Triethylamine forms an addition compound, aminate, with germanic iodide in which five moles of the former are combined with 1 mole of the iodide.

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The Complex Ions Formed by Iodine Cyanide with Cyanide and Iodide Ions. The Vapor Pressure, Free Energy and Dissociation of Iodine Cyanide

BY DON M. YOST AND WILLIAM E. STONE

Introduction

Former investigations[1] of the equilibria involving iodine cyanide had as their object the determination of the free energy of formation of cyanogen. Since the results led to a negative value for the entropy of this substance, which would be a contradiction of the third law, it was considered of importance to reinvestigate some of the reactions involved.

One of the reversible [2,1] reactions employed was

$$ICN + H^+ + I^- = I_2 + HCN \qquad (1)$$

but the measurements indicated that it was complicated by the formation of the complex ions I_2CN^- and $I(CN)_2^-$. By means of distribution experiments we have determined the stabilities of these ions and estimated their effect on reaction (1).

Another reaction previously studied[3] was the dissociation of solid iodine cyanide into iodine and cyanogen

$$ICN(s) = \tfrac{1}{2}I_2(g) + \tfrac{1}{2}C_2N_2(g) \qquad (2)$$

In this case we have considered it better to redetermine the dissociation with all substances present as gases than to have a solid phase present with its possible catalytic effect on the formation of paracyanogen.

In this paper are presented the results of measurements (1) on the stabilities of the ions $I(CN)_2^-$ and I_2CN^-, (2) on the vapor pressures and solubility of iodine cyanide, and (3) on the dissociation of the latter into iodine and cyanogen. There are also presented the free energy calculations made by combining our results with those of other investigators.

Preparation of the Materials and Experimental Methods

The iodine cyanide was prepared by adding iodine to a moderately concentrated solution of potassium cyanide, and extracting the resulting mixture with ether after

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[1] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, p. 591.

[2] Laura Kovach, *Z. physik. Chem.*, **80**, 107 (1912).

[3] Ref. 1, p. 592.

the iodine color had disappeared. The ether layer was removed, washed several times with water and finally evaporated to dryness. The residue, consisting principally of iodine cyanide, was purified by sublimation at 90–100° in an atmosphere free from water vapor. The resulting material was snow white, consisted of long needle-like crystals, and was, of course, free from the mercury salts that may be present when some other methods of preparation are used.

The iodine cyanide in the solutions was determined by adding a 25.0-cc. sample to 200 cc. of dilute hydrochloric acid containing potassium iodide, and titrating the liberated iodine with standard thiosulfate.

It was found that the distribution ratios of iodine cyanide between aqueous solutions and carbon tetrachloride were easily measurable and that equilibrium was established rapidly.

In the vapor pressure experiments a quantity of the iodine cyanide was caused to sublime into a highly evacuated bulb equipped with an all-glass click gage. The bulb with its contents was kept connected with high vacuum pumps for several hours at room temperature in order to remove any more easily volatile impurities. Finally the bulb was cooled with liquid air, sealed off and attached to the manometer system. Both the bulb and click gage were submerged in an oil-bath equipped with a stirrer, thermoregulator and a Reichsanstalt thermometer graduated in tenths of a degree. Equilibrium was approached from both a lower and a higher temperature.

Results of the Distribution and Solubility Experiments.—In Table I are presented representative results of the distribution experiments in which the water layer contained no added salts. The solubility of solid iodine cyanide in water is given just below the table. All experiments were made at 25°. All concentrations are given in moles per liter of solution.

TABLE I

DISTRIBUTION RATIOS OF IODINE CYANIDE BETWEEN CARBON TETRACHLORIDE AND PURE WATER AT 25°

Concentration of ICN in moles per liter of solution Water layer	 CCl_4 layer	Distribution ratio $\frac{(ICN)\text{ in }CCl_4}{(ICN)\text{ in }H_2O}$
0.02480	0.004460	0.1798
.02596	.004673	.1800
.03312	.006007	.1814
.05144	.009441	.1835
.06697	.01239	.1850
.07173	.01330	.1854
.07960	.01482	.1862

Solubility of ICN in water at 25°, 0.2523 mole/liter.

It is clear from these results that the distribution ratio increases slightly but definitely with increase in concentration. If solutions of iodine cyanide in carbon tetrachloride are assumed to be perfect, and if the activity coefficient of the solute in aqueous solution is taken as unity at infinite dilution, then the activity coefficient of the iodine cyanide in aqueous solution at the concentration C may be calculated, and is given by the empirical formula

$$\gamma = 1 + 0.661\ C \qquad (3)$$

The distribution ratio r_0 at infinite dilution was determined graphically and found to be 0.1771.

The solubility of iodine cyanide in carbon tetrachloride may be calculated from its solubility in water by using equation (3) and the value just given for r_0. The calculated value is 0.0521 mole/liter or 5.02 g./1000 g. of carbon tetrachloride.

In Table II are given the results of the distribution experiments in which the aqueous layer contained potassium cyanide. The concentrations of iodine cyanide in the aqueous phase were obtained by the use of r_0 and equation (3). Corrections were applied for the hydrolysis of potassium cyanide by employing the relation $(HCN)(OH^-)/(CN^-) = 0.77 \times 10^{-5}$ obtained from the free energy values of Lewis and Randall.[4]

TABLE II

DISTRIBUTION OF IODINE CYANIDE BETWEEN CARBON TETRACHLORIDE AND POTASSIUM CYANIDE SOLUTIONS AT 25°

Concentration in moles per liter of solution							
ICN CCl_4 layer	ICN + $I(CN)_2^-$ H_2O layer	ICN H_2O layer	$I(CN)_2^-$	KCN	CN^- + $I(CN)_2^-$	CN^-	K_5
0.01135	0.07482	0.06157	0.01325	0.09796	0.09709	0.08384	2.57
.008011	.06350	.04396	.01954	.1919	.1907	.1712	2.60
.008488	.06611	.04650	.01961	.1959	.1947	.1751	2.41
.005037	.04651	.02792	.01859	.2939	.2924	.2738	2.43
.007018	.06418	.03864	.02554	.2939	.2924	.2669	2.48
.003767	.03878	.02098	.01780	.3639	.3622	.3444	2.46
.002935	.03419	.01639	.01780	.4455	.4436	.4258	2.55
						Mean	2.50

The value of K_5 given in the last column is the equilibrium constant for the reaction

$$ICN + CN^- = I(CN)_2^- \tag{4}$$

where

$$(I(CN)_2^-)/(ICN)(CN^-) = K_5 \tag{5}$$

TABLE III

DISTRIBUTION OF IODINE CYANIDE BETWEEN CARBON TETRACHLORIDE AND POTASSIUM IODIDE SOLUTIONS

Concentration in moles per liter of solution						
ICN CCl_4 layer	ICN + $I(CN)_2^-$ H_2O layer	ICN H_2O layer	I_2CN^-	KI	I^-	K_7
0.01483	0.08866	0.07958	0.00908	0.1000	0.0909	1.26
.01414	.08436	.07601	.00835	.1000	.0916	1.20
.008965	.05688	.04903	.00785	.1500	.1421	1.13
.01107	.07374	.06013	.01361	.2000	.1864	1.21
.01091	.07178	.05926	.01252	.2000	.1875	1.13
.004941	.03564	.02741	.00823	.2500	.2418	1.24
.005192	.03637	.02877	.00760	.2500	.2424	1.09
.004495	.03327	.02497	.00830	.3000	.2917	1.14
.005910	.04341	.03266	.01075	.3000	.2892	1.14
					Mean	1.17

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(4) Ref. 1, pp. 607 and 608.

The experiments in which the aqueous layer consisted of potassium iodide solution were carried out in the same way as those just given. No correction for the hydrolysis of the potassium iodide was necessary in this case. Otherwise the calculations were made as indicated above. The results are presented in Table III.

The values given for K_7 refer to the reaction

$$\mathrm{ICN} + \mathrm{I}^- = \mathrm{I_2CN}^- \tag{6}$$

where

$$(\mathrm{I_2CN}^-)/(\mathrm{ICN})(\mathrm{I}^-) = K_7 \tag{7}$$

The Free Energy of Formation of Solid Iodine Cyanide.—The results given in the above tables may now be used to correct the equilibrium constant, K_1, found by other investigators for the reaction

$$\mathrm{ICN(aq.)} + \mathrm{H}^+ + \mathrm{I}^- = \mathrm{HCN(aq.)} + \mathrm{I_2(aq.)} \tag{1}$$

where

$$(\mathrm{HCN})(\mathrm{I_2})/(\mathrm{ICN})(\mathrm{H}^+)(\mathrm{I}^-) = K_1$$

L. Kovach[2] as well as Lewis and Keyes[5] have studied this reaction which is known to be rapid and reversible. We have chosen to apply our data to the results of the former investigator who found $K_1 = 1.37$, since more dilute solutions were used. When this is done the average value of the constant for reaction (1) at 25° is found to be $K_1 = 1.50$ and $\Delta F^\circ_{298} = -RT \ln K_1 = -240$ cal. From the solubility of iodine cyanide given above, together with the activity coefficient given by equation (3), there results

$$\mathrm{ICN(s)} = \mathrm{ICN(aq.)} \qquad \Delta F^\circ_{298} = 725 \text{ cal.}$$

The following reactions and their free energy changes at 25° may now be written down.

$$\begin{aligned}
\mathrm{ICN(aq.)} + \mathrm{H}^+ + \mathrm{I}^- &= \mathrm{HCN(aq.)} + \mathrm{I_2(aq.)} && \Delta F^\circ = -240 \text{ cal.}\\
\mathrm{ICN(s)} &= \mathrm{ICN\ (aq.)} && \Delta F^\circ = 725 \text{ cal.}\\
\mathrm{I_2(aq.)} &= \mathrm{I_2(s)} && \Delta F^\circ = -3926 \text{ cal.}^1\\
\tfrac{1}{2}\mathrm{H_2(g)} + \tfrac{1}{2}\mathrm{I_2(s)} &= \mathrm{H}^+ + \mathrm{I}^- && \Delta F^\circ = -12{,}361 \text{ cal.}^1\\
\mathrm{HCN(aq.)} &= \mathrm{HCN(g)} && \Delta F^\circ = 1390 \text{ cal.}^1\\
\mathrm{HCN(g)} &= \tfrac{1}{2}\mathrm{H_2(g)} + \mathrm{C(s)} + \tfrac{1}{2}\mathrm{N_2(g)} && \Delta F^\circ = -27{,}600 \text{ cal.}
\end{aligned}$$

Hence

$$\tfrac{1}{2}\mathrm{I_2(s)} + \mathrm{C(s)} + \tfrac{1}{2}\mathrm{N_2(g)} = \mathrm{ICN(s)} \qquad \Delta F^\circ = 42{,}010$$

The value found for the free energy of formation of solid iodine cyanide, 42,010 cal., is in satisfactory agreement with that given by Lewis and Keyes, 42,790 cal.

The free energy of formation of HCN(g) was calculated from its heat of formation,[6] 30,100 cal., and the entropies at 25° of hydrogen, 31.23 cal./deg.,[7] carbon, 1.3 cal./deg.,[1] nitrogen, 45.77 cal./deg.,[8] and hydrogen

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[5] Lewis and Keyes, This Journal, **40**, 472 (1918).

[6] "International Critical Tables," Vol. V, p. 176.

[7] Giauque, This Journal, **52**, 4816 (1930).

[8] Badger, private communication.

cyanide gas, 48.23 cal./deg.[9] The value given, 27,600 cal., is in good agreement with those found by Lewis and Randall (Ref. 1, p. 608), 28,910 cal., and Badger[10] 29,700 cal., from equilibrium measurements. It may therefore be considered that the above free energies do not depend on the application of the third law of thermodynamics.

The Vapor Pressure of Solid Iodine Cyanide.—In Table IV are presented the results of the vapor pressure measurements made on solid iodine cyanide.

TABLE IV

RESULT OF THE VAPOR PRESSURE MEASUREMENTS ON SOLID IODINE CYANIDE

Temp., °C.	25.0	46.15	49.88	51.49	55.42	66.44	70.69	73.34	81.42	100.93
Pressure, mm.	1.2	4.7	5.9	7.1	8.9	18.3	23.6	28.7	43.4	121.7

$$\log_{10} p_{\text{mm.}} = -\frac{13{,}940}{2.3026\ RT} + 10.225$$

The change in heat content attending vaporization is found to be ΔH = 13,940 cal., and the standard free energy change at 25° for the vaporization is $\Delta F^\circ_{298} = 3926$ cal.

By combining this last free energy value with the one in the previous section for the free energy of solid iodine cyanide there results

$$\tfrac{1}{2}\text{I}_2(\text{s}) + \text{C(s)} + \tfrac{1}{4}\text{N}_2(\text{g}) = \text{ICN(g)} \qquad \Delta F^\circ_{298} = 45{,}940$$

This value is probably not subject to an error greater than 1500 cal.

The Dissociation of Gaseous Iodine Cyanide.—A number of experiments were made, starting with pure iodine cyanide, to determine the equilibrium constant for the reaction

$$\text{ICN(g)} = \tfrac{1}{2}\text{I}_2\ (\text{g}) + \tfrac{1}{2}\text{C}_2\text{N}_2(\text{g})$$

but the values found were neither reproducible nor in agreement with those found by Lewis and Keyes.[5] Thus at 150°, $K = (\text{I}_2)^{1/2}(\text{C}_2\text{N}_2)^{1/2}/(\text{ICN})$ varied from 0.0054 to 0.012 and at 220° from 0.0028 to 0.012. Three values at 200° were quite consistent with K = 0.016, but the consistency seems to be accidental since at the neighboring temperature of 180°, such values as 0.0049 and 0.0087 were obtained. Moreover, the variation with temperature was not uniform. The results obtained could not be correlated with the amount of material present nor with the time of heating.

These results indicated that true equilibrium had not been reached and that slow catalyzed reactions were involved. To determine if the reaction were really reversible, mixtures of gaseous iodine and cyanogen were heated at 120 and 165° for several hours in a thermostat. No iodine cyanide whatever could be observed, although if either the above experiments or those of Lewis and Keyes showed only approximately the true equilibrium state a large fraction of the mixture should have reacted. To determine whether iodine cyanide or mercuric iodide (an impurity

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(9) Badger, and Woo, THIS JOURNAL **54**, 3523 (1932).

(10) Badger, *ibid.*, **46**, 2166 (1924).

sometimes present in iodine cyanide) would catalyze the reaction, small amounts were added to the iodine–cyanogen mixtures. No observable combination of iodine and cyanogen resulted. It is concluded, therefore, that the dissociation reaction is not reversible. By this is meant that either only a very small amount of iodine cyanide is formed from cyanogen and iodine or that the rate of formation is extremely slow.

Lewis and Keyes found that the dissociation was quite extensive under certain conditions, and they ascribed this behavior to the formation of paracyanogen. What seems most likely is that the dissociation reaction is slow and very sensitive to catalysts, and that true equilibrium is reached only when all but a very small amount of the iodine cyanide has decomposed. This view is supported by the results of calculations given below in which the third law is invoked.

If, as the experiments indicate, the dissociation proceeds almost to completion, then it may be easily shown by use of known[11] heat data that the entropy of cyanogen is a positive quantity. That is, no contradiction of the third law can be said to have been shown in this case.

Very recently the heat of combustion of cyanogen has been redetermined in this Laboratory by McMorris and Badger. From their value and the heat of combustion of carbon they find the change in heat content accompanying the formation of cyanogen to be

$$2C(s) + N_2(g) = C_2N_2(g) \quad \Delta H = 65{,}930 \text{ cal.}$$

a value not greatly different from that found by Thomsen. Badger (private communication) has also calculated the entropy of cyanogen gas from spectroscopic data and finds $S^{\circ}_{298} = 59.0 \pm 2$ cal./deg. From these values and the entropies of carbon and nitrogen the free energy of formation of cyanogen gas becomes $\Delta F^{\circ}_{298} = 62{,}770$ cal. This value may be in error by as much as but not more than 1800 cal. as a result of the present uncertainty in the value for the entropy and heat of formation of cyanogen. This error would have to be over ten times greater in order to invalidate the conclusions that follow.

When this free energy value for cyanogen is combined with those for gaseous iodine cyanide and iodine the following equation results

$$ICN(g) = \tfrac{1}{2}I_2(g) + \tfrac{1}{2}C_2N_2(g) \qquad \Delta F^{\circ}_{298} = -12{,}240 \text{ cal.}$$

This result, which cannot be in error by more than 2800 cal., shows definitely that gaseous iodine cyanide tends to decompose extensively into iodine and cyanogen at 25°. At higher temperatures the extent of decomposition would be still greater since $\Delta H = -16{,}000$ cal. This conclusion is in agreement with the experimental results.

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(11) The ΔH attending formation of ICN(s) (Ref. 5) from the elements in their standard states at 25° is 42,300. For the formation of ICN(g) we find $\Delta H = 56{,}240$, the heat of vaporization used being that given above. It may be remarked that this value, when combined with the above free energy and the known entropies of iodine gas, 62.29, nitrogen, 45.77 and graphite, 1.3, leads to the value 72.7 cal./deg. for the entropy of iodine cyanide gas at 25° and one atmosphere.

Summary

The distribution of iodine cyanide between carbon tetrachloride and water and aqueous solutions of potassium iodide and cyanide has been determined. From the results the equilibrium constants, $1.17 = (I_2CN_2^-)/(ICN)(I^-)$ and $2.50 = (I(CN)_2^-)/(ICN)(CN^-)$, have been calculated. These values were used to correct the equilibrium constants given by Kovach for the reaction

$$ICN + H^+ + I^- = HCN + I_2$$

Measurements of the vapor pressure of solid iodine cyanide were made and the results were found to be well represented by

$$\log_{10} p_{\text{mm.}} = -\frac{13{,}940}{2.3026\,RT} + 10.225$$

By combining these values with those of others the standard free energy of formation of gaseous iodine cyanide was found to be $\Delta F^\circ_{298} = 45{,}940$ cal.

It was found that gaseous iodine and cyanogen do not react to form appreciable amounts of iodine cyanide. This fact led to the conclusion that the entropy of cyanogen is, in all probability, not negative as has previously appeared to be the case. Calculations based on the third law confirmed the experimentally found result.

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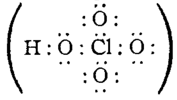
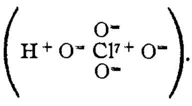
The Formulas of Antimonic Acid and the Antimonates

BY LINUS PAULING

The formula of a compound should not only express its chemical composition, but also give some information concerning the nature of the atomic aggregates present under the ordinary conditions for the substance. Thus the formula KH_2PO_4 indicates that the substance is an acid salt rather than a hydrated normal salt $KPO_3 \cdot H_2O$, etc. It is pointed out in the following pages that from this viewpoint the formulas of oxygen acids of elements in their highest valence states have been correctly assigned in most cases, the principal exception being antimonic acid, the correct formula of which has not previously been suggested; and it is shown that, when the existence of highly polymerized forms of the acids and their salts is recognized, a simple consideration of ionic sizes leads to the assignment of correct formulas on theoretical grounds.

Molecules of the oxygen acids can be represented as containing either covalent bonds  $\left(\mathrm{H}:\underset{\cdot\cdot}{\ddot{\mathrm{O}}}:\overset{:\ddot{\mathrm{O}}:}{\underset{:\underset{\cdot\cdot}{\mathrm{O}}:}{\mathrm{Cl}}}:\underset{\cdot\cdot}{\ddot{\mathrm{O}}}:\right)$ or ionic bonds  $\left(\mathrm{H^+\,O^-}\overset{\mathrm{O^-}}{\underset{\mathrm{O^-}}{\mathrm{Cl^{7+}}}}\mathrm{O^-}\right)$. Actually