securely stoppered and shaken, thus bringing the samples into contact with the aqueous solution. In this manner the liberated iodine, as well as the remainder of the halogen in the compound, was converted into sodium halides. Boiling the solution with dilute nitric acid, and the subsequent addition of an excess of silver nitrate solution precipitated all of the halogen in the compound as mixed silver chloride and iodide. The results of the determinations check the theoretical factor, noted above, and confirm the formula $(CrO_2Cl_2)_2.P_2I_4$.

Compound (g.).	AgCl.AgI (g.).	Factor, found.	Factor, theory.
0.1872	0.3468	1.715	1.719
0.1169	0.2004	1.714	. . .

Summary.

The extended study of the interaction of chromyl chloride and phosphorus halides in anhydrous carbon tetrachloride solutions reveals the following facts:

1. While the interaction between chromyl chloride and phosphorus trichloride, or tribromide, is an *oxidation-reduction reaction* conforming to the equation

$$2CrO_2Cl_2 + 3PX_3 \longrightarrow 2CrOCl.POX_3 + PX_3Cl_2 (X = Cl \text{ or } Br),$$

the interaction with phosphorus triiodide unexpectedly gave an *addition compound* of the formula $CrO_2Cl_2.PI_3$.

2. The interaction with phosphorus pentachloride likewise resulted in the formation of an addition compound, $CrO_2Cl_2.PCl_5$.

3. The interaction with phosphorus pentabromide gave no definite compound but, presumably, a mixture of compounds, $CrOCl.POBr_3$ and $CrO_2Cl_2.PBr_5$.

4. The interaction with phosphorus diiodide gave a compound corresponding in composition to the formula $(CrO_2Cl_2)_2.P_2I_4$, or, more briefly, $CrO_2Cl_2.PI_2$. This substance is similar in composition and properties to the compound $CrO_2Cl_2.PI_3$ noted in (1).

5. None of these compounds has been prepared before. Their constitution is unknown, and they do not lend themselves to classification according to the Werner coördination formulas.

CINCINNATI, O.

THE OXIDIZING POWER OF CYANATES AND THE FREE ENERGY OF FORMATION OF CYANIDES.

BY GILBERT N. LEWIS AND THOMAS B. BRIGHTON.

In attacking the difficult problem of free energy changes in organic reactions it has seemed at the outset necessary to determine the free energy of formation, through reversible synthesis from the elements of several

fundamental organic substances. Two such substances, urea and formic acid, have already been reversibly synthesized.[1]

Hydrocyanic acid, which enters into so many different types of reactions, is an especially important point of departure for organic preparations. Since its reversible formation from the elements is known to occur at very high temperatures, it would seem that a study of this reaction would lead most directly to a knowledge of its free energy of formation. Indeed von Wartenberg[2] has determined the amount of hydrogen cyanide obtained by passing a mixture of hydrogen and nitrogen past a rod of carbon kept at 1908° to 2148° A., but the difficulty of measuring these high temperatures, the fact that the yield of hydrogen cyanide depended upon the rate of flow, and the possibility of a reversal of the reaction before the gas was cooled, make it uncertain whether the yield which he obtained represented true equilibrium.

By an extremely indirect method, but nevertheless through a series of reactions, each of which lends itself to an exact study of equilibrium at moderate temperatures, we have obtained data from which the free energy of formation of hydrocyanic acid may be calculated. From the equilibrium between KCNO, CO, KCN and CO_2, which will be discussed in the following section, and from experiments which will also be described in this paper permitting the calculation of the free energy of solution of potassium cyanate and potassium cyanide, we calculate the equilibrium in the reaction

$$CNO^- + CO(g.) = CN^- + CO_2(g.).$$
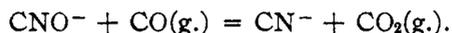
The free energy of formation of CNO^- being known from the work of Lewis and Burrows, and that of CO and CO_2 from the calculations of Lewis and Randall on the free energy of the carbon compounds,[3] the free energy of formation of cyanide ion follows directly. From this the free energy of formation of hydrogen cyanide may be immediately obtained since its dissociation constant is known.

The Equilibrium between KCNO, KCN, CO and CO_2.

It is known that fused cyanide is readily oxidized by the air to cyanate. It seemed likely therefore that, by the use of a milder oxidizing agent, a reaction leading to a definite equilibrium would occur. Eiloart[4] found that fused cyanide was oxidized by carbon dioxide, and a few experiments sufficed to show us that fused cyanate is in part reduced by carbon monoxide.[5]

[1] Lewis and Burrows, THIS JOURNAL, **34**, 1515 (1912); Branch, *Ibid.*, **37**, 2316 (1916).

[2] Von Wartenberg, *Z. anorg. Chem.*, **52**, 299 (1907).

[3] Lewis and Randall, THIS JOURNAL, **37**, 458 (1915).

[4] Eiloart, *Chem. News*, **54**, 88 (1886).

[5] The preliminary study of the reversibility of this reaction was made in this laboratory by Dr. H. Ehrenberg.

Before proceeding to the study of the equilibrium in this reaction it was decided, for the sake of convenience in the later calculations, to use a fused mixture of potassium cyanide and potassium cyanate of the same composition as that which is in equilibrium with the two solid salts at their eutectic point. The composition of this eutectic mixture was found by mixing the salts in trial proportions. Eleven of these mixtures were made up, 100% KCNO, 90% KCNO, ..., 10% KCNO, 100% KCN, by weight. The salts were first fused to secure thorough mixing and then, after cooling, were put into a fused nitrate bath which was heated and allowed to cool until the least fusible mixtures were eliminated. It was soon found that the eutectic mixture would contain between 10% and 20% KCN; more tubes were then prepared containing 11, 12, 13, ..., 20% KCN. The three most easily fusible contained 14, 15 and 16% KCN. Then a small Dewar tube made of Jena glass was used, and carefully weighed mixtures containing 14, 15 and 16% KCN were fused. Each was allowed to cool very slowly, and when partly solidified the liquid was drawn through a plug of glass wool into a small tube. This liquid was then allowed to solidify, weighed, and analyzed for potassium cyanide by titrating with standard silver nitrate solution. The sample from the 14% mixture contained 14.58% KCN, from the 15% mixture in two experiments 14.55% and 14.71%, from the 16% mixture 14.61% and 14.63%. The eutectic mixture contains, therefore, 14.6% KCN and this mixture was used in all the following work. The eutectic temperature was found to be 282° C.[1]

The experiments about to be described were made in the apparatus[2] shown in Fig. 1. The air thermostat was composed of a 9-inch iron pipe, wrapped with nichrome wire for heating, and enclosed in alundun cement.
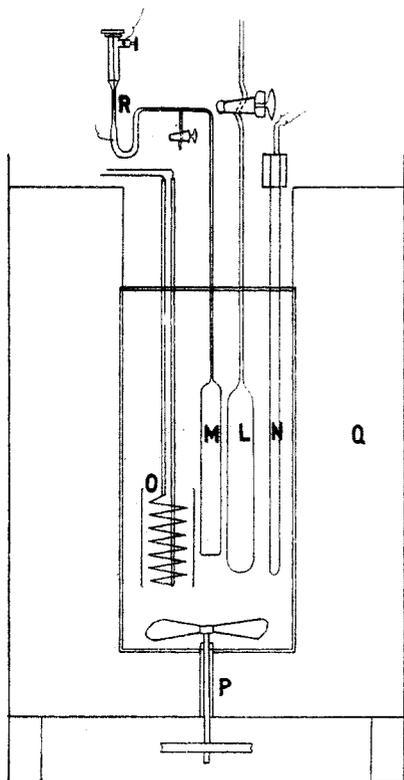
Fig. 1.

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[1] It seemed highly improbable that KCN and KCNO would form solid solutions, and there was nothing in the experiments described above which would indicate the existence of such solutions.

[2] This apparatus was in part designed by Professor Randall for another purpose.

It was further insulated by a 6-inch layer of magnesia asbestos mixture, Q, this packing being held in place by a galvanized iron casing. Through the bottom of the bath, which was made of soapstone, ran a shaft, P, leading to a fan of monel metal, with a bearing of graphite. The top of the bath was made of two pieces of transite board cut to fit the glass tubes leading to the reaction vessel, and covered with six inches of loose asbestos.

Through this top was also led a silver tube connected to a silver bulb, M, which, operating as an air thermometer, communicated with the temperature regulator R. It operated an auxiliary heater, O, of nichrome wire within the bath. This heater was surrounded by a shield of monel metal to protect the regulator and reaction vessel from direct radiation. Owing to the fact that the equilibrium under consideration changes only slightly with the temperature, it was sufficient to keep the temperature constant within two or three degrees. The temperature was read by means of a resistance thermometer, N.

The reaction vessel L was a bulb of Jena glass 7 inches long and 1.5 inches in diameter. A small Jena glass tube led from this bulb out of the bath. In order to diminish the volume of gas of unknown temperature this tube was nearly filled by a rod of quartz. Outside the bath the Jena glass tube was connected by means of de Khotinski cement to ordinary glass tubing leading to the vacuum pump, the carbon dioxide supply, and the analytical apparatus.

The cyanide and cyanate used contained only a small trace of carbonate and were free from any appreciable amount of any other impurity except water. Since both substances react with water at high temperatures, they were dried as far as possible in a vacuum desiccator and then were brought into the reaction vessel with as little exposure to the air as possible. The vessel was then exhausted and heated very gradually while attached to the pump. After several hours' heating *in vacuo* dry carbon dioxide was allowed to enter at atmospheric pressure and to remain until equilibrium was established.

It was found possible to introduce the salts in such quantities as to give just the eutectic composition as shown by analysis. Potassium cyanide may be readily determined in the presence of cyanate by titrating with silver nitrate and a few drops of iodide solution as indicator, but the determination of cyanate is attended with greater difficulties. We first attempted to analyze for cyanate by acidifying and converting to ammonium ion according to the reaction

$$CNO^- + H_2O + 2H^+ = CO_2 + NH_4^+.$$

However, when acid is added to a cyanate solution, a gas of pungent odor escapes with the carbon dioxide. Even when the cyanate was placed in one arm of an H tube and dilute acid in the other, and the tube sealed, shaken and kept at 100° for an hour, the results obtained, either by de-

termining the ammonia produced, or the amount of acid neutralized, did not correspond to more than 92% of the cyanate used.

Satisfactory results were finally obtained by treating with an excess of silver nitrate of known concentration, diluting to a known volume, filtering off an aliquot portion from the silver cyanate and titrating the excess silver nitrate with potassium thiocyanate. The silver cyanate is sufficiently insoluble in the presence of an excess of silver ion to prevent appreciable error. Error will be caused, however, if the solution of cyanate is allowed to stand long enough for decomposition according to the reaction $CNO^- + 2H_2O = HCO_3^- + NH_3$. When cyanide is also present it must first be determined separately.

Since in the reaction one mol of carbon monoxide is formed from one mol of carbon dioxide, small portions of the gas in the reaction chamber could be withdrawn for analysis from time to time without disturbing the equilibrium. The gas to be analyzed was transferred by a mercury pump to the measuring pipet, brought to known concentration, and the pressure measured. The gas was then pumped through a concentrated solution and then over moist sticks of potassium hydroxide. After sufficient time for the complete absorption of carbon dioxide, the gas was pumped back over phosphorus pentoxide into the measuring pipet where, at the original volume, its pressure was again measured. In the first experiments this process was repeated in order to ensure the complete absorption of carbon dioxide. In a number of cases the residual gas was exploded with air and, by absorption of the resulting carbon dioxide, was shown to be pure carbon monoxide. In no case was there found a measurable amount of any other gas.

The attainment of equilibrium required less than two days at 550° C., from four to six days at 500°, and in the three determinations at 450° equilibrium appeared to be established in about a month; but a comparison of the results with those at the two higher temperatures seemed to indicate that even in that period equilibrium was not fully established. At 500°, however, there can be no question that true equilibrium was established, since it was approached several times from higher as well as from lower temperatures with identical results. Table I gives the absolute tem-

TABLE I.

T.	K.	T.	K.
721	(1.86)	781	1.99
724	(1.92)	816	2.22
770	1.98	823	2.28
774	1.98	840	2.35
776	1.97	840	2.29
778	2.03	841	2.26
778	2.03	846	2.46
780	2.06	847	2.33

peratures of the measurements and the ratio of the partial pressures of the two gases, $K = [CO_2]/[CO]$, at each temperature.

Nothing is known as to the specific heats of the two fused salts, but we can make no great error in assuming that the change in heat capacity in our reaction is negligible. If so, the heat of reaction is constant and log K will be a linear function of $1/T$. We have plotted these two quantities against one another and have drawn the best straight line through the individual points. From this line produced we find at the eutectic point, $555° A$, $K_{555} = 0.89$. From the slope of the line we find for the reaction involving the fused salts $\Delta H = 3130$ cal., which is not very different from the value $\Delta H = 4300$, obtained from the data of Thomsen and Berthelot for the corresponding reaction involving the solid salts at room temperature.

Since all the measurements were made with a mixture having the same composition as the eutectic mixture, the ratio of the pressures of the two gases over the solid salts at the eutectic temperature will be the same, namely, $K = 0.89$. Hence for the reaction

$$KCNO(s.) + CO(g.) = KCN(s.) + CO_2(g.); \Delta F^{\circ '}_{555} = - R'T \ln K = 126.$$

The specific heats of the two solids are not known, but if we apply Kopp's law we see that the heat capacity of the cyanate will be greater than that of the cyanide by about as much as that of carbon dioxide is greater than carbon monoxide. Hence we may write $\Delta \Gamma = 0$. We have seen that $\Delta H = 4300$, and in the equation $\Delta F = \Delta H_0 + IT$, substituting the above value of ΔF, we find $I = -7.52$, and finally

$$KCNO(s.) + CO(g.) = KCN(s.) + CO_2(g.); \Delta F^{\circ}_{298} = 2060. \quad (1)$$
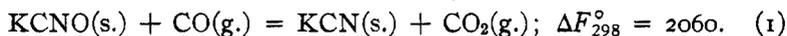
The Free Energy of Solution of Potassium Cyanide and Cyanate.

The determination of the difference in free energy between a very soluble solid salt and its ions at hypothetical molal concentration in aqueous solution has rarely been made. Fortunately at the time this work was being carried on a general study of the free energy of solution was being carried on in this laboratory by Dr. W. H. Rodebush, and in collaboration with him data were obtained from which the free energy of solution of potassium cyanide and cyanate may be calculated. The chief data required are the freezing points determined over the widest possible range of temperature. For the two salts in question the freezing points of their aqueous solutions were obtained down to the cryohydric points which were found to be $-29.61°$ for potassium cyanide and $-18.14°$ for potassium cyanate. The results are given in Tables II and III, the first column showing the number of grams of salt per 1000 g. of water, and the second the freezing point.

The solubilities at $25°$ were also determined and found to be 716 g. potassium cyanide per 1000 g. of water and 750 g. potassium cyanate per 1000 g. of water. The latter quantity was a little difficult to obtain on account of the rapid decomposition of the solution, but reproducible results were ob-

tained by violent shaking in the thermostat for a short time, and four determinations differed from the mean by only 0.3%.

TABLE II.—KCN.		TABLE III.—KCNO.	
460.1	—24.83°	320	—17.40°
408.1	—21.93	270	—13.58
359.3	—18.99	264	—13.00
309.2	—16.18	212.5	— 9.94
266.5	—14.36	141.8	— 6.29
251.0	—13.37	98.4	— 4.18
209.0	—10.88		
113.1	— 5.64		

The utilization of these data, together with familiar thermodynamic equations, for the calculation of the free energy of solution of the two salts will be fully discussed in the paper by Dr. Rodebush and need not be discussed in detail here.   As a result of these calculations we find for the dilution of the saturated solution to the point where the ions are at hypothetical molal concentration, or, in other words, in passing from solid salt to the ions of hypothetical molal concentration,

$$KCN(s.) = K^+ + CN^-; \quad \Delta F^o_{298} = -2130 \qquad (2)$$

$$KCNO(s.) = K^+ + CNO^-; \quad \Delta F^o_{298} = -1440 \qquad (3)$$
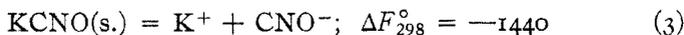
The Free Energy of Formation of Cyanide Ion and of Aqueous Hydrocyanic Acid.

If we combine Equations 1, 2 and 3 we find

$$CNO^- + CO(g.) = CN^- + CO_2(g.); \quad \Delta F^o_{298} = 1370. \qquad (4)$$

Of these four substances the free energy of the first, second and fourth are known from existing data.   Thus for cyanate ion we may combine the following six equations:

$CO(NH_2)_2(M) = NH_4^+ + CNO^-$	$\Delta F^o_{298} =$	2766[1]
$CO_2 + 2NH_3 = CO(NH_2)_2(M) + H_2O(l)$	$\Delta F^o_{298} =$	-3334[1]
$C_G + O_2 = CO_2$	$\Delta F^o_{298} =$	-94360[2]
$N_2 + 3H_2 = 2NH_3$	$\Delta F^o_{298} =$	-9480[3]
$NH_4^+ + \ominus = 2H_2 + \frac{1}{2} N_2$	$\Delta F^o_{298} =$	19895[3]
$H_2O(l) = H_2 + \frac{1}{2} O_2$	$\Delta F^o_{298} =$	56620[4]

Whence by addition,

$$C_G + \frac{1}{2}N_2 + \frac{1}{2}O_2 + \ominus = CNO^-; \quad \Delta F^o_{298} = -27893. \qquad (5)$$
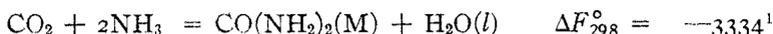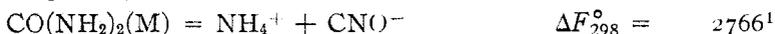
From the paper by Lewis and Randall on "The Free Energy of Carbon Compounds" we have

$$CO + \frac{1}{2}O_2 = CO_2; \quad \Delta F^o_{298} = -61800.$$
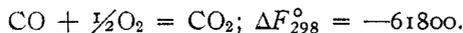
[1] Lewis and Burrows, THIS JOURNAL, **34**, 1515 (1912).
[2] Lewis and Randall, *Ibid.*, **37**, 458 (1915).
[3] Lewis and Adams, *Ibid.*, **37**, 1983 (1915).
[4] Lewis and Randall, *Ibid.*, **36**, 1969 (1914).

Combining this equation with (4) and (5) we find the free energy of formation of cyanide ion,

$$C_G + \tfrac{1}{2}N_2 + \ominus = CN^-; \quad \Delta F^\circ_{298} = 35277. \tag{6}$$
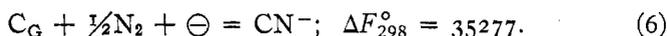
Since we take the free energy of formation of hydrogen ion as zero, this equation also gives the free energy of formation of hydrocyanic acid in a solution molal with respect to each ion, namely,

$$\tfrac{1}{2}H_2 + C_G + \tfrac{1}{2}N_2 = H^+ + CN^-; \quad \Delta F^\circ_{298} = 35277.$$
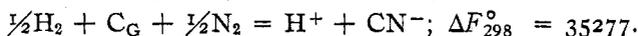
In order to determine the free energy of undissociated hydrocyanic acid we may use the results of Walker and Cormack[1] who found from conductance measurements that the dissociation constant at $18°$ is 13.2×10^{-10}. For the heat of dissociation von Steinwehr[2] found 11100 cal. and Thomsen[3] 10930. Taking 11000 as the best value we find by means of the van't Hoff equation $K_{298} = 2.06 \times 10^{-9}$. Hence

$$HCN(aq.) = H^+ + CN^-; \quad \Delta F^\circ_{298} = 11856. \tag{7}$$

Finally, combining Equations 6 and 7, we have
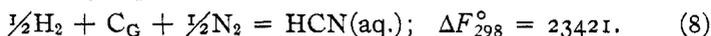
$$\tfrac{1}{2}H_2 + C_G + \tfrac{1}{2}N_2 = HCN(aq.); \quad \Delta F^\circ_{298} = 23421. \tag{8}$$

BERKELEY, CAL.

THE SPECIFIC HEATS AT LOW TEMPERATURES OF SODIUM, POTASSIUM, MAGNESIUM AND CALCIUM METALS, AND OF LEAD SULFIDE.

BY E. D. EASTMAN AND W. H. RODEBUSH.

The empirical law of Dulong and Petit, in its original form, states that the heat capacity per gram atom of all the solid elements, excluding those of very low atomic weight, is the same and equal to 6.4 calories per degree. This is the average value of C_p, the atomic heat at constant pressure. Lewis[4] has shown that if C_v, the atomic heat at constant volume, be considered, not only are the deviations from the average considerably smaller, but that the new value 5.9 calories per degree is identical with that calculated on the basis of the theory of equipartition. According to this principle the change of kinetic energy with the temperature is $3R/2$ per gram atom for any substance whose individual atoms are able to move in every direction. The usual assumption that the atoms of a solid element are in harmonic oscillation about more or less fixed positions requires that they possess potential as well as kinetic energy, and that the time averages of the two be equal. This would give as the atomic heat $3R$ or 5.97 calories

[1] Walker and Cormack, *J. Chem. Soc.*, **77**, 16 (1900).

[2] Von Steinwehr, *Z. physik. Chem.*, **38**, 198 (1901).

[3] Thomsen, "Thermochemistry," **1908**, p. 252.

[4] Lewis, THIS JOURNAL, **29**, 1165 (1907); *Z. anorg. Chem.*, **55**, 200 (1907).