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# Thermodynamics of Metal–Cyanide Coördination. I. pK, $\Delta H^0$, and $\Delta S^0$ Values as a Function of Temperature for Hydrocyanic Acid Dissociation in Aqueous Solution[1a]

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*Received December 8, 1961*

The thermodynamic dissociation constant of HCN in aqueous solution has been determined from 10 to 45°. The p$K$ values obtained with their indicated 95% confidence limits are: 10°, 9.63 ± 0.01; 15°, 9.49 ± 0.01; 20°, 9.36 ± 0.01; 25°, 9.21 ± 0.01; 30°, 9.11 ± 0.01; 35°, 8.99 ± 0.01; 40°, 8.88 ± 0.02; 45°, 8.78 ± 0.02. The $\Delta H^0$ value for HCN dissociation in aqueous solution was determined at 8 and 25° by a thermometric titration procedure. The values obtained with their 95% confidence limits are: 8°, 11.3 ± 0.2; and 25°, 10.4 ± 0.2 kcal./mole. $\Delta S^0$ values of $-7.4$ and $-3.9$ e.u. were calculated from the $\Delta H^0$ and $\Delta G^0$ values at 8 and 25°, respectively. The $\Delta G^0$ value at 8° was obtained by extrapolation from $\Delta G^0$ values in the 10 to 45° region.

## Introduction

The dissociation of HCN in aqueous solution has been studied several times, but no extensive study has previously been made as a function of temperature.

The previously reported p$K$ data[2,3] are not in sufficiently good agreement nor have they been determined over a sufficiently wide temperature range to permit calculation of reliable $\Delta H^0$ values from their temperature dependence. The only reported value for $\Delta H$ was determined calorimetrically in the last century.[2]

This study was undertaken to obtain p$K$ and $\Delta H^0$ values for HCN dissociation as a function of temperature in order to interpret equilibrium constant and heat data determined by us for metal cyanide interaction. Calorimetrically determined $\Delta H^0$ values are reported here for HCN dissociation at 8 and 25°. p$K$ values have been determined as a function of temperature, thus providing data for (1) interpretation of the calorimetric results; and (2) an independent estimation of $\Delta H^0$.

## Experimental

**Materials.**—Reagent grade NaCN (Baker), $HClO_4$ (Baker and Adamson), and NaOH (Baker and Adamson) were used in the preparation of solutions for p$K$ and heat determinations. An HCN stock solution was prepared by passing a 0.05 $F$ NaCN solution through an ion exchange column containing a cation exchange resin (Amberlite GC-120, Type I) until the [$Na^+$] as determined by a flame test was less than 0.05% of that originally present. $HClO_4$, carbonate-free NaOH, and NaCN solutions were prepared and standardized by conventional means.

Potenitial sources of error with respect to the handling and storage of cyanide solutions are (1) volatilization of the molecular HCN species and (2) hydrolytic decomposition of the cyanide ion. The first error was minimized by avoiding acidic solutions. The main body of data in the present work was obtained by titrating $HClO_4$ into NaCN solutions, thus keeping the solution basic during the major part of the titration. The second source of error was minimized by frequent preparation of fresh NaCN stock solutions. The $CN^-$ concentration of the stock solutions was found by Liebig titration to decrease about 0.1% per day; however, the base concentration of these solutions as determined by $HClO_4$ titration remained constant. The decomposition products of the reaction between $CN^-$ and water have been reported by Marsh, *et al.*,[4] to be CO and $NH_3$. Infrared spectra obtained in this Laboratory showed substantial quantities of formate ion to be present also in $CN^-$ solutions. Formation of any of these products is consistent with the observed change in total cyanide concentration and the constancy of the base concentration.

**p$K$ Determinations.**—NaCN solutions were titrated with $HClO_4$ at temperature intervals from 10 to 40°. All titrations were carried out in a water bath whose temperature was controlled to ±0.1° at each temperature studied. The titration vessel was filled with $N_2$ prior to each titration; however, $N_2$ was not bubbled through or passed over the solution during a titration since it was found that this resulted in loss of HCN due to volatilization. pH measurements were made at appropriate intervals using a Beckman Model GS pH meter or a Leeds and Northrup pH indicator (cat. no. 7664) equipped with a 1000-ohm

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[1] (a) Supported in part by Brigham Young University Research Grant No. 115-74-661 and A. E. C. Contract AT (04-3)-299; (b) to whom inquiries concerning this article should be sent; (c) participant, NSF Summer Research Participation Institute, 1961 (NSF Grant No. G-15613).

[2] J. Bjerrum, G. Schwarzenbach, and L. G. Sillén, "Stability Constants," Special Publication 6, The Chemical Society, London, 1957, p. 33.

[3] K. P. Ang, *J. Chem. Soc.*, 3822 (1959).

[4] J. D. F. Marsh, W. B. S. Newling, and J. Rich, *J. Appl. Chem.* (London), **2**, 681 (1952).

heliopot with a microdial giving sensitivity equivalent to that of the Beckman Model GS pH meter. The Beckman E-2 glass and saturated calomel electrodes used in the determinations were calibrated throughout the titration range against a pH 9.18 buffer solution which was prepared using borax (NBS Standard Sample No. 187a) and instructions obtained from the National Bureau of Standards.

**Heat Determinations.**—The heat of dissociation of HCN in aqueous solution was determined by a thermometric titration procedure at 8 and 25°. Equilibrium was approached from both directions with the heat of dissociation being determined by titrating tetramethylammonium hydroxide into HCN solutions and the heat of formation by titrating $HClO_4$ into NaCN solutions. The equipment and procedure used in these determinations have been described[5]; however, certain refinements of the equipment and thermistor calibration procedure have been incorporated into the present study. These are (1) the use of two thermistors in the bridge circuit giving approximately double the response to temperature changes, (2) introduction into the circuit of an amplifier making possible measurements over a hundredfold ionic strength, $\mu$, range which is about ten times greater than that previously obtainable, and (3) a thermistor calibration procedure in which the thermistors and a 1° Beckmann thermometer were placed in a water bath which was controlled at the temperature of interest (8 or 25°) to ±0.001°. The resistance change of the thermistors then was obtained at several temperatures covering the range to be used in the subsequent determinations (7.9 to 8.4° and 24.8 to 25.3°). Data from this procedure showed the resistance of the thermistors in each temperature interval to be a linear function of the temperature. This calibration made possible subsequent estimation in the calorimeter of temperature changes as small as 0.03° to ±1%.

**Calculations.**—The method used to calculate $\Delta H^0$ values from the thermometric titration data has been described.[5,6]

A p*K* value corrected to $\mu = 0$ was obtained in the following manner from the p*K* data of a given titration. $\mu$ was calculated in the usual manner. A Debye–Hückel equation of the form $-\log \gamma = (A\sqrt{2\mu}/1 + B\sqrt{2\mu})$ was used to convert pH to $[H^+]$ and the p*Q* (where *Q* is the molarity quotient at a finite $\mu$) to p*K*. A value of 4 Å. was used in the Debye–Hückel expression for the ionic diameter as Hamer[7] has shown from literature data that best agreement is obtained between p*K* values calculated from potentiometric and spectrophotometric data using this value. p*K* was calculated by the $\bar{n}$ method.[8] $\bar{n}$ was calculated from electroneutrality and mass balance expressions using titration readings in the $\bar{n}$ region 0.4 to 0.6. All calculations including a recycling process between $\mu$ and $\gamma$ until the approximation attained the desired self-consistence were done on an IBM 650 electronic computer.

## Results

p*K* values corrected to $\mu = 0$ for HCN dissociation at the various temperatures studied are given in Table I together with the $\mu$ value of the solution used in the p*K* determination. At least two titrations were made at each $\mu$ value and individual p*K* values were calculated from six readings in each determination. The averages of these p*K* values are given in Table I together with their 95% confidence limits[9] (double the standard deviation). The 95% confidence limits were calculated before "rounding-off" the data.

Calculation of the heat of dissociation of HCN at 8° required a value for the heat of formation of water at 8°. This value was determined calorimetrically to be −14.54 ± 0.05 kcal./mole using the same method[5] that was used to determine the corresponding value at 25°. In Table II are given the calorimetrically determined heats of HCN dissociation as a function of $\mu$ at 8 and 25°.

The data in Table II vary significantly with temperature, but not with either $\mu$ or the mode of titration. For these reasons, a 95% confidence limit[9] was calculated based on all data at each temperature, and the $\Delta H$ value thus obtained was taken to be $\Delta H^0$. The $\Delta H^0$ values obtained in this manner are 10.4 ± 0.2 kcal./mole at 25°, and 11.3 ± 0.2 kcal./mole at 8°.

Combination of the $\Delta H^0$ values at 8 and 25° with the corresponding $\Delta G^0$ values ($\Delta G^0$ at 8° was obtained by extrapolation of the data from higher temperatures) gives $\Delta S^0 = -3.9$ (8°) and $-7.4$ (25°) e.u., respectively, for HCN dissociation.

## Discussion

The p*K* value determined in the present study at 25° is in excellent agreement with that determined spectrophotometrically by Ang,[3] 9.22, but not with that determined by Britton and Dodd,[10] 9.31. Ang states that freshly prepared cyanide solutions were used in his study while no mention is made of such precautions by Britton and coworkers[10,11] in their studies at 18 and 25°. It is likely that their value at 25° is high because of failure to account for the difference between the cyanide and total base concentrations resulting from cyanide decomposition. Failure to account for this difference in our calculations would place

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[5] J. J. Christensen and R. M. Izatt, *J. Phys. Chem.*, **66**, 1030 (1962).

[6] J. J. Christensen, R. M. Izatt, and L. Hansen, "Proceedings of the Seventh International Conference on Coördination Chemistry," Stockholm, 1962, Paper 7F1, p. 354.

[7] W. J. Hamer in "The Structure of Electrolytic Solutions," W. J. Hamer, ed., John Wiley and Sons, New York, N. Y., 1959, Chapter 15, p. 236.

[8] F. J. C. Rossotti and H. Rossotti, "The Determination of Stability Constants," McGraw-Hill Book Co., New York, N. Y., 1961.

[9] W. J. Youden, "Statistical Methods for Chemists," John Wiley and Sons, New York, N. Y., 1951, pp. 9–20.

[10] H. T. S. Britton and E. N. Dodd, *J. Chem. Soc.*, 2332 (1931).

[11] H. T. S. Britton and R. A. Robinson, *ibid.*, 458 (1931).

TABLE I

p*K* VALUES (CORRECTED TO $\mu = 0$) AS A FUNCTION OF TEMPERATURE FOR HCN DISSOCIATION IN AQUEOUS SOLUTION
$\mu$ VALUES ARE THOSE OF THE SOLUTIONS USED IN THE p*K* DETERMINATIONS

| | Temperature, °C. | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $\mu \times 10^3$ | 10 | 15 | 20 | 25 | 30 | 35 | 40 | 45 |
| 24 | | | | 9.19 | | | | |
| 15 | 9.63 | 0.48 | 9.36 | 9.21 | 9.10 | 8.99 | 8.87 | 8.78 |
| 5.5 | | | | 9.23 | | | | |
| 1.7 | 9.62 | 9.50 | 9.36 | 9.21 | 9.11 | 8.99 | 8.89 | |
| 0.90 | | | | 9.22 | | | | |
| 0.33 | | | | 9.19 | | | | |
| Average | 9.63 | 9.49 | 9.36 | 9.21 | 9.11 | 8.99 | 8.88 | 8.78 |
| 95% confidence limit | ±0.012 | ±0.010 | ±0.012 | ±0.014 | ±0.008 | ±0.014 | ±0.018 | ±0.020 |

our 25° p*K* value at 9.28. p*K* values reported previously[2,11] at 18°, 7.58, 8.89, and 9.32, differ appreciably from each other and from those determined in the present study at 15 and 20°, probably because of the previously mentioned errors which are inherent in the preparation and handling of HCN solutions.

One calormetric $\Delta H$ value, 10.96 kcal./mole, has been reported[2] for HCN dissociation. This value, obtained at 18° in 1882, together with our $\Delta H^0$ data at 8 and 25°, would suggest a small, but definite, increase in $\Delta H^0$ from 25 to 8°. The p*K* change with temperature found in the present work is consistent with this observation. In Fig. 1 is seen a plot of p*K* *vs.* $1/T$, where the limits of uncertainty are the 95% confidence limits given in Table I. These data show a slight curvature over the temperature range studied which is consistent with the observed $\Delta H$ change with temperature. Drawing the best straight lines through the 40 to 25° and 10 to 25° data one obtains for $\Delta H^0$ 9.4 and 10.7 kcal./mole, which can be assigned to 32.5 and 18°, respectively. The average of these values, 10.1 kcal./mole, agrees well with the 25° calorimetric value. The 18° value, 10.7 kcal./mole, is in good agreement with the 18° calorimetric value, and the extrapolated 8° value, 11.6 kcal./mole, is in good agreement with the 8° calorimetric value.

Canady, *et al.*,[12] present evidence that in the dissociation of a molecular acid in aqueous solution the contribution of the proton to $\Delta S^0$ is approximately −4 e.u., and the total $\Delta S^0$ for such an ionization is −14 to −18 e.u. Recent data obtained by us[5] confirm this observation. The $\Delta S^0$ values obtained in the present study for HCN dissociation are much lower than expected at 25°, and are still lower at 8°. These low $\Delta S^0$ values are consistent with the observation that a high degree of solvent ordering would be expected of the highly polar HCN(aq) molecular species (dielectric constant of HCN(l) = 117 compared to $H_2O$(l) = 82) counterbalancing the contribution

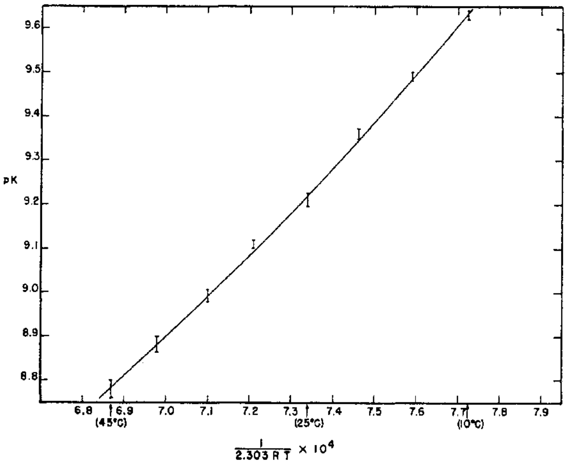

Fig. 1.—Plot of p*K* for HCN dissociation *vs.* $1/T$.

TABLE II

$\Delta H$ VALUES (KCAL./MOLE) AS A FUNCTION OF $\mu$ FOR HCN DISSOCIATION AT 8 AND 25°

| (a) Titration of $CN^-$ with $H^+$ | | | (b) Titration of HCN with $OH^-$ | |
|---|---|---|---|---|
| $\mu \times 10^3$ | $\Delta H$ (25°) | $\Delta H$ (8°) | $\mu \times 10^3$ | $\Delta H$ (25°) |
| 26.3 | 10.44 | 11.18 | 10.9 | 10.64 |
| | 10.45 | 11.28 | | 10.56 |
| | 10.20 | 11.32 | 8.75 | 10.32 |
| | | 11.46 | 5.47 | 10.34 |
| 13.3 | 10.32 | 11.28 | | 10.19 |
| | 10.30 | 11.62 | 3.28 | 10.55 |
| | 10.39 | 11.32 | | 10.36 |
| | 10.09 | 11.38 | 2.19 | 10.31 |
| 6.75 | 10.48 | 11.09 | | 10.42 |
| | 10.36 | 11.03 | 1.31 | 10.25 |
| | 10.41 | 11.29 | | |

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[12] W. J. Canady, H. M. Papee, and K. J. Laidler, *Trans. Faraday Soc.*, **54**, 502 (1958).

to $\Delta S^0$ of the $CN^-$. Thus, the observed $\Delta S^0$ is essentially that resulting from the contribution of the proton. The molecules previously studied by Canady, *et al.*, and by us had low polarity and, thus, did not show this effect to an appreciable extent.

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CONTRIBUTION FROM THE INSTITUTE FOR PHYSICAL CHEMISTRY,
UNIVERSITY OF COPENHAGEN, DENMARK, AND THE
DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, NEW YORK 27, NEW YORK

# The Electronic Structures and Magnetic Properties of the Chromyl and Molybdenyl Ions

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*Received April 19, 1962*

The electron spin resonance spectra and the magnetic susceptibilities of $(NH_4)_2[MoOCl_5]$ and $Rb_2[CrOCl_5]$ are reported. The results are consistent with an electronic structural description which includes considerable oxygen-to-metal $\pi$-bonding. Complete consistency between the e.s.r. and the susceptibility data is found for $(NH_4)_2[MoOCl_5]$. The lack of consistency of the data for $Rb_2[CrOCl_5]$ is attributed to the presence of a small amount of $Cr^{3+}$ impurity. Comparison of e.s.r. data with reported susceptibility data for $Mo^{5+}$ solutions of varying HCl concentration is interpreted in terms of the nature of the species present.

## Introduction

In a previous report[1] the electronic structures and spectra of the chromyl ($CrO^{3+}$) and molybdenyl ($MoO^{3+}$) ions were discussed. Both the charge transfer and the "crystal field" d-d spectra could be accounted for by the molecular orbital energy level scheme derived for the electronically equivalent ($d^1$) vanadyl ($VO^{2+}$) ion.[2] The most striking feature of the electronic structures of these oxycations is the existence of considerable oxygen-to-metal $\pi$-bonding.

In the present paper the electron spin resonance spectra and the temperature dependencies of the magnetic susceptibilities of $(NH_4)_2[MoOCl_5]$ and $Rb_2[CrOCl_5]$ are investigated and the results are interpreted in terms of the previously proposed electronic structural description. The magnetic susceptibilities of solid samples of $(NH_4)_2[MoOCl_5]$[3] and $Rb_2[CrOCl_5]$[4] and solutions of $Mo^{5+}$[5] have been reported in the literature, but for only room temperature.

A comparison of the results of the present e.s.r. measurements on $Mo^{5+}$ solutions with the susceptibility results of Sacconi and Cini[5] allows an interpretation of the magnetic nature of the species present in these solutions.

## Results

**Chromyl Ion.**—The electron spin resonance spectrum of a solid sample of $Rb_2[CrOCl_5]$ shows a single broad resonance line centered at $g = 1.986$. The $g$ value indicates an orbitally nondegenerate ground state, as expected for a compound containing $CrO^{3+}$. The $g$ factor for a paramagnetic molecule with an orbitally nondegenerate ground state differs from 2.0023 due to the mixing of ground state and excited states *via* spin–orbit coupling. The expressions for the $g$ values for $d^1$ transition metal oxycations in $C_{4v}$ ligand fields are[2]

$$g_\perp = 2.0023\left(1 - \frac{\xi}{\Delta E(^2B_2 \longrightarrow {}^2E(I))}\right) \qquad (1)$$

$$g_\parallel = 2.0023\left(1 - \frac{4\xi}{\Delta E(^2B_2 \longrightarrow {}^2B_1)}\right) \qquad (2)$$

with

$$\langle g\rangle^2 = 1/3\,(2g_\perp^2 + g_\parallel^2) \qquad (3)$$

In these equations $\xi$ is the spin–orbit coupling constant for $Cr^{5+}$ in $CrO^{3+}$ and the $\Delta E$'s are the energies of known crystal field transitions in $Rb_2[CrOCl_5]$.[1] The $\xi$ value for $CrO^{3+}$ is calculated to be 65 cm.$^{-1}$, using the observed $\langle g\rangle$ value and the known $\Delta E$ values ($\Delta E(^2B_2 \rightarrow {}^2E(I)) = 12{,}900$ cm.$^{-1}$, $\Delta E(^2B_2 \rightarrow {}^2B_1) = 23{,}500$ cm.$^{-1}$).

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[1] H. B. Gray and C. R. Hare, *Inorg. Chem.*, **1**, 363 (1962).

[2] C. J. Ballhausen and H. B. Gray, *ibid.*, **1**, 111 (1962).

[3] B. T. Tjabbes, *Proc. Acad. Sci. Amsterdam*, **35**, 693 (1932); *Chem. Abstr.*, **26**, 4987 (1932).

[4] R. W. Asmussen, "Magnetokemiske Undersøgelser over Uorganiske Kompleksforbindelser," Gjellerups Forlag, Copenhagen, 1944.

[5] L. Sacconi and R. Cini, *J. Am. Chem. Soc.*, **76**, 4239 (1954).