is identical with that in water from 0.01 N up to 50% acid. The same values were obtained either by dissolving or precipitating the radium sulfate indicating a true state of solution.

3. The value found is that predicted from comparison with the decreasing solubilities of calcium, strontium and barium sulfates.

4. Excess of sulfuric acid does not have a repressive effect on the solubility of radium sulfate.

5. On increasing the concentration of sulfuric acid above 65%, a marked rise in solubility of radium sulfate takes place, and it is more than 12 times as soluble in 70% as in 65% acid.

6. An explanation is given of the "effective solubility" of radium sulfate (when precipitated together with large excess of barium) which is found to be far below the actual solubility of radium sulfate.

7. The solubility of radium sulfate in sulfuric acid solutions up to 25% acid is about 50% higher at 35° than at 25° and again increases about 50% in the temperature interval 35° to 45°.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

EQUILIBRIA INVOLVING CYANOGEN IODIDE; THE FREE ENERGY OF FORMATION OF CYANOGEN.

BY GILBERT N. LEWIS AND DONALD B. KEYES.

Received December 12, 1917.

While there is doubtless an equilibrium between carbon, nitrogen and cyanogen at the temperature of the electric arc, it has not hitherto been found practicable to determine the free energy of formation of cyanogen through a study of this simple equilibrium. It is, however, possible, when the free energy of formation of hydrocyanic acid is known, to obtain that of cyanogen by the aid of two reversible reactions. The study of the equilibrium in these reactions will form the subject of this paper.

The Dissociation of Cyanogen Iodide.

The two reactions to which we have referred both involve the interesting substance cyanogen iodide (or as it might perhaps better be called, iodine cyanide). This is a white substance which, on moderate heating, decomposes readily according to the reaction

$$2\,CNI = (CN)_2 + I_2.$$

When the substance is heated in a closed tube the dissociation evidently occurs until a definite equilibrium is established, and solid cyanogen iodide remains in the presence of its own vapor, gaseous iodine, and cyanogen. Since the vapor of cyanogen iodide dissociates without change of volume, and since the reaction is evidently too rapid to permit a determination of the equilibrium by a sudden cooling of the vapors, no ordinary means of determining the degree of dissociation is available. Since, however, cyanogen iodide and cyanogen are both colorless, it seemed feasible to determine the concentration of iodine vapor colorimetrically.[1]

For this purpose two similar tubes of quartz, each closed at the ends by polished quartz windows, were employed. These are shown as A and C in Fig. 1, where the tube A is connected by a quartz side tube to the bulb B, containing an excess of solid cyanogen iodide. The side tube leading from C emerges from the air thermostat containing the tubes and leads to the bulb D filled with solid iodine and immersed in a small oil thermostat H. The air thermostat was provided with the necessary stirrer, heater and regulator, not shown in the diagram, and with glass windows, E and F, through which the light from a frosted incandescent lamp could pass through the tubes A and C into the optical parts of a colorimeter placed above the window E.

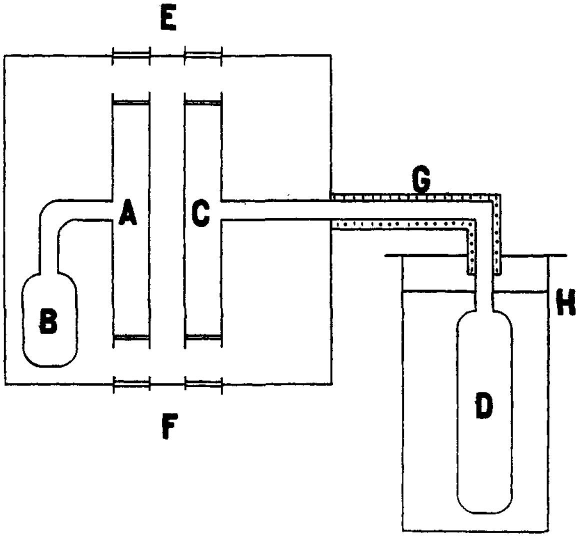

Fig. 1.

When the air thermostat is heated to the desired temperature, the oil thermostat may be kept at a lower temperature such that the intensity of color of the pure iodine in C just matches that of the iodine in the mixed vapor in A. In order to avoid a condensation of the iodine vapor between the two thermostats, this portion of the connecting tube was heated by a coil of wire G. Some trouble was caused at first by the condensation of the solids upon the quartz windows; this was subsequently avoided by the aid of small auxiliary heating coils placed near these windows, and not shown in the figure. These coils were removed shortly before the final equilibrium was established. The tubes containing iodine and cyanogen iodide were completely exhausted of air before the experiments began.

The first experiments were disappointing. When the air thermostat was kept at a constant temperature, in the neighborhood of 100°, the in-

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[1] The apparatus was largely constructed by Dr. R. L. Sebastian, to whom we are also indebted for some preliminary measurements in this reaction and in the one discussed in the following section.

tensity of color in the cyanogen iodide tube increased slowly until, at the end of several hours, equilibrium seemed to be established; but, on further standing, the color once more deepened and continued to do so without apparent limit. This phenomenon we attributed to the removal of cyanogen by the deposition of para-cyanogen upon the walls of the tube. This conversion of cyanogen into para-cyanogen is markedly autocatalytic, but it was found that with the exercise of reasonable precautions, such as keeping the tube free from dust and avoiding all cyanogen iodide at the point where the tube was sealed off after filling, it was possible to reach and maintain equilibrium for an hour or two, before the formation of para-cyanogen set in.

When the dissociation had reached the constant value, the temperature of the oil thermostat was varied until a color match was procured (a slight correction being made for lack of exact equality in the length of the two quartz tubes). Since the partial pressure of iodine is now the same in both tubes it is only necessary to know the vapor pressure of solid iodine at the temperature of the oil bath, in order to find its pressure over the cyanogen iodide; and this vapor pressure of solid iodine can be obtained at once from a plot in which we incorporated the data of Baxter, Hickey and Holmes,[1] and of Ramsay and Young.[2]

Four measurements were made, each with a complete refilling of the apparatus in order to avoid the accumulation of para-cyanogen. The results are given in Table I. The first column shows the temperature of the air bath, and the second gives the values of p, the partial pressure of the iodine expressed in mm. Since one mol of cyanogen is produced for each mol of iodine the two partial pressures are the same, and the product of these two, expressed in atmospheres, $K = p^2/760^2$, is the equilibrium constant for the reaction

$$2\ \mathrm{CNI(s.)} = \mathrm{(CN)_2(g.)} + \mathrm{I_2(g.)}.$$

TABLE I.

t.	p.	K.
90.0	3.42	2.00×10^{-5}
110.0	21.08	7.76×10^{-4}
116.5	33.1	1.91×10^{-3}
123.0	56.7	5.63×10^{-3}

The values of log K plotted against the reciprocal of the absolute temperature fall very nearly upon a straight line which, extrapolated to 25°, gives log $K_{298} = -10.95$. From the slope of this line we may find the heat absorbed in the reaction $\Delta H = 48000$ cals. Berthelot made two determinations of this heat.[3] From the first $\Delta H = 41800$; from the second

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[1] Baxter, Hickey and Holmes, THIS JOURNAL, **29**, 127 (1907).

[2] Ramsay and Young, *J. Chem. Soc.*, **49**, 453 (1886).

[3] Berthelot, *Ann. chim. phys.*, **5**, 433 (1875); **23**, 252 (1881).

$\Delta H = 9100$. Each of these determinations was based upon a large number of separate reactions, and in the absence of any more direct determinations we shall adopt the value calculated from equilibrium measurements, and also therefore the value of log K_{298} given above.

We may now calculate the free energy of the reaction from the equation $\Delta F°_{298} = -1364.9 \log K_{298}$; or, substituting the given value

$$2\text{CNI(s.)} = (\text{CN})_2\text{(g.)} + \text{I}_2\text{(g.)};\ \Delta F°_{298} = 14950. \qquad (1)$$

Equilibrium in the Reaction between Cyanogen Iodide and Hydriodic Acid.

In order to determine the free energy of formation of cyanogen iodide we have investigated a reaction which was shown to be reversible by von Meyer,[1] namely,

$$\text{CNI} + \text{HI} \rightleftarrows \text{HCN} + \text{I}_2.$$

If a mixture of solid cyanogen iodide and iodine is treated with a dilute aqueous solution of hydriodic acid, prepared according to the method of Bray and MacKay,[2] equilibrium is readily established, but there are numerous difficulties in the determination of the composition of the equilibrium mixture. We have attempted to measure the vapor pressure of hydrogen cyanide over the mixture and to determine the concentration of hydrogen ion and iodide ion in solution.

For this purpose the mixture was placed in a bubbler of simple construction so designed as to permit the gas which passes through to remain for some time in contact with the solution, while the pressure throughout the apparatus is kept essentially constant. In order to avoid errors due to oxidation of the hydriodic acid, pure nitrogen, prepared from ammonium nitrite, was passed through the bubbler. This nitrogen was stored over water which was protected from the oxygen of the air by a tube containing moist phosphorus. The measurements were made in a thermostat at 25°. Each experiment lasted from twelve to fifteen hours, about two liters of nitrogen passing through the apparatus. From the bubbler this gas was led through glass wool to catch any spray and thence out of the thermostat into another bubbler containing 0.1 *M* sodium hydroxide to absorb the vapor of hydrogen cyanide. This solution was later slightly acidified and treated with silver nitrate, the silver cyanide being filtered and weighed.

In order to obtain the concentration in the aqueous phase from the partial pressure of the HCN the distribution constant must be known. A rough determination of this constant, which will suffice for our present purpose, was made with the apparatus just described. If P is the pressure in atmospheres and m the concentration in mols per thousand grams of water, $K = P/m = 0.096$. Hence,

$$\text{HCN(aq.)} = \text{HCN(g.)};\ \Delta F°_{298} = 1390. \qquad (2)$$

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[1] Von Meyer, *J. prakt. Chem.*, 36, 292 (1887).

[2] THIS JOURNAL, 32, 1195 (1910).

Returning to the main reaction which we may write in the form $CNI(s.) + H^+ + I^- = HCN(g.) + 2I(s.)$, the results of five equilibrium measurements are given in Table II. The first column gives the molal concentration of the original solution of hydriodic acid, and the second the partial pressure of hydrogen cyanide.

Owing to our ignorance of the amount of cyanogen iodide dissolved as such and of the products of its hydrolysis, the determination of the concentration of H^+ and I^- is far from simple. If we find the concentration of hydrogen cyanide produced in the reaction by dividing its partial pressure by the distribution constant, and if this concentration is subtracted from the original concentration of hydrogen iodide the result should equal the concentration of hydrogen iodide and hydrogen tri-iodide remaining, provided that no other reaction occurs except the one under consideration. If the concentration so obtained is multiplied by the degree of dissociation[1] we obtain the concentration of H^+ given in Col. 3.

TABLE II.

HI(orig.).	P(HCN).	H^+	I^-.	K.
0.0296	0.00115	0.0161	0.0065	11.0
0.1038	0.00605	0.0361	0.0144	11.6
0.1020	0.00675	0.0285	0.0118	20.2
0.0677	0.00360	0.0268	0.0100	13.4
0.0764	0.00471	0.0246	0.0106	18.0

If we could be sure that no anions were present in solution except I^- and I_3^-, the concentration of I^- could readily be determined from that of H^+ by means of data at hand on the equilibrium between iodine, iodide, and tri-iodide. This seemed, however, an unsafe assumption, and numerous methods were considered, all of which failed owing, we believe, to the peculiar reactivity of the dissolved cyanogen iodide. Finally, after the first two experiments were completed, a method was devised which seemed capable of giving definite information as to the composition of the solution.

The reaction vessel was reconstructed so that after attainment of equilibrium the solution could be forced, without change of composition or temperature, into an electrode vessel of the pipet type containing a platinum electrode. This, stationed in a thermostat at 25°, could be connected to other electrode vessels of the same type containing solid iodine and hydrogen iodide of several known concentrations. In this way it was possible to find a definite concentration of hydrogen iodide in the second half-cell such that the e. m. f. of the combination became zero. Since both solutions are saturated with solid iodine this would mean, if no other substance besides hydrogen iodide and hydrogen tri-iodide were present, an identity

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[1] If we assume the corrected degree of dissociation in the mixture of hydrogen iodide and hydrogen tri-iodide to be the same as that of hydrogen chloride we may take for the degree of dissociation 0.91 in the first experiment, 0.88 in the second, and 0.89 in the remainder.

of the two solutions. As a matter of fact, however, the concentration of acid in the comparison electrode proved to be less in each case than that which was calculated by the above method for the concentration of acid left in the equilibrium chamber, being 81.3% of the latter in the third experiment, 72.5% in the fourth, and 84.7% in the fifth, average 79.5%. Since the e. m. f. depends only upon the concentration of I^-, we are unable to explain the difference, except upon the assumption that cyanogen iodide, like iodine, forms a complex ion with I^-, thus diminishing the concentration of the latter. We shall assume therefore that in the first two experiments where the direct measurements were not made the sum of the concentrations of I^- and I_3^- is smaller than the concentration of H^+ in the ratio just given for the last three experiments namely 0.795. Of this concentration about half is due to I^- and one-half to I_3^-. According to the measurements of Bray and MacKay[1] the ratio of iodide to tri-iodide is 1.03 at the highest of our concentrations at 1.05 at the lowest. Using these data we obtain the concentration I^- given in Col. 4 of Table II.

The equilibrium constant as determined by our equation is equal to the pressure of hydrogen cyanide divided by the product of the concentrations of H^+ and I^-, $K = [\mathrm{HCN}]/(\mathrm{H}^+)(\mathrm{I}^-)$. The values of K so calculated are given in the last column of Table II. The last experiment can be given little weight owing to the fact that in this case only about one-third as much nitrogen was passed through the bubbler as in the other cases, and the determination of the presence of hydrogen cyanide is therefore uncertain.

Unquestionably the interesting reactions involved in this equilibrium are worthy of a far more careful investigation than we have been able to make at the present time, but the results are adequate for our present purpose and we shall take as a sort of a weighted mean $K = 13$. Hence we find,

$$\mathrm{CNI(s.)} + \mathrm{H}^+ + \mathrm{I}^- = \mathrm{HCN(g.)} + 2\mathrm{I(s.)};\ \Delta F^\circ_{298} = -1520. \quad (3)$$

Combining this with Equation 2 gives

$$\mathrm{CNI(s.)} + \mathrm{H}^+ + \mathrm{I}^- = \mathrm{HCN(aq.)} + 2\mathrm{I(s.)};\ \Delta F^\circ_{298} = -2910. \quad (4)$$

We may combine with this equation the following:

$$\mathrm{HCN(aq.)} = {}^1/_2\mathrm{H}_2 + \mathrm{C}_G + {}^1/_2\mathrm{N}_2;\quad \Delta F^\circ_{298} = -23421,^2$$
$$\mathrm{I(s.)} = \mathrm{I}^- + \oplus;\quad \Delta F^\circ_{298} = -12304,^3$$
$${}^1/_2\mathrm{H}_2 + \oplus = \mathrm{H}^+;\quad \Delta F^\circ_{298} = 0.^4$$

Whence,

$$\mathrm{C}_G + {}^1/_2\mathrm{N}_2 + \mathrm{I\ (s.)} = \mathrm{CNI(s.)};\ \Delta F^\circ_{298} = 38635. \quad (5)$$

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[1] Bray and MacKay, THIS JOURNAL, **32**, 914 (1910).

[2] Lewis and Brighton, *Ibid.*, **40**, 482 (1918).

[3] Lewis and Randall, *Ibid.*, **36**, 2259 (1914).

[4] Lewis and Randall, *Ibid.*, **36**, 1969 (1914).

If we combine Equations 1 and 5 of this paper with the equation for the free energy of iodine vapor,[1]

$$2I(s.) = I_2(g.);\ \Delta F^\circ_{298} = -4640$$

we obtain finally the free energy of formation of cyanogen gas,

$$2C_G + N_2 = (CN)_2(g.);\ \Delta F^\circ_{298} = 87580. \qquad (6)$$

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI.]

REACTIONS IN NON-AQUEOUS SOLVENTS. II. THE ACTION OF CHROMYL CHLORIDE UPON PHOSPHORUS HALIDES.

BY HARRY SHIPLEY FRY AND JOSEPH L. DONNELLY.

Received December 18, 1917.

In the first paper of this series[2] it was shown that the dangerously explosive interaction between chromyl chloride and the phosphorus trihalides could be controlled and studied quantitatively by conducting the reactions in anhydrous carbon tetrachloride solutions. Equimolar solutions of chromyl chloride and phosphorus trichloride and tribromide were found to interact in the ratio of two volumes of the former to three volumes of the latter, *i. e.*, $2CrO_2Cl_2 : 3PX_3 (X = Cl \text{ or } Br)$, yielding new compounds of the formulas $CrOCl.POX_3$ according to the general equation

$$2CrO_2Cl_2 + 3PX_3 \longrightarrow 2CrOCl.POX_3 + PX_3Cl_2.$$

The determination of these ratios by volumetric methods was rendered possible through the use of acetyl bromide as an indicator for the detection of minute traces of chromyl chloride, the end point of the reaction depending upon the formation of the unstable but intensely colored (violet-red) chromyl bromide.[3]

This paper presents briefly the results of a further quantitative study of the action of chromyl chloride upon the following phosphorus halides: (A) Triiodide, (B) Pentachloride, (C) Pentabromide, and (D) Diiodide.

A. Interaction of Chromyl Chloride and Phosphorus Triiodide.

A volumetric study of the interaction of 0.2 *M* solutions of chromyl chloride and phosphorus triiodide in anhydrous carbon tetrachloride using acetyl bromide as an indicator (method described in Part I, Section A, *loc. cit.*) could not be effected because the slightly violet-red color of the phosphorus triiodide solution, due to inevitable traces of free iodine, invariably obscured the end point of the reaction. However, equimolar (0.2 *M*) solutions of chromyl chloride and phosphorus triiodide interacted exothermally, and instantaneously, yielding a voluminous dark brown precipitate, which, after being filtered, and repeatedly washed with carbon tetrachloride

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[1] Lewis and Randall, THIS JOURNAL, 36, 2259 (1914).

[2] Fry and Donnelly, *Ibid.*, 38, 1923 (1916).

[3] Fry, *Ibid.*, 33, 697 (1911).