The Cyanogen Halides. Part III. Their Heats of Formation and Free Energies.*

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The heats of formation of the cyanogen halides have been determined by measuring the sum of the heats of alkaline hydrolysis of cyanogen and of the cyanogen halides, and the heat of reaction of iodine with an alkali cyanide. The values for cyanogen chloride, bromide, and iodide in their standard and gaseous states at 25°, the heat of sublimation of the bromide (found from the redetermined vapour-pressures), and the free energies in the gas phase at 25° (from the recalculated entropies) are reported. The dissociations to molecules, atoms, and ions are discussed.

The heats of formation and free energies of the cyanogen halides are required, first to confirm that cyanogen bromide and iodide are really as metastable with respect to cyanogen and the halogens as the old data imply, especially in view of the ready equilibration of the nitrosyl and interhalogen halides; secondly, to see whether the free energy of cyanogen bromide is the mean of those for the chloride and iodide as assumed in Part I *; thirdly, for the determination of the heats of formation of the double halides described in Part II.* By comparing these heats with those of the corresponding ionic nitrosyl compounds it is hoped to draw some conclusions about the bonding in the cyanogen complexes.

Since all previous data depend to some extent on Berthelot's values (*Ann. Chim. Phys.*, 1875, **5**, 455), these have been redetermined where necessary. The heats of the alkaline hydrolyses, $CNX + 2NaOH = NaCNO + NaX + H_2O$ ($X = Cl$, Br, or I) have been measured, and the stoicheiometry of this reaction has been established for cyanogen bromide and iodide, where there had been some doubt (Migrdichian, " Organic Cyanogen Compounds," Reinhold Publ. Corp., N.Y., 1947, p. 101; Williams, " Cyanogen Compounds," Arnold and Co., London, 1948, p. 9).

There is a possibility of considerable error in the heat of formation of sodium cyanate found by Lemoult (*Ann. Chim. Phys.*, 1899, **16**, 338) from the heat change on acid hydrolysis, because of the difficulty of complete retention, or expulsion, of carbon dioxide from the hydrolysate. An alternative procedure, in which the recently determined heat of formation of cyanogen (Knowlten and Prosen, *J. Res. Nat. Bur. Stand.*, 1951, **46**, 489) is used, involves the heats of the reactions $NaCN + I_2 = NaI + ICN$, $ICN + 2NaOH = NaCNO + NaI + H_2O$ and $C_2N_2 + 2NaOH = NaCNO + NaCN + H_2O$. Their sum enables the heat of formation of sodium cyanate to be determined. A value for sodium cyanide can also be derived.

To obtain the heats of formation of cyanogen bromide and iodide in the gas phase, the respective heats of sublimation are required. Two values have been recorded for the latter and are given equal weight (Yost and Stone, *J. Amer. Chem. Soc.*, 1933, **55**, 1889; Ketelaar and Kruyer, *Rec. Trav. chim.*, 1943, **62**, 550). Only one value for cyanogen bromide is available (Baxter, Bezzenberger, and Wilson, *J. Amer. Chem. Soc.*, 1920, **42**, 1368) so the vapour pressure has been redetermined. The entropies of the cyanogen halides, calculated by Stevenson (*J. Chem. Phys.*, 1939, **7**, 171), have been redetermined in view of the accurate bond-length data now available, as well as the small changes in fundamental constants.

Experimental

The calorimeter was similar to that described previously (Woolf, *J.*, 1951, 231). In the electrical calibration, the heater resistance was determined on a standardized Wheatstone bridge, and the applied e.m.f. on a vernier potentiometer. All measurements, with the inclusion of chemical analysis, were made to within 0·2%. Care was taken to bring the calorimeter and contents to temperature equilibrium before and after heat changes. The cyanogen halides were prepared, and purified shortly before use, by the methods described in Part I (*loc. cit.*).

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* Part I, *J.*, 1953, 4121; Part II, *J.*, 1954, 252.

Heat of Hydrolysis of Cyanogen Halides.—(i) *Chloride.* An evacuated glass bulb (250 ml.) fitted radially with two taps was filled with cyanogen chloride almost to atmospheric pressure at room temperature (18—20°). The amount of gas was found by direct weighing. One side was connected to a mercury reservoir, the other to an inlet tube terminated by a sintered disc (2·5 cm. diam., no. 2 porosity) and immersed just below the stirrer in 500 ml. of 0·5N-sodium hydroxide. After equilibration at 25° both taps were opened, and the gas was forced into the alkali by raising the mercury reservoir. The gas was expelled within 1½ min. and the heat rise was completed within 2 min. Calibration was effected after the heat rise due to stirring was again uniform. The solution which remained was analysed for chloride, since only about 98% of the gas was hydrolysed under the above conditions. This was not due to the rate of hydrolysis (Eden and Wheatland, *J. Soc. Chem. Ind.*, 1950, **69**, 166) or to the non-stoicheiometry of the reaction (Douglas and Winkler, *Canad. J. Res.*, 1947, **25**, *B*, 381) but to the failure to absorb gas at the high rate of flow employed. A finer sinter, or slower rate, would have ensured more complete absorption.

(ii) *Bromide.* Powdered cyanogen bromide, obtained by distillation *in vacuo* to liquid-air temperature, was placed in a weighed, thin-ended tube, the other end of which was ground flat and closed with a cover-slip and picein wax. After a reweighing, the tube was immersed in 500 ml. of N-sodium hydroxide and pierced with a pointed rod when a steady state had been attained.

The stoicheiometry was checked in separate experiments by estimation of cyanate and bromide formed. The absence of cyanide, bromate, and hypobromite was shown by qualitative tests. This confirms Moeller's results (*Kgl. Danske Videnskab. Selsk.*, 1934, **12**, 17).

(iii) *Iodide.* The iodide, which could not be powdered, was weighed into a glass tube whose ends were closed with rubber bungs. This was held at 25° in the thermostat before the bungs were removed and the rest dropped into the alkali. The iodide adhering to the bungs was estimated by titration of the iodide formed with standard iodate (Andrews's method). In these reactions the maximum temperature was obtained after about 20 min., compared with about 1 min. with cyanogen bromide. The observed times are in agreement with values calculated from hydrolysis rates. [A large excess of hydroxide is used so that its concentration is approximately constant, and the rate law is pseudo-unimolecular. The reaction is 99·9% complete in ten half-life periods and this is numerically equal to $10 \log_e 2/k[\text{OH}]$, where k is the velocity constant. At 25°, k is approx. 0·3, 50, and 530 for cyanogen iodide, bromide, and chloride, respectively (Griffith and McKeown, *Trans. Faraday Soc.*, 1938, **34**, 316; Eden and Wheatland, *loc. cit.*), so the time of hydrolysis in normal alkali is 23, 0·14, and 0·013 min., respectively.] The results for alkaline hydrolyses are tabulated, ΔT being the rise in temperature. The water equivalent is the heat (in cal.), determined electrically, to raise the calorimeter and contents by 1°. The quantities of cyanogen bromide and iodide were determined by direct weighing, those of cyanogen chloride by analyses.

Water equiv. (cal./°)	ΔT	Wt. (g.)	Heat/mole (kcal.)	Water equiv. (cal./°)	ΔT	Wt. (g.)	Heat/mole (kcal.)
CNCl in 500 ml. of N/2-NaOH.							
532·5	1·387°	0·685 [1]	66·29	533·3	1·353	0·671	66·11
532·9	1·458	0·719	66·43	534·6	1·412	0·699	66·39
535·9	1·381	0·685	66·41			Mean	66·3(3) ± 0·10
CNBr in 500 ml. of N-NaOH.							
541·4	0·974°	0·9994	55·89	539·4	0·979°	0·9940	56·27
539·0	0·941	0·9588	56·04	540·8	1·000	1·0279	55·73
541·2	0·929	0·9450	56·36			Mean	56·0(6) ± 0·17
543·2	0·950	0·9746	56·08				
ICN in 500 ml. of N-NaOH.							
539·4	0·823°	1·466 [2]	46·28	539·5	0·845°	1·500	46·46
538·4	0·852	1·517	46·23	537·4	0·862	1·529	46·33
540·0	0·843	1·498	46·44			Mean	46·3(5) ± 0·08

[1] The percentage of CNCl utilized was 97·4, 96·8, 98·2, 95·6, 98·4, respectively. Gravimetric and volumetric analyses agreed to the last figure. [2] Weight of ICN as determined by Andrews's titration of iodide, 1·465, 1·515, 1·496, 1·500, 1·529 g., respectively.

Heat of Formation of Sodium Cyanate.—(1) *By acid hydrolyses.* Sodium cyanate (20 g.) was recrystallised from methanol–water (2 : 1) (600 c.c.), giving 8 g. of pure cyanate, and because of its bulky nature this was compressed into pellets. About 1 g. of cyanate (2 or 3 pellets) was dropped into 500 ml. of water, and the heat of solution measured. N-Hydrochloric acid (38 ml.) was then added by piercing an ampoule suspended in the cyanate solution, and the heat of hydrolysis was measured. The acid normality at the end was 0·02N and it was assumed that all carbon dioxide remained in solution. In another type of experiment sodium cyanate pellets were added to a large excess of N-sulphuric acid. The assumption here was that all carbon dioxide was eliminated. There was a pronounced hump, corresponding with the cooling caused by evolution of carbon dioxide gas, in the time–temperature curves of the latter experiments. The heat of solution of sodium cyanate in N-sodium hydroxide was also determined.

An attempt to determine the carbon dioxide was only semi-quantitative because of its loss during transfer of the 80—90% saturated solutions. The solution was acidified, and the dioxide steam-distilled into excess of baryta, which was then back-titrated with acid. Equivalent solutions were employed with sodium carbonate in place of cyanate. About 74% of the carbon dioxide was found after 7 min. (the time for the mid-point of the temperature rise) which decreased to 53% after 42 min. Although the absolute values were not significant, the demonstration of a loss of gas under the experimental conditions was important. A 10% loss corresponds to 0·4 kcal. An estimation under the conditions of the sulphuric acid experiments showed that some carbon dioxide was retained. It can only be concluded that the agreement between the methods must be due to a cancellation of errors. The results were as follows:

NaCNO in 500 ml. of N-H_2SO_4: Heat/mole, 22·85, 22·79, 22·76; mean 22·8(0) ± 0·03.
NaCNO in 500 ml. of H_2O: Heat/mole, −4·62, −4·67; mean −4·64 ± 0·03.
Addition of 38 ml. of N-HCl: Heat/mole, 27·51, 27·74; mean 27·6(2) ± 0·10.
NaCNO in 500 ml. of N-NaOH: Heat/mole, −4·54, −4·52; mean −4·53 ± 0·01.

(2) *By the cyanogen route.* (i) Heat of reaction of iodine with alkali cyanides. Powdered iodine was added to excess of sodium cyanide solution in this series of experiments. The heat of solution of cyanogen iodide in a solution of the same concentrations of sodium iodide and cyanide as that left after the reaction, was determined separately:

500 ml. of 6% NaCN solution + 19 g. of iodine: Heat/mole, 9·04, 9·08, 9·11, 9·09, 9·07, 9·12; mean 9·09 ± 0·02.
ICN in NaCN + NaI solution: Heat/mole, −1·29, −1·25, mean −1·27 ± 0·02.
The corresponding figures for potassium cyanide were 8·69, 8·73, 8·77, 8·73, 8·78 (mean 8·74 ± 0·03) and −1·33.

(ii) Heat of hydrolysis of cyanogen. The cyanogen, prepared by heating dry silver cyanide at 360° *in vacuo*, was purified by fractionation *in vacuo*. It was hydrolysed in the same way as cyanogen chloride, and the hydrolysate analysed, because of incomplete absorption (98·2 ± 0·4% of the gas reacted in these experiments). The cyanide was determined by the Liebig–Denigès method, and the total cyanide and cyanate by Volhard's procedure. The latter results, all about 0·5% low because of the appreciable solubility of silver cyanate, were used as a rough check on the stoicheiometry of the hydrolysis. The results were:

C_2N_2 in 500 ml. of 0·1N-NaOH. Mean water equiv. 530·0 ± 1·1 cals./°C.

Wt. of C_2N_2 (g.)	Temp. rise	Heat/mole (kcal.)	Wt. of C_2N_2 (g.)	Temp. rise	Heat/mole (kcal.)
0·586	0·703°	33·10	0·577	0·689	32·95
0·582	0·700	33·19	0·582	0·701	33·21
0·583	0·695	32·89		Mean 33·0(5) ± 0·12	
0·580	0·693	32·95			

The heat of formation of solid sodium cyanate calculated from the experiments with sulphuric acid is −97·1, the following heats of formation being used: −211·50 for H_2SO_4, 331·2 for $(NH_4)_2SO_4$, −280·1 for Na_2SO_4, and −94·05 for carbon dioxide gas. The experiments in hydrochloric acid give −92·5 for the aqueous heat of formation using −39·6 for HCl, −71·7 for NH_4Cl, and −98·7 for aqueous carbon dioxide. The difference between these figures, *viz.*, 4·6, agrees with the determined heat of solution.

The heat of formation of sodium cyanate calculated from the cyanogen route is −98·1 for the solid and −93·4(5) for the aqueous solution. The heats involved are: C_2N_2, 73·84; NaOH, −112·15; H_2O, −68·3; heat of solution of CNI, −1·27, and the heat of dilution of NaCN (45—4800 mols. of H_2O). Direct measurement of the last gave approximately 0·06, but a value of 0·1, the figure for the heats of dilution of the other sodium halides, was used.

The heats of formation of sodium cyanide from these data are NaCN_c −21·4 and NaCN(135 H_2O) −21·85; for aqueous potassium cyanide, −25·05 is found from the difference in the heats of reaction of iodine with potassium and sodium cyanides.

The heats of formation of cyanogen chloride, bromide, and iodide were calculated to be 31·6, 32·5, and 38·3 in their standard states, the following heats of formation being used: NaCl −97·24, NaBr −86·12, NaI −70·59, NaCNO −93·4. In the gas phase the heats of formation became 43·3 and 52·4 for cyanogen bromide and iodide; the latent heats of sublimation were taken as 10·8 and 14·1, respectively.

Vapour Pressure of Cyanogen Bromide.—This was determined statically by means of a mercury manometer. (It has already been shown that mercury is only slowly attacked by molten cyanogen bromide; Part I, *loc. cit.*). The manometer and cyanogen bromide bulb were filled by the usual vacuum technique and then kept in a thermostat at various temperatures. Between each reading the cyanogen bromide bulb was cooled in liquid nitrogen to recondense any cyanogen bromide which had distilled on to the glass surfaces. All measurements were made with respect to a reference mark on the mercury limb unexposed to bromide vapour. The results (T in °K and p in terms of mm. of Hg at 0°) are given below; the last three were obtained after an interval of 3 days at room temperature. The manometer could still be read after a month. With less carefully purified specimens, attack was appreciable after a few days.

T ...	273·3	284·5	288·2	288·8	291·5	293·3	298·3	303·0	303·5	308·6	313·1	289·0	298·2	308·2
p	22·2	49·3	63·8	66·0	77·6	89·8	120·0	159·8	163·6	221·8	281·8	65·8	119·0	216·0

The vapour pressure equation is $\log_{10}p = 9{\cdot}993 - 2{\cdot}360/T$; the latent heat of sublimation 10·8(1) kcal.

Entropies.—The entropies are only required to a slightly higher accuracy than the heats of formation (0·1 kcal.). Smith, King, Smith, and Gordy's bond lengths (*Phys. Review*, 1948, **74**, 370) have been used. The more recent data for cyanogen bromide and iodide hardly affect these values (Simmons and Anderson, *ibid.*, 1950, **80**, 338; Tetenbaum, *ibid.*, 1952, **86**, **444**). The entropy values are given in the order CNCl, CNBr, CNI: translational entropy, 38·256, 38·877, 40·972; rotational, 15·800, 16·532, 17·014; vibrational, 2·222, 2·663, 3·349. Total entropy, 56·28, 59·07, 61·33 (Stevenson, *loc. cit.*, gave 54·72, 58·26, 60·76).

The only source of appreciable error in this determination is in the uncertainties of the fundamental frequencies. West and Farnsworth's data (*J. Chem. Phys.*, 1933, **1**, 402) are used. Wagner's more recent values (*Z. physikal. Chem.*, 1941, *B*, **48**, 309; 1943, *A*, **193**, 55), which differ by 11 wave-numbers in the worst instance, would give a difference of less than 0·05 kcal. in the free energies at 25°, compared with 0·46 kcal. obtained with Stevenson's figures.

The free energies of gaseous cyanogen chloride, bromide, and iodide at 298·2°K, calculated from the entropy and thermal data, are 30·0, 38·3, and 45·5, respectively. The value for the bromide is within 1 kcal. of the mean of the other two.

DISCUSSION

The heat of formation of cyanogen chloride was determined by Berthelot (*loc. cit.*) from the heat of its alkaline hydrolysis at 21°. The cyanogen chloride was introduced in the liquid state, so the heat of vaporization was required. His figure of 8·76 kcal. was higher than more recent values (Cook and Robinson, *J.*, 1935, 1001, 6·36 kcal.; Douglas and Winkler, *Canad. J. Res.*, 1947, **25**, *B*, 381, 6·40 kcal.). In the procedure described, which resulted in a more rapid reaction, the heat of formation of the gas was measured directly at 25°.

The heat of formation of cyanogen bromide has not been recorded, although Berthelot attempted to use the reaction of bromine with a cyanide. The secondary reaction of cyanogen bromide and the cyanide interfered.

Values for cyanogen iodide have been measured by two methods. Berthelot found the heat of reaction of iodine with potassium cyanide solution at 20° to be 6·3 kcal. Our value obtained at 25° is 8·74 ± 0·03 kcal. (This reversal of values compared with the latent-heat figures is probably coincidental.) A measure of the free energy of cyanogen iodide was determined from an approximate equilibrium constant for $\text{ICN} + \text{H}^+ + \text{I}^- \rightleftharpoons \text{HCN} + \text{I}_2$ (Lewis and Keys, *J. Amer. Chem. Soc.*, 1918, **40**, 472). Yost and Stone (*ibid.*, 1933, **55**, 1889) obtained a more consistent value from Kovach's results (*Z. physikal. Chem.*, 1912, **80**,

107) corrected for the formation of complex ions, $I(CN)_2^-$ and I_2CN^-. Gauguin has estimated the equilibrium constant from measurements on the redox potential of the CN^-–I_2 couple (*Bull. Soc. chim.*, 1948, 1048). Values of the free energy calculated from these data depend on the heat of formation of hydrogen cyanide determined by Berthelot and Thomsen. The free energies found in this work are independent of the old thermochemical data and are reliable to 0·6 kcal. The main errors are in the heat of formation of cyanogen, the heats of sublimation of cyanogen iodide and bromide, and in the measured heats of reaction.

The dissociations of cyanogen halides to halogens and cyanogen, expressed as $\log_{10} K$, where K is the equilibrium constant, are —4·0(3), 1·7(6), and 5·5(6) for the chloride, bromide, and iodide, respectively, in the gas state. Thus cyanogen chloride at equilibrium is less dissociated than nitrosyl chloride ($\log_{10} K = -3{\cdot}57$), and the metastability of cyanogen iodide is as great as the old figures indicate. It has already been emphasized by Yost and Stone (*loc. cit.*) that the gaseous iodide does not equilibrate so that dissociation measurements yield false values for the free energy.

The carbon–halogen bond-dissociation energies, the heat of reaction for $CNX = CN + X$, can be given greater precision because of recent values for the heat of formation of the cyanogen radical. Two independent methods lead to values of 94·3, and 92·7 ± 6 kcal. (Brewer, Templeton, and Jenkins, *J. Amer. Chem. Soc.*, 1951, **73**, 1462; McDowell and Warren, *Trans. Faraday Soc.*, 1952, **48**, 1084). The dissociation energies for cyanogen chloride, bromide, and iodide are 91·4, 77·4, and 67·1 ± 7 kcal. if the heat of formation of cyanogen radical is 94 kcal. These energies have been measured by observations on the absorption limit in the ultra-violet spectra (Badger and Woo, *J. Amer. Chem. Soc.*, 1931, **53**, 2573; Mooney and Reid, *Proc. Roy. Soc. Edin.*, 1932, **52**, 152). From their mean wave-length limits, and an excitation energy of 26·4 kcal. for the excited cyanogen radical formed in the photodissociation, the dissociation energies are 102, 88, and 69 kcal. These are maximum values because the experimental wave-length limits are only rough minimum values. Recently Stevenson (*J. Chem. Phys.*, 1950, **18**, 1347) has used the electron-impact method to obtain possible values for the dissociation energy of cyanogen chloride, which however depend on the state of the cyanogen radical formed in these experiments (compare McDowell and Warren, *loc. cit.*).

The heats of formation of cyanogen halides from cyanogen and halogens in the gas phase are equal to Pauling's ionic resonance energies if the cyanogen radical can be considered equivalent to a halogen atom. Only for cyanogen chloride is the reaction exothermic (+5·3 kcal.), and the derived electronegativity coefficient, 2·5, implies that the cyanogen radical is close to iodine. The heats of formation for cyanogen bromide and iodide, —2·7 and —8·1 kcal., show that there is no stabilization by covalent-ionic resonance. However, it is doubtful whether the simple electronegativity ideas are applicable to the cyanogen or nitrosyl halides. (For nitrosyl chloride and bromide, the derived coefficients of 2·4 and 2·3 respectively, would lead to a large electron affinity for the nitrosyl radical.)

For a series of related molecules there is usually some connection between bond energy and length. In the simplest instance contraction in length is associated with a strengthening of the bond. The bond contraction for carbon–halogen double bonds compared with single bonds are all 0·18—0·20 Å (Bernstein, *J. Chem. Phys.*, 1947, **15**, 285). The bonds in cyanogen chloride, bromide, and iodide are respectively 0·13, 0·12, and 0·10 Å less than single bonds. [The variation of carbon–nitrogen distance in these molecules shows a barely perceptible movement in sympathy (Smith *et al.*, *loc. cit.*) but the constancy of bond length to within ±0·01 Å in the cyanogen radical when joined to groups as diverse as H, CH_3, CN, Cl, Br, and I is remarkable.] One would expect this contraction to be reflected in an increasing bond strength from the iodide to chloride. The carbon–halogen bond dissociation energies for normal single bonds are taken as 81, 68, and 53 ± 2—3 kcal., the mean of values for alkyl halides (Lane, Linnett, and Oswin, *Proc. Roy. Soc.*, 1953, *A*, **216**, 361); the bond strength in cyanogen halides, i.e., the heats of dissociation $CNX = CN + X$, is therefore enhanced by 10·5, 9·8, and 14·0 kcal. as compared with the single bond energies. The carbon–iodide bond is strengthened by more than the carbon–chlorine bond. It may well be that this contradiction arises from errors in the heats of dissociation, although the largest uncertainty, that in the heat of formation of the cyanogen radical, is eliminated when the cyanogen halides are treated as a group.

The dissociation of cyanogen halides into ions can also be calculated. The real interest is in the dissociation in solution, but unfortunately no data for the solvation energies of positive halogen or cyanogen ions are available unless assumptions are made about ionic radii in solution. In the gas phase the heats of formation of positive and negative cyanogen ions are uncertain. The electron affinity of cyanogen is very near that of bromine. Various methods yield a value of 83 kcal. (Pritchard, *Chem. Reviews*, 1953, **52**, 529) and hence the heat of formation of the cyanide ion is 11 kcal., 94 kcal. being used for the cyanogen radical. The ionization potential of the cyanogen radical is assumed to be not less than that of bromine atom (275 kcal.) [Stevenson's value of 335 kcal. (*loc. cit.*) is probably high because the cyanogen radical formed in his experiments may have excess of kinetic energy.] This leads to a heat of formation for the positive cyanogen ion of 369 kcal. and the following heats of reaction :

$$\mathrm{CNCl} \longrightarrow \mathrm{CN^+ + Cl^-},\ -278;\quad \mathrm{CNCl} \longrightarrow \mathrm{CN^- + Cl^+},\ -307.$$
$$\mathrm{CNBr} \longrightarrow \mathrm{CN^+ + Br^-},\ -270;\quad \mathrm{CNBr} \longrightarrow \mathrm{CN^- + Br^+},\ -268.$$
$$\mathrm{CNI} \longrightarrow \mathrm{CN^+ + I^-},\ -266;\quad \mathrm{CNI} \longrightarrow \mathrm{CN^- + I^+},\ -226.$$

Hence, for cyanogen iodide but not for the chloride, the ionization to a positive cyanogen ion and a halide ion is more endothermic than to a positive halogen ion and a cyanide ion : there is little difference for cyanogen bromide. Because of the uncertainty in the ionization potential of cyanogen radicals the only certain conclusion, however, is that the heat of reaction $\mathrm{X^- + CN^+ \longrightarrow X^+ + CN^-}$ becomes progressively more endothermic from cyanogen chloride to iodide.

The minuteness of the ionization of cyanogen halides in aqueous solution is also demonstrated by the above figures. The solvation energy for cyanogen halides may be assumed to be of the same order as those of the alkali halides since the sizes of the positive halogen ions are approximately those of the alkali cations. Thus the maximum solvation energy available is only about 190 kcal. and the ionizations in solution would still remain considerably endothermic. The extent of ionization would appear to increase from chloride to iodide and it seems likely that the apparently greater ionization of cyanogen chloride is due to its more rapid hydrolysis rather than to a primary ionization.

The mechanism of alkaline hydrolysis of cyanogen chloride may differ from that of cyanogen iodide, although the stoicheiometry is the same for both reactions. This point will be discussed in Part IV.

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