene solution and the aqueous solution were pipetted into solutions of potassiun iodide in 5 % acetic acid and titrated with an 0.01 N. solution of sodium thiosulphate.

The results of the distribution experiments for iodine cyanide between water and benzene are given in the table I. Here the column ICN, H_2O is the molar concentration of iodine cyanide in the aqueous layer and the column ICN, C_6H_6 the molar concentration in the benzene layer. d is the distribution ratio, i. e. the ratio of the iodine cyanide concentration in the benzene layer to the concentration in the aqueous layer.

It may be seen from the table, that the value of d is the same for the three lowest iodine cyanide concentrations. We may accept, therefore, for the distribution ratio at infinite dilution, d_0, the value:

$$d_0 = 1.421.$$

Assuming that the activity of the iodine cyanide in the benzene solution is equal to the concentration for the entire range of concentrations in the table, the activity coefficient of the iodine cyanide in the aqueous solution is given by:

$$f = \frac{d}{d_0}.$$

The values of f together with the value of log f are given in the table.

Table I.

The distribution of iodine cyanide between water and benzene at 25°.

ICN, H_2O Molarity	ICN, C_6H_6 Molarity	d	f	log f
0.0005411	0.0007690	1.421		
0.001077	0.001532	1.422	1.000	0.0000
0.002163	0.003075	1.421		
0.003217	0.004578	1.423	1.002	0.0009
0.003235	0.004607	1.424		
0.004759	0.006781	1.425	1.003	0.0013
0.006423	0.009177	1.429	1.006	0.0026
0.009644	0.01383	1.434	1.009	0.0039
0.01278	0.01841	1.441	1.014	0.0060
0.01600	0.02310	1.444	1.016	0.0069

Table II.

The distribution of iodine cyanide between water and carbon tetrachloride at 25°. YOST & STONE's experiments recalculated with $d_0 = 0.1755$.

ICN, H_2O Molarity	ICN, CCl_4 Molarity	log f Y. & S.	log f recalculated
0.02480	0.004460	0.0066	0.0105
0.02596	0.004673	0.0071	0.0110
0.03312	0.006007	0.0104	0.0143
0.05144	0.009441	0.0154	0.0193
0.06697	0.01239	0.0190	0.0229
0.07173	0.01330	0.0199	0.0238
0.07960	0.01482	0.0218	0.0257

In fig. 1 the curve (ICN) gives the values of log f plotted against the iodine cyanide concentration in the aqueous layer.

Yost & Stone (l. c.) have estimated the distribution of iodine cyanide between water and carbon tetrachloride for iodine cyanide concentrations higher than the here applied,

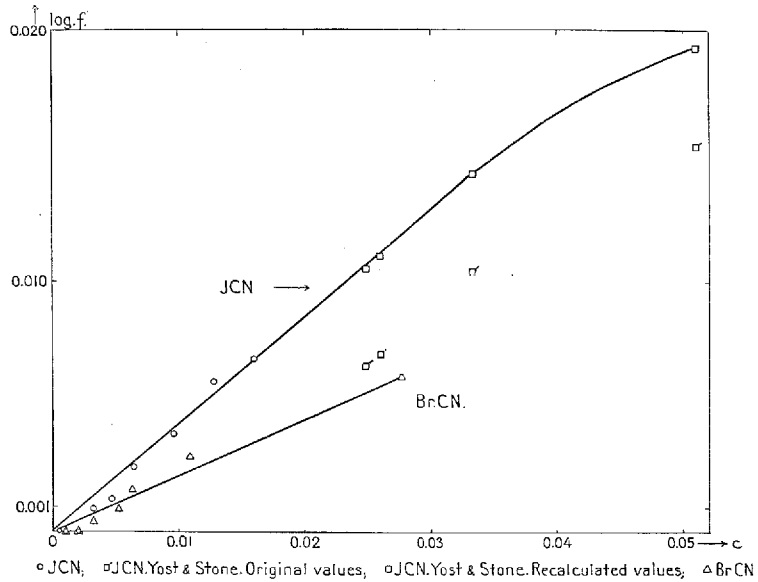

Fig. 1.

and have by a graphic method extrapolated to the value of d_0, the distribution ratio at infinitive dilution. If the activity coefficient of the iodine cyanide in the aqueous solution is calculated from Yost & Stone's experiments and their value for d_0 (table II column log f, Y & S), the results do not fit in with the experiments in table I. However, it appears that the curve for Yost & Stone's values of log f, plotted against the iodine cyanide concentration, is not directed toward the zeropoint at infinitive dilution. When the distribution ratios are plotted against the concen-

trations of iodine cyanide in the aqueous layer, it appears, that in the extrapolation to the value of $d_0 = 0.1771$, these authors have omitted the two lowest concentrations. When these are taken into consideration the value obtained is $d_0 = 0.1755$. When the activity coefficient is calculated by means of this value (table II, log f recalculated), the results fit in nicely with the experiments in table I (see fig. 1).

Table III.

The distribution of cyanogen bromide between water and benzene at 25°.

BrCN, H_2O Molarity	BrCN, C_6H_6 Molarity	d	f	log f
0.001040	0.003646	3.506	1.000	0.0000
0.002091	0.007331	3.506		
0.003119	0.01094	3.508	1.001	0.0004
0.003187	0.01117	3.505		
0.005207	0.01829	3.512	1.002	0.0009
0.006340	0.02232	3.520	1.004	0.0017
0.01089	0.03845	3.530	1.007	0.0030
0.02773	0.07065	3.548	1.012	0.0052

The distribution ratio of cyanogen bromide between water and benzene are given in table III. Here BrCN, H_2O and BrCN, C_6H_6 are the cyanogen bromide concentrations in the aqueous layer and the benzene layer respectively, when the distribution equilibrium is attained. The value of the distribution ratio at infinitive dilution is found to $d_0 = 3.506$. By means of this value the activity coefficient of cyanogen bromide in the aqueous solution has been calculated (f and log f in the table), and in fig. 1 the values of log f have been plotted against the cyanogen bromide concentrations (curve BrCN).

It may be observed that the two curves in fig. 1 are of a similar shape, but that the "self-salting-out effect" is less for cyanogen bromide than for iodine cyanide.

6. The Distribution of Iodine Cyanide and Cyanogen Bromide between Benzene and Aqueous Salt Solutions.

These experiments were made in a manner similar to the distribution of the halogen cyanides between water and benzene. The solutions of the salts, potassium chloride, sodium chloride, potassium bromide, sodium bromide, potassium nitrate, sodium nitrate, sodium perchlorate and sodium sulphate, were made by weighing out the dry, anhydrous salts and dissolve to a definite volume with water.

After addition of a measured volume of a halogen cyanide solution of a known concentration to a measured volume of the salt solution (all the aqueous solutions were made from water saturated with benzene at 25°), an equal volume of benzene (saturated with water) was added, and the mixture rotated in a thermostate at $25° \pm 0.02°$. When the equilibrium had been attained, samples of the two layers were drawn by means of pipettes, runned into acidified solutions of potassium iodide and the liberated iodine titrated with a 0.01 N. solution of sodium thiosulphate. From the results of the two titrations the distribution coefficient (d in the following tables III to XVII) was calculated. By means of this value and the distribution coefficient d'_0 (obtained from table I or III) for the halogen cyanide distribution between pure water and benzene, when the benzene layer has the same halogen cyanide concentration as the benzene layer in the distribution experiment in question, the quantity f, the "apparent activity coefficient", has been calculated. This is defined by the equation:

$$f = \frac{d}{d'_0}.$$

The values of f are given in the tables, and in the graphs, figs. 2 and 4, the values of log f have been plotted against the normal salt concentration.

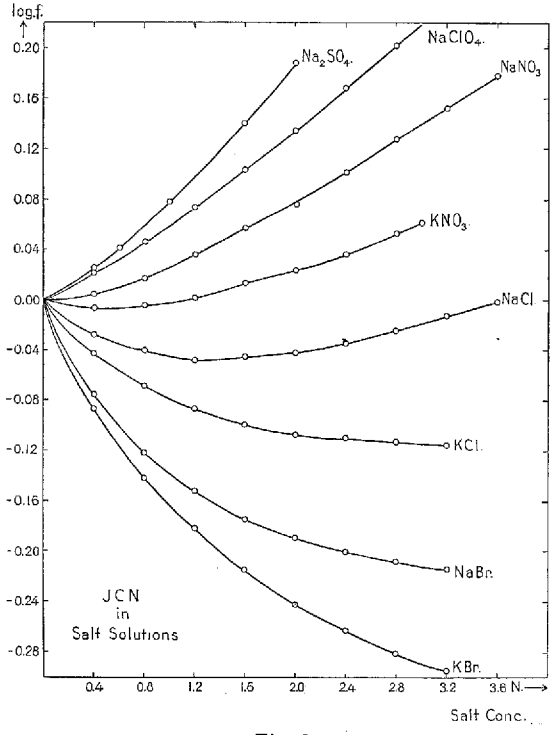

Fig. 2.

Further a quantity k has been calculated, defined by the equation:

$$\log f = k \cdot c,$$

where f is the apparent activity coefficient of the halogen cyanide in the salt solution of the normal concentration c. The values of k are given in the tables, and in the graphs, figs. 3 and 5, k has been plotted against the normal salt concentration.

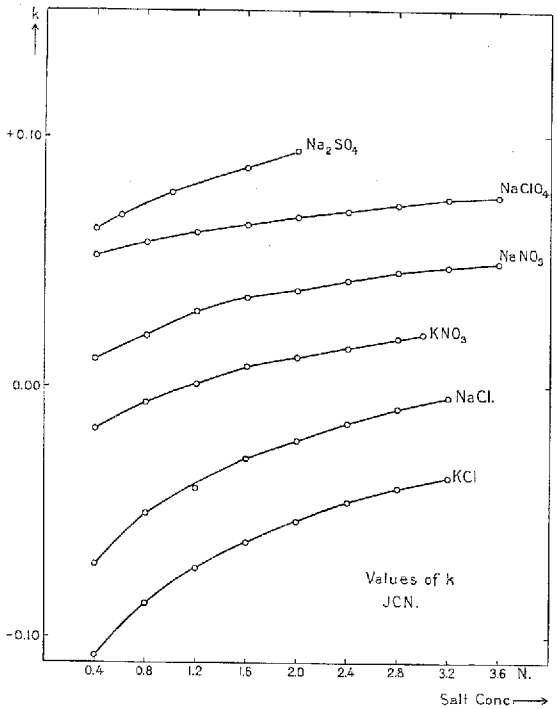

Fig. 3 a.

Table IV.

The distribution of ICN between benzene and aqueous solutions of KCl at 25°.

KCl conc. Normality	ICN, Salt, aq. Molarity	ICN, C_6H_6 Molarity	d	f	log f	k
		$d'_0 = 1.424$				
0.4000	0.003581	0.004617	1.289	0.9055	— 0.0432	— 0.1080
0.8000	0.003703	0.004493	1.213	0.8520	— 0.0696	— 0.0870
1.200	0.003786	0.004410	1.165	0.8180	— 0.0872	— 0.0727
1.600	0.003846	0.004350	1.131	0.7944	— 0.1000	— 0.0625
2.000	0.003883	0.004313	1.111	0.7802	— 0.1078	— 0.0539
2.400	0.003896	0.004301	1.104	0.7754	— 0.1105	— 0.0460
2.800	0.003908	0.004287	1.097	0.7704	— 0.1133	— 0.0405
3.200	0.003922	0.004275	1.090	0.7654	— 0.1161	— 0.0363

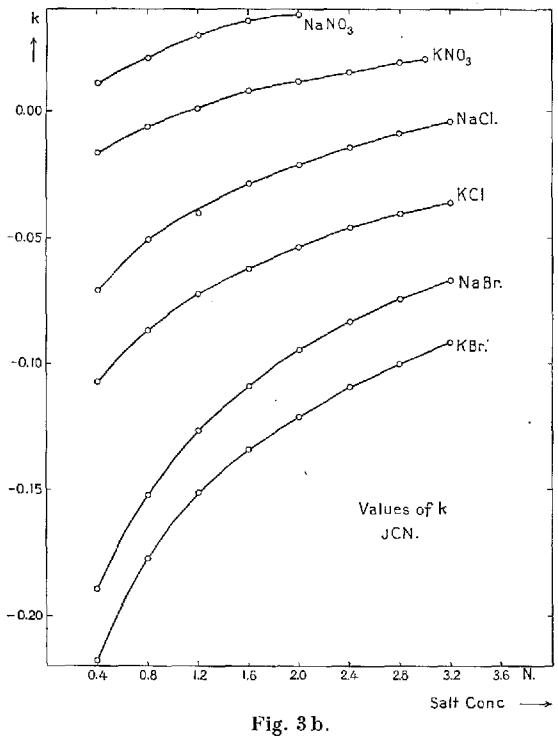

Fig. 3 b.

Table V.

The distribution of ICN between benzene and aqueous solutions of NaCl at 25°.

NaCl conc. Normality	ICN, Salt, aq. Molarity	ICN, C_6H_6 Molarity	d	f	log f	k
		$d'_6 = 1.424$				
0.4000	0.004385	0.005845	1.333	0.9375	—0.0280	—0.0710
0.8000	0.004493	0.005823	1.296	0.9110	—0.0405	—0.0506
1.200	0.004480	0.005703	1.273	0.8948	—0.0483	—0.0403
1.600	0.004517	0.005785	1.281	0.9008	—0.0454	—0.0284
2.000	0.004484	0.005789	1.291	0.9068	—0.0425	—0.0213
2.400	0.004418	0.005795	1.312	0.9226	—0.0350	—0.0146
2.800	0.004360	0.005855	1.343	0.9442	—0.0249	—0.00888
3.200	0.004321	0.005967	1.381	0.9707	—0.0129	—0.00403

Table VI.

The distribution of ICN between benzene and aqueous solutions of KBr at 25°.

KBr conc. Normality	ICN, Salt, aq. Molarity	ICN, C_6H_6 Molarity	d	f	log f	k
		$d'_0 =$	1.425			
0.4000	0.005332	0.006208	1.164	0.8180	— 0.0872	— 0.2180
0.8000	0.005689	0.005843	1.027	0.7208	— 0.1422	— 0.1778
1.200	0.005963	0.005577	0.9357	0.6577	— 0.1820	— 0.1517
1.600	0.006175	0.005354	0.8670	0.6084	— 0.2158	— 0.1344
2.000	0.006353	0.005176	0.8146	0.5717	— 0.2428	— 0.1214
2.400	0.006484	0.005045	0.7779	0.5459	— 0.2629	— 0.1095
2.800	0.006743	0.005029	0.7459	0.5234	— 0.2812	— 0.1004
3.200	0.006700	0.004840	0.7225	0.5077	— 0.2944	— 0.0920

Table VII.

The distribution of ICN between benzene and aqueous solutions of NaBr at 25°.

NaBr conc. Normality	ICN, Salt, aq. Molarity	ICN, C_6H_6 Molarity	d	f	log f	k
		$d'_0 =$	1.424			
0.4000	0.004765	0.005694	1.195	0.8392	— 0.0761	— 0.1902
0.8000	0.005038	0.005410	1.074	0.7541	— 0.1225	— 0.1531
1.200	0.005224	0.005235	1.002	0.7037	— 0.1526	— 0.1271
1.600	0.005345	0.005088	0.9520	0.6685	— 0.1749	— 0.1093
2.000	0.005435	0.004998	0.9196	0.6460	— 0.1899	— 0.09495
2.400	0.005480	0.004913	0.8966	0.6300	— 0.2009	— 0.08370
2.800	0.004586	0.004830	0.8802	0.6182	— 0.2089	— 0.0746
3.200	0.005541	0.004816	0.8690	0.6103	— 0.2145	— 0.0670

Table VIII.

The distribution of ICN between benzene and aqueous solutions of $NaClO_4$ at 25°.

$NaClO_4$ conc. Normality	ICN, Salt, aq. Molarity	ICN, C_6H_6 Molarity	d	f	log f	k
		$d'_0 = 1.424$				
0.4000	0.004006	0.005987	1.494	1.049	0.0209	0.0523
0.8000	0.003871	0.006127	1.583	1.112	0.0460	0.0575
1.200	0.003708	0.006253	1.686	1.184	0.0734	0.0615
1.600	0.003568	0.006448	1.807	1.269	0.1035	0.0647
2.000	0.003397	0.006607	1.945	1.366	0.1354	0.0677
2.400	0.003233	0.006778	2.097	1.472	0.1680	0.0700
2.800	0.003068	0.006971	2.272	1.596	0.2029	0.0725
3.200	0.002906	0.007185	2.472	1.736	0.2396	0.0749
3.600	0.002730	0.007293	2.671	1.876	0.2732	0.0759

Table IX.

The distribution of ICN between benzene and aqueous solutions of KNO_3 at 25°. Conc. of ICN in benzene layer before distribution 0.009914 molar.

KNO_3 conc. Normality	ICN, Salt, aq. Molarity	ICN, C_6H_6 Molarity	d	f	log f	k
		$d'_0 = 1.424$				
0.4000	0.004127	0.005787	1.402	0.9845	—0.0068	—0.0170
0.8000	0.004118	0.005796	1.408	0.9888	—0.0049	—0.0061
1.200	0.004085	0.005829	1.427	1.002	0.0009	0.0008
1.600	0.004021	0.005893	1.466	1.030	0.0126	0.0079
2.000	0.003964	0.005950	1.502	1.055	0.0232	0.01160
2.400	0.003894	0.006020	1.547	1.087	0.0360	0.01500
2.800	0.003802	0.006112	1.608	1.129	0.0528	0.01886
3.000	0.003737	0.006134	1.642	1.153	0.0619	0.02063

Table X.

The distribution of ICN between benzene and aqueous solutions of $NaNO_3$ at 25°. Conc. of ICN in benzene layer before distribution 0.009964 molar.

$NaNO_3$ conc. Normality	ICN, Salt, aq. Molarity	ICN, C_6H_6 Molarity	d	f	log f	k
		$d'_0 = 1.424$				
0.4000	0.004089	0.005875	1.437	1.0093	0.0040	0.0110
0.8000	0.004022	0.005942	1.478	1.038	0.0162	0.0203
1.200	0.003915	0.006049	1.546	1.086	0.0357	0.0298
1.600	0.003797	0.006167	1.624	1.141	0.0571	0.0357
2.000	0.003697	0.006267	1.696	1.191	0.0759	0.0380
2.400	0.003563	0.006401	1.797	1.262	0.1010	0.0421
2.800	0.003424	0.006540	1.911	1.342	0.1278	0.0456
3.200	0.003303	0.006661	2.017	1.417	0.1513	0.0472
3.600	0.003171	0.006793	2.143	1.506	0.1778	0.0493

Table XI.

The distribution of ICN between benzene and aqueous solutions of Na_2SO_4 at 25°.

Na_2SO_4 conc. Normality (2·Molarity)	ICN, Salt, aq. Molarity	ICN, C_6H_6 Molarity	d	f	log f	k
		$d'_0 = 1.422$				
0.4000	0.002551	0.003842	1.506	1.059	0.0249	0.0623
0.6000	0.002498	0.003901	1.562	1.099	0.0408	0.0680
1.000	0.002366	0.004020	1.700	1.195	0.0775	0.0775
1.600	0.002161	0.004241	1.962	1.380	0.1398	0.0874
2.000	0.002008	0.004401	2.192	1.541	0.1879	0.0940

Table XII.

The distribution of BrCN between benzene and aqueous solutions of KCl at 25°.

KCL conc. Normality	BrCN, Salt, aq. Molarity	BrCN, C_6H_6 Molarity	d	f	log f	k
		d'_0 =	3.505			
0.4000	0.003157	0.01126	3.565	1.017	0.0073	0.0182
0.8000	0.003097	0.01132	3.653	1.042	0.0180	0.0225
1.200	0.003035	0.01139	3.752	1.070	0.0295	0.0246
1.600	0.002964	0.01145	3.863	1.102	0.0422	0.0264
2.000	0.002892	0.01154	4.022	1.147	0.0597	0.0299
2.400	0.002787	0.01162	4.171	1.190	0.0755	0.0315
2.800	0.002710	0.01171	4.322	1.233	0.0910	0.0325
3.200	0.002632	0.01179	4.476	1.277	0.1062	0.0332

Table XIII.

The distribution of BrCN between benzene and aqueous solutions of NaCl at 25°.

NaCl conc. Normality	BrCN, Salt, aq. Molarity	BrCN, C_6H_6 Molarity	d	f	log f	k
		d'_0 =	3.510			
0.4000	0.004639	0.01700	3.663	1.044	0.0186	0.0465
8.0000	0.004479	0.01718	3.835	1.093	0.0385	0.0481
1.200	0.004239	0.01714	4.043	1.152	0.0614	0.0512
1.600	0.004055	0.01734	4.276	1.218	0.0857	0.0536
2.000	0.003854	0.01749	4.538	1.293	0.1116	0.0558
2.400	0.003654	0.01755	4.812	1.371	0.1370	0.0571
2.800	0.003472	0.01764	5.081	1.448	0.1607	0.0574
3.200	0.003302	0.01775	5.376	1.532	0.1852	0.0578
3.600	0.003154	0.01788	5.665	1.614	0.2079	0.0578

Table XIV.

The distribution of BrCN between benzene and aqueous solutions of KBr at 25°.

KBr conc. Normality	BrCN, Salt, aq. Molarity	BrCN, C_6H_6 Molarity	d	f	log f	k
		$d'_0 =$	3.505			
0.4000	0.003231	0.01118	3.460	0.9872	—0.0056	—0.0140
0.8000	0.003243	0.01115	3.436	0.9804	—0.0086	—0.0108
1.200	0.003247	0.01116	3.438	0.9808	—0.0084	—0.0070
1.600	0.003238	0.01115	3.444	0.9826	—0.0076	—0.0047
2.000	0.003219	0.01119	3.477	0.9920	—0.0035	—0.0018
2.400	0.003184	0.01123	3.527	1.006	0.0027	0.0011
2.800	0.003156	0.01126	3.566	1.017	0.0075	0.0026
3.200	0.003120	0.01129	3.618	1.032	0.0138	0·0043

Table XV.

The distribution of BrCN between benzene and aqueous solutions of NaBr at 25°.

NaBr conc. Normality	BrCN, Salt, aq. Molarity	BrCN, C_6H_6 Molarity	d	f	log f	k
		$d'_0 =$	3.505			
0.4000	0.003133	0.01109	3.538	1.009	0.0041	0.0102
0.8000	0.003085	0.01109	3.596	1.026	0.0111	0.0139
1.200	0.003020	0.01112	3.680	1.050	0.0211	0.0176
1.600	0.002955	0.01118	3.782	1.079	0.0330	0.0206
2.000	0.002885	0.01117	3.870	1.104	0.0430	0.0215
2.400	0.002793	0.01115	3.990	1.139	0.0563	0.0234
2.800	0.002712	0.01120	4.126	1.177	0.0709	0.0253
3.200	0.002625	0.01119	4.260	1.215	0.0847	0.0265

Table XVI.

The distribution of BrCN between benzene and aqueous solutions of $NaClO_4$ at 25°.

$NaClO_4$ conc. Normality	BrCN, Salt, aq. Molarity	BrCN, C_6H_6 Molarity	d	f	log f	k
		$d'_0 =$	3.506			
0.4000	0.001979	0.007101	3.589	1.023	0.0102	0.0255
0.8000	0.001925	0.007099	3.688	1.052	0.0220	0.0275
1.200	0.001867	0.007094	3.799	1.084	0.0349	0.0291
1.600	0.001817	0.007158	3.939	1.123	0.0506	0.0316
2.000	0.001737	0.007233	4.164	1.188	0.0747	0.0374
2.400	0.001686	0.007306	4.334	1.236	0.0921	0.0384
2.800	0.001626	0.007406	4.556	1.300	0.1138	0.0406
3.200	0.001571	0.007470	4.755	1.356	0.1324	0.0414
3.600	0.001507	0.007480	4.963	1.416	0.1510	0.0419

Table XVII.

The distribution of BrCN between benzene and aqueous solutions of KNO_3 at 25°.

KNO_3 conc. Normality	BrCN, Salt, aq. Molarity	BrCN, C_6H_6 Molarity	d	f	log f	k
		$d'_0 =$	3.506			
0.4000	0.002334	0.008236	3.529	1.0063	0.0027	0.0067
0.8000	0.002316	0.008254	3.563	1.016	0.0069	0.0086
1.200	0.002294	0.008276	3.609	1.0295	0.0126	0.0105
1.600	0.002250	0.008320	3.698	1.055	0.0232	0.0145
2.000	0 002201	0.008369	3.803	1.085	0.0354	0.0177
2.400	0.002150	0.008420	3.915	1.117	0.0480	0.0200
2.800	0.002103	0.008467	4.027	1.149	0.0602	0.0215
3.000	0.002071	0.008499	4.095	1.168	0.0674	0.0225

Table XVIII.

The distribution of BrCN between benzene and aqueous solutions of $NaNO_3$ at 25°.

$NaNO_3$ conc. Normality	BrCN, Salt, aq. Molarity	BrCN, C_6H_6 Molarity	d	f	log f	k
		$d'_0 =$	3.507			
0.4000	0.002300	0.008298	3.609	1.0295	0.0126	0.0315
0.8000	0.002240	0.008358	3.733	1.065	0.0273	0.0341
1.200	0.002174	0.008425	3.874	1.105	0.0432	0.0360
1.600	0.002104	0.008494	4.039	1.152	0.0614	0.0384
2.000	0.002010	0.008588	4.275	1.219	0.0861	0.0431
2.400	0.001937	0.008661	4.472	1.275	0.1056	0.0440
2.800	0.001866	0.008732	4.687	1.337	0.1261	0.0450
3.200	0.001790	0.008808	4.929	1.406	0.1479	0.0462
3.600	0.001718	0.008880	5.176	1.476	0.1692	0.0470

Table XIX.

The distribution of BrCN between benzene and aqueous solutions of Na_2SO_4 at 25°.

Na_2SO_4 conc. Normality	BrCN, Salt, aq. Molarity	BrCN, C_6H_6 Molarity	d	f	log f	k
		$d'_0 =$	3.506			
0.4000	0.002506	0.009894	3.947	1.126	0.0515	0.1287
0.6000	0.002398	0.01005	4.190	1.195	0.0774	0.1290
1.000	0.002155	0.01023	4.748	1.354	0.1317	0.1317
1.600	0.001821	0.01052	5.774	1.647	0.2167	0.1354
2.000	0.001629	0.01069	6.560	1.871	0.2721	0.1365

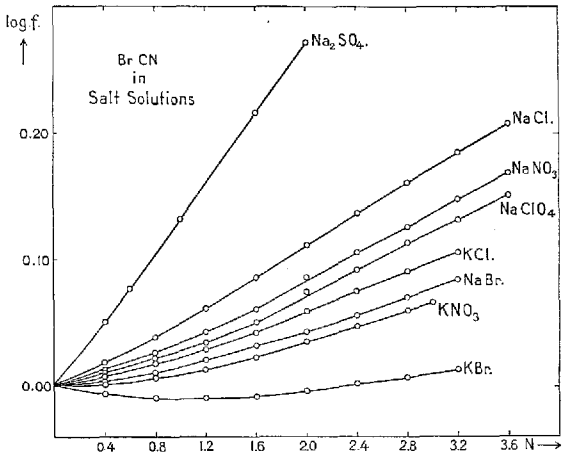
log f.
Br CN
in
Salt Solutions
Na_2SO_4.
Na Cl.
$Na NO_3$
$Na ClO_4$
KCl.
Na Br.
KNO_3
KBr.
0.20
0.10
0.00
0.4
0.8
1.2
1.6
2.0
2.4
2.8
3.2
3.6 N
Salt Conc.

Fig. 4.

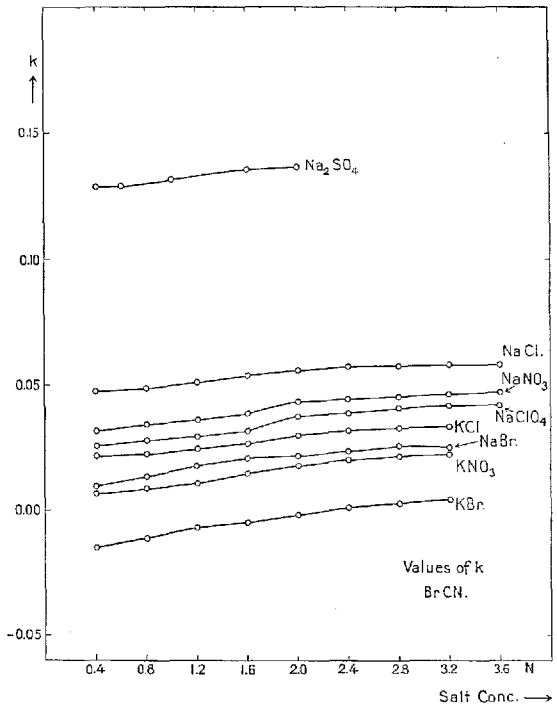
k
0.15
0.10
0.05
0.00
-0.05
Na_2SO_4
Na Cl.
$Na NO_3$
$Na ClO_4$
KCl
Na Br.
KNO_3
KBr.
Values of k
Br CN.
0.4
0.8
1.2
1.6
2.0
2.4
2.8
3.2
3.6 N
Salt Conc.

Fig. 5.

7. Discussion of the Distribution Experiments.

a. Introduction.

Observing the plots of log f against the salt concentration (figs. 2 and 4) one is struck immediately by the difference in the appearance of the curves for iodine cyanide and cyanogen bromide. While the iodine cyanide curves are wide apart and show a curvature in the entire range of salt solutions investigated, the cyanogen bromide curves are much closer together, and from a salt concentration of about 1.2 or 1.6 N. the curves are straight lines (excepting the curves for NaBr and KBr).

It may also be observed that the sodium chloride and the sodium nitrate curves of cyanogen bromide are placed above the sodium perchlorate curve, while the opposite is the case for iodine cyanide. Further, for cyanogen bromide the sodium chloride curve is above the sodium nitrate curve and the potassium chloride curve above the potassium nitrate curve, while the opposite is the case for iodine cyanide. Similar differences may be observed also in other cases.

Still more striking is the difference in the appearance of the curves which have been obtained by plotting the values of k against the salt concentrations (figs. 3a, 3b and 5).

The iodine cyanide curves are wide apart and, in the majority of cases, have a strong curvature. The curves of two salts with a common anion are parallel and the distance between the curves for a sodium salt and a potassium salt is almost the same in all cases independent of the anion. But the curves of such salts which have a common cation are not parallel.

In the case of cyanogen bromide all of the k-curves are practically parallel (with the exception of the curves for the bromides which differ slightly) and at higher salt concentrations almost straight lines.

Among the k-curves of iodine cyanide the only one of the same shape as the k-curves of cyanogen bromide is the sodium perchlorate curve. The perchlorate ion, however, is a perfectly "saturated" ion, which has no or at least only a very minute tendency to form complex ions. The shape of the sodium perchlorate k-curve of cyanogen bromide, therefore, must be due entirely to the "salting out effect" of the sodium and the perchlorate ions and not to complex formation. Since the other k-curves for cyanogen bromide have the same shape (the curves for the bromides differ slightly), it may be concluded that cyanogen bromide does not form complex ions with the sulphate, the nitrate and the chloride ion. Since the curves for sodium and potassium bromide differ, if only slightly, from the other, it is likely that this is due to a complex formation. This, however, must be very slight.

As the sodium perchlorate-k-curve of iodine cyanide is practically of the same shape as the k-curves of cyanogen bromide, it may further be concluded that iodine cyanide does not form complex ions with the perchlorate ion. That the other iodine cyanide-k-curves have a different appearence must be due to a complex formation with the anions of the salts. From the shape and the relative position of the curves one might expect that iodine cyanide forms complex ions more readily with bromide ions than with cloride ions, and more readily with these than with nitrate and sulphate ions.

b. Salting out Effect and Complex Formation.

The value of the salting out effect of a certain salt solution with a certain non-electrolyte cannot, in general, be predicted with any degree of certainty[1].

It is impossible, therefore, to apply directly any universal formula for the salting out coefficient, similar to the formula for the activity coefficient of an ion in a dilute solution of an electrolyte, when the salting out effect has to be separated from the effect due to a complex formation.

The quantity f, the "apparent activity coefficient", in the previous tables includes simultaneously the change in the activity due to the salting out effect and the change in the concentration of the free halogen cyanide due to the complex formation.

Let it be assumed, however, that the distribution ratio, entirely due to the salting out effect, is d′, defined by the equation:

$$d' = \frac{J_b}{J_f}, \tag{1}$$

where J_b is the concentration of the halogen cyanide in the benzene layer, and J_f is the concentration of free, not complex bound halogen cyanide in a certain salt solution of a certain concentration. The actual salting out coefficient is then defined by the equation:

$$f' = \frac{d'}{d'_0}, \tag{2}$$

where d'_0 is the distribution ratio of the halogen cyanide between benzene and water as previously discussed.

[1] See for instance Randall & Fairbanks Faily: Chem. Rev. **4** (1927) 285; Åkerlof: J. Amer. Chem. Soc. **51** (1929) 984.

When the equation for the complex formation is:

$$J + X^- \rightleftarrows JX^-,$$

where J is the halogen cyanide and X^- a certain monovalent ion, the equilibrium constant K_{JX^-} is obtained from the equation:

$$K_{JX^-} = \frac{a_{JX^-}}{a_J \cdot a_{X^-}}, \tag{3}$$

where a_{JX^-}, a_J and a_{X^-} are the activities of the substances in question.

If the total concentration of the halogen cyanide in the salt solution, after the distribution equilibrium has been attained between this and the benzene layer, is J_w, we have that:

$$J_w = J_f + J_c, \tag{4}$$

where J_f is the concentration of the free halogen cyanide and J_c the concentration of the complex bound halogen cyanide.

If the total halogen cyanide concentration in the aqueous salt solution, before the distribution between a certain volume of the salt solution and the same volume of benzene, is J_0, we may write:

$$J_0 = J_w + J_b. \tag{5}$$

The apparent distribution ratio of the halogen cyanide between an aqueous salt solution containing the ion X^- and benzene is then:

$$d_x = \frac{J_b}{J_w}. \tag{6}$$

This gives

$$J_0 = J_w (1 + d_x) \text{ or } J_w = \frac{J_0}{1 + d_x}, \tag{7}$$

and

$$J_b = J_0 - J_w = \frac{J_0 \cdot d_x}{1 + d_x}. \tag{8}$$

The actual distribution ratio, however, is:

$$d'_x = \frac{J_b}{J_f},$$

which gives:

$$J_f = \frac{J_b}{d'_x} = \frac{J_0 \cdot d_x}{(1 + d_x)\, d'_x}. \tag{9}$$

Introducing these values in (4) we get:

$$J_c = \frac{J_0 (d'_x - d_x)}{(1 + d_x)\, d'_x}. \tag{10}$$

Introducing these values of the concentrations in the equation for the equilibrium constant we have:

$$K_x = \frac{J_c \alpha_c}{J_f \alpha_f [X^-]\, \alpha_x}. \tag{11}$$

Here α_c is the activity coefficient of the complex ion JX^-, $[X^-]$ the concentration and α_x the activity of the X^- ions, and finally α_f the activity coefficient of the free halogen cyanide.

As the halogen cyanide concentration in the previous experiments is very small compared to the salt concentration, the concentration of the free X^- ions may be put equal to the total salt concentration c. Further, according to previous considerations, we have that $\alpha_f = f'_x$, and the equation for the complexity constant may be written, therefore:

$$\frac{\alpha_x}{\alpha_c} \cdot K_x = \frac{J_c}{J_f \cdot f'_x \cdot c}, \tag{12}$$

or, by introducing the values J_c and J_f from (9) and (10),

$$\frac{\alpha_x}{\alpha_c} \cdot K_x = \frac{d'_x - d_x}{d_x \cdot f'_x \cdot c}. \tag{13}$$

On division by d'_0 in nominator and denominator this equation is transformed to:

$$\frac{\alpha_x}{\alpha_c} \cdot K_x = \frac{1}{c} \cdot \left(\frac{1}{f_x} - \frac{1}{f'_x}\right). \tag{14}$$

Here α_c is unknown, while α_x may be obtained from the measurements of other authors and f'_x has not yet been estimated.

c. The estimation of f'_x, the actual salting out coefficient of iodine cyanide in salt solutions.

As previously discussed it may be concluded that cyanogen bromide does not form complex compounds with any other of the investigated anions than with the bromide ion, and here the complex formation, judged from the shape of the k-curve, must be very slight, so slight that it may be considered negligible in the following investigation. In the case of cyanogen bromide the values of f_x, which have been found in the experiments and are given in the tables XII to XIX (f in the tables), must be the actual salting out coefficients.

Iodine cyanide, on the other hand, as judged from the position of the apparent activity curves in comparison with the corresponding cyanogen bromide curves and from

the shape of the k-curves, forms complex ions, to different extent, with the bromide, the chloride and the nitrate ions, but not with the perchlorate ion. The k-curves for iodine cyanide and cyanogen bromide in sodium perchlorate solutions are parallel.

In table XX the value $\Delta = k_{ICN,\ NaClO_4} - k_{BrCN,\ NaClO_4}$ at different salt concentrations has been calculated, and it may be observed that it is fairly constant within the experimental error, as an error in the estimation of f of about 0.2 per cent. may cause deviations from the average value of Δ, which are very closely equal to the deviations observed in table XX.

Table XX.

$NaClO_4$ conc. Normality	k ICN, $NaClO_4$	k BrCN, $NaClO_4$	Δ
0.400	0.0523	0.0255	0.0268
0.800	0.0575	0.0275	0.0300
1.200	0.0615	0.0291	0.0324
1.600	0.0647	0.0316	0.0331
2.000	0.0677	0.0374	0.0303
2.400	0.0700	0.0384	0.0316
2.800	0.0725	0.0406	0.0319
3.200	0.0749	0.0414	0.0335
3.600	0.0759	0.0419	0.0340
		Mean...	0.0315

It has now been assumed, since cyanogen bromide and iodine cyanide are closely related and differ in structure probably only by a displacement of a pair of shared electrons, that the actual salting out effect on iodine cyanide by a sodium salt of a monovalent ion X^- may be expressed by the same equation, i. e.

$$\Delta = k'_{ICN,\ NaX} - k_{BrCN,\ NaX}$$

or:

$$k'_{ICN,\ NaX} = k_{BrCN,\ NaX} + \Delta.$$

Here $k'_{ICN,\ NaX}$ is the k-value which corresponds to the actual salting out coefficient, $f'_{ICN,\ NaX}$, of iodine cyanide in solutions of the salt NaX, and these two naturally are connected by the equation:

$$\log f'_{ICN,\ NaX} = c \cdot k'_{ICN,\ NaX} ,$$

where c as usual is the concentration of the salt, NaX, in the solution. The values of $k_{BrCN,\ NaX}$ are the k-values in the tables XIII, XV and XVIII.

By means of the value of Δ obtained in the table XX the values of the logarithm of the actual salting out coefficient of iodine cyanide, $\log f'$, in solutions of sodium bromide, sodium chloride and sodium nitrate have been calculated in the table XI, XII and XIII respectively.

By introducing these computed values of f' and the previously estimated values of f (the apparent activity coefficient) in the equation (14), the values of the quantity $\frac{\alpha_x}{\alpha_c} \cdot K_x$ have been calculated for the various salts at various salt concentrations and are given in the tables and in the graph fig. 6.

Table XXI.

Estimation of the complexity constant of the complex ion $ICNBr^-$.

$\Delta = 0.0315.$

NaBr conc.	k BrCN, NaBr	k′ ICN, NaBr	log f′ ICN, NaBr	log f ICN, NaBr	$\frac{\alpha_{Br}}{\alpha_c} \cdot K_{Br}$	α_{Br}	α_c
0.0000	Extrapolated graphically				0.650		
0.4000	0.0102	0.0417	0.0167	—0.0761	0.575	0.71	0.81
0.8000	0.0139	0.0454	0.0363	—0.1225	0.508	0.69	0.88
1.200	0.0176	0.0491	0.0589	—0.1526	0.457	0.69	1.01
1.600	0.0206	0.0521	0.0834	—0.1749	0.419	0.69	1.10
2.000	0.0215	0.0530	0.1060	—0.1899	0.382	0.73	1.24
2.400	0.0234	0.0549	0.1318	—0.2009	0.354	0.76	1.39
2.800	0.0253	0.0568	0.1590	—0.2089	0.330	0.80	1.58
3.200	0.0265	0.0580	0.1856	—0.2145	0.308	0.85	1.79

Table XXII.

Estimation of the complexity constant of the complex ion $ICNCl^-$.

$\Delta = 0.0315$.

NaCl conc.	k BrCN, NaCl	k′ ICN, NaCl	log f′ ICN, NaCl	log f ICN, NaCl	$\frac{\alpha_{Cl}}{\alpha_c} \cdot K_{Cl}$	α_{Cl}	α_c
0.0000	Extrapolated graphically				0.39		
0.4000	0.0465	0.0780	0.0312	—0.0280	0.339	0.70	0.81
0.8000	0.0481	0.0796	0.0637	—0.0405	0.293	0.67	0.89
1.200	0.0512	0.0827	0.0992	—0.0483	0.264	0.66	0.98
1.600	0.0536	0.0851	0.1362	—0.0454	0.238	0.67	1.10
2.000	0.0558	0.0873	0.1746	—0.0425	0.221	0.67	1.18
2.400	0.0571	0.0886	0.2126	—0.0350	0.206	0.69	1.22
2.800	0.0574	0.0889	0.2489	—0.0249	0.194	0.71	1.43
3.200	0.0578	0.0893	0.2858	—0.0129	0.182	0.73	1.56

Table XXIII.

Estimation of the complexity constant of the complex ion $ICNNO_3^-$.

$\Delta = 0.0315$.

$NaNO_3$ conc.	k BrCN, $NaNO_3$	k′ ICN, $NaNO_3$	log f′ ICN, $NaNO_3$	log f ICN, $NaNO_3$	$\frac{\alpha_{NO_3}}{\alpha_c} \cdot K_{NO_3}$	α_{NO_3}	α_c
0.0000	Extrapolated graphically				0.14		
0.4000	0.0315	0.0630	0.0252	0.0040	0.118	0.64	0.76
0.8000	0.0341	0.0656	0.0525	0.0162	0.0965	0.57	0.83
1.2000	0.0360	0.0675	0.0810	0.0357	0.0759	0.53	0.98
1.600	0.0384	0.0699	0.1118	0.0571	0.0647	0.50	1.08
2.000	0.0431	0.0746	0.1492	0.0759	0.0651	0.47	..
2.400	0.0440	0.0755	0.1812	0.1010	0.0557	0.45	1.13
2.800	0.0450	0.0765	0.2142	0.1278	0.0479	0.43	1.26
3.200	0.0462	0.0777	0.2486	0.1513	0.0443	0.41	1.30

As it may be observed, the value of this quantity is not constant, but decreases with increasing salt concentration. By a graphical extrapolation (see fig. 6), however, it is possible to obtain the approximate value at the salt concentration zero. When the salt concentration approaches

zero the values of α_x and α_c both approach unity, and thus the value obtained in the extrapolations is the approximate value of K_x.

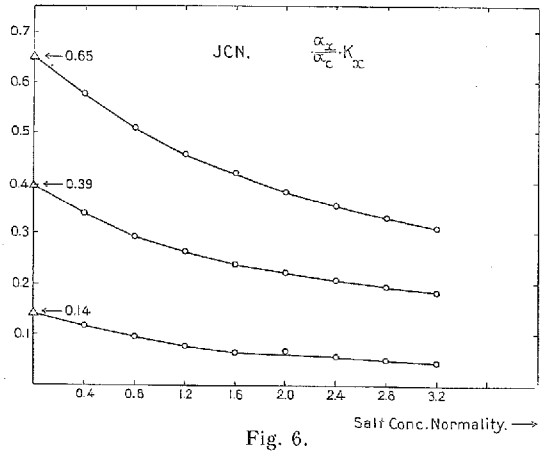

Fig. 6.

In this manner the complexity constants have been estimated as follows:

$$\frac{[ICNBr^-]}{[ICN] \cdot [Br^-]} = 0.65 \qquad A = -255 \text{ cal.}$$

$$\frac{[ICNCl^-]}{[ICN] \cdot [Cl^-]} = 0.39 \qquad A = -557 \text{ cal.}$$

$$\frac{[ICNNO_3^-]}{[ICN] \cdot [NO_3^-]} = 0.14 \qquad A = -1163 \text{ cal.}$$

The brackets here indicate the activities of the substances within the brackets.

By means of the equation:

$$A = RT \ln K_x$$

the affinity, A, of the complex formation at 25° may be calculated and is given above.

The values of α_{Br}, α_{Cl} and α_{NO_3} in the tables XXI, XXII and XXIII respectively have been taken from the tables of activity coefficients in Landolt Börnsteins tables (II Erg. Bd. 1931). By means of these, the value of K_x obtained in the extrapolation, and the values of $\frac{\alpha_x}{\alpha_c} \cdot K_x$, the values of α_c have been calculated and are given in the tables XXI to XIII.

The increase in the value of the complex-ion activity coefficients with increasing salt concentration is unusual but not improbable high.

d). Reflections on the structure of cyanogen bromide and iodine cyanide.

From an investigation of the Raman spectrum of cyanogen chloride[1] the conclusion has been drawn that this molecule is Cl–C≡N, and that, similar to hydrogen cyanide, H–C≡N, it probably is linear[2].

Since the three substances cyanogen chloride, cyanogen bromide and iodine cyanide show the same type of absorption spectre[3], it may be concluded that all three substances have the general structure X–C≡N (X is a halogen atom), and that their molecules are linear.

Cyanogen bromide and iodine cyanide in aqueous solutions (and in several other solvents) are non-electrolytes[4], and even if they may behave abnormally in certain solvents, this is probably due to a chemical reaction with the solvent molecules[5]. The bromine and the iodine in cyanogen

[1] West & Farnsworth: Jour. Chem. Phys. **1** (1933) 402.

[2] Badger & Binder: Phys. Rev. **37** (1931) 800.

[3] Badger & Sho-Chow Wo: Jour. Amer. Chem. Soc. **53** (1933) 2572.

[4] Max Møller: Det Kgl. Danske Vid. Selskabs Math.-fysiske Medd. XII, 17. Walden: Z. phys. Chem. **43** (1903) 401.

[5] Audrieth & Birr: Jour. Amer. Chem. Soc. **55** (1933) 672.

bromide and iodine cyanide respectively, therefore, are bound to the carbon atom of the cyanide group with a homopolar bond.

However, in the alkaline hydrolysis of cyanogen bromide and iodine cyanide (and in several other reactions[1]) a great difference in their behaviour is observed. With silver hydroxide, for instance, cyanogen bromide gives silver bromide and silver cyanate, while iodine cyanide gives silver iodide, silver iodate and silver cyanide. This seems to indicate that these halogen cyanides form polar molecules, and while bromine in the cyanogen bromide seems to be the electronegative part of the molecule, iodine in cyanogen iodide seems to be the electropositive part.

As far as it can be seen this, however, may meen nothing more than the pair of shared electrons in cyanogen bromide is pulled fairly close to the bromine atom, while in iodine cyanide they are pulled close to the cyanide group, (or that in cyanogen bromide the probability of their occurance is greater close to the bromine atom than to the cyanide group, and naturally the opposite for iodine cyanide.) The greater ability of iodine cyanide to form complex ions with cations may be due just to this displacement of the electronic bond.

Since the actual salting out coefficient is greater for iodine cyanide than for cyanogen bromide, it might be expected that the dipole momentum of iodine cyanide is smaller than the dipole momentum of cyanogen bromide, but this will be taken up for an experimental investigation in a following paper.

[1] See for instance CHATTAWAY & WADMORE: Jour. Chem. Soc. **81** (1902) 197.

8. Summary.

The molecular weight of iodine cyanide has been determined in water and benzene.

The distribution between water and benzene of iodine cyanide and cyanogen bromide has been investigated and the activities in very dilute aqueous solutions estimated.

The distribution of iodine cyanide and cyanogen bromide between benzene and aqueous solutions of the bromides, the chlorides, the nitrates, the sulphates and the perchlorates (of sodium only) of sodium and potassium has been investigated.

In the case of cyanogen bromide these experiments permit a direct calculation of the salting out effect, as cyanogen bromide does not form complex ions with any of the anions mentioned above, probably with the exception of the bromide ion. But here the complex formation is exceedingly slight and may be disregarded in this connection.

In the case of iodine cyanide the salting out effect is complicated by a simultaneous complex formation, to a different extent, with the bromide, the chloride, the sulphate and the nitrate ion. But no complex formation is observed with the perchlorate ion. By application of this fact, and by means of the salting out effect on cyanogen bromide it has been possible to separate, at least with a certain approximation, the effect due to the complex formation of iodine cyanide with the anion in question and the salting out effect.

The following complexity constants have been estimated:

$$\frac{[ICNBr^-]}{[ICN]\cdot[Br^-]} = 0.65; \quad \frac{[ICNCl^-]}{[ICN]\cdot[Cl^-]} = 0.39; \quad \frac{[ICNNO_3^-]}{[ICN]\cdot[NO_3^-]} = 0.14.$$

Here the brackets indicate the activity of the substances.

Finally the structure of the cyanogen bromide and the iodine cyanide molecules has been discussed.

A part of this work has been made in the Jones Chemical Laboratory of Chicago University, and it is a dear duty to express my thanks to the Head of the Department, Professor, Dr. J. STIEGLITZ, for his interest and the readiness with which all I needed was placed to my disposal.

The other part of this work has been made in the Department of Chemistry for Chemical Engineers of the Royal Polytechnic Institute, Copenhagen. I wish to thank the Head of the Department Professor, Dr. J. A. CHRISTIANSEN for his kind interest.

The author is also much indebted to the Carlsberg Foundation for a grant, which made it possible to continue the investigation.

May 1935.

Færdig fra Trykkeriet den 8. Oktober 1936.