product, $C_7H_8Cr(CO)_3$ (0.19 g.); the other was the morpholine product, $C_4H_8NOCr(CO)_5$. *Anal.* Calcd. for $C_9H_9CrNO_6$: C, 38.4; H, 3.2; N, 5.0; mol. wt., 281. Found: C, 38.4; H, 3.2; N, 5.6; mol. wt., 352.

(ii) Morpholine Molybdenum Pentacarbonyl.—Molybdenum hexacarbonyl (1 g.) was refluxed with morpholine (0.35 g.) in benzene for 6 hr.; the solution was cooled and filtered, and the filtrate was evaporated *in vacuo* to give a pale yellow solid (1.1 g.), m.p. 105–108°. *Anal.* Calcd. for $C_9H_9MoNO_6$: C, 33.4; H, 2.8; N, 4.3; mol. wt., 323. Found: C, 33.4; H, 3.1; N, 4.4; mol. wt., 362.

(iii) Morpholine Tungsten Pentacarbonyl.—Tungsten hexacarbonyl (1 g.) was refluxed with morpholine (0.25 g.) in toluene for 6 hr.; a pale yellow solid (0.9 g.), m.p. 139–141°, was obtained from the filtered reaction mixture. *Anal.* Calcd. for $C_9H_9WNO_6$: C, 26.9; H, 2.2; N, 3.4. Found: C, 26.7; H, 2.4; N, 3.5.

Bis-morpholine Molybdenum Tetracarbonyl.—Molybdenum hexacarbonyl (1 g.) was refluxed with excess morpholine in benzene until yellow crystals suddenly precipitated from solution. The crystals (1 g.) were filtered, washed twice with benzene, and kept *in vacuo*. *Anal.* Calcd. for $C_{12}H_{18}MoN_2O_6$: C, 37.7; H, 4.7; N, 7.3. Found: C, 37.2; H, 4.7; N, 7.4.

Bis-morpholine tungsten tetracarbonyl was prepared from tungsten hexacarbonyl by the method described for the molybdenum analog. *Anal.* Calcd. for $C_{12}H_{18}WN_2O_6$: C, 30.6; H, 3.8; N, 5.9. Found: C, 30.9; H, 3.8; N, 5.9.

Tris-morpholine Molybdenum Tricarbonyl.—Morpholine was distilled onto a frozen, evacuated benzene solution of π-$(CH_3)_3$-$C_6H_3Mo(CO)_3$.[7] The reactants were allowed to warm to room temperature, and the white, air-sensitive precipitate formed after 3 hr. was filtered and analyzed. *Anal.* Calcd. for $C_{15}H_{27}MoN_3$-O_6: C, 40.8; H, 6.1; N, 9.6. Found: C, 40.3; H, 5.8; N, 9.8.

(2) Pyrrolidine Reactions.—These reactions were carried out under the same conditions as the morpholine reactions, and the following compounds were isolated.

(i) Pyrrolidine Molybdenum Pentacarbonyl.—Pale yellow powder, m.p. 53–55°, soluble in benzene. *Anal.* Calcd. for $C_9H_9MoNO_5$: C, 35.2; H, 2.9; N, 4.6; mol. wt., 307. Found: C, 35.0; H, 2.6; N, 4.6; mol. wt., 358.

(ii) Pyrrolidine Tungsten Pentacarbonyl.—Yellow powder, m.p. 71–73°, soluble in benzene. *Anal.* Calcd. for C_9H_9-WNO_5: C, 27.3; H, 2.3; N, 3.5; mol. wt., 395. Found: C, 27.1; H, 2.0; N, 3.3; mol. wt., 417.

(iii) Bis-pyrrolidine Molybdenum Tetracarbonyl.—Yellow crystals, insoluble in benzene, soluble in acetone, sparingly soluble in nitromethane. *Anal.* Calcd. for $C_{12}H_{18}MoN_2O_4$: C, 41.1; H, 5.1; N, 8.0. Found: C, 40.9; H, 5.2; N, 7.7.

(iv) Bis-pyrrolidine Tungsten Tetracarbonyl.—Yellow crystals, less easily oxidized than the Mo analog. *Anal.* Calcd. for $C_{12}H_{18}WN_2O_4$: C, 32.9; H, 4.1; N, 6.4. Found: C, 32.9; H, 4.05; N, 6.6.

(3) Piperazine Reactions. (i) Piperazine Dimolybdenum Decacarbonyl.—Molybdenum hexacarbonyl (4 g.) and piperazine (0.7 g.) were refluxed in benzene for 12 hr., when yellow crystals deposited together with a brown decomposition product. The crystals were dissolved in acetone, and the filtered solution was evaporated to yield a pale yellow powder (1.1 g.). *Anal.* Calcd. for $C_{14}H_{10}Mo_2N_2O_{10}$: C, 30.1; H, 1.8; N, 5.0. Found: C, 30.5; H, 1.9; N, 5.1.

(ii) Piperazine Ditungsten Decacarbonyl.—Tungsten hexacarbonyl (2.4 g.) and piperazine (0.3 g.) were refluxed in toluene for 6 hr. and the reaction products were worked up as for those of the analogous molybdenum reaction. *Anal.* Calcd. for C_{14}-$H_{10}W_2N_2O_{10}$: C, 22.9; H, 1.4; N, 3.8. Found: C, 23.3; H, 1.5; N, 3.8.

(iii) Tris-piperazine Molybdenum Tricarbonyl.—Benzene was distilled onto a mixture of toluene molybdenum tricarbonyl (0.7 g.) and piperazine (0.7 g.) *in vacuo*, and the mixture was warmed to room temperature under nitrogen and shaken for 2 hr. The white precipitate (0.8 g.) was filtered, dried, and analyzed. *Anal.* Calcd. for $C_{15}H_{30}MoN_6O_3$: C, 41.1; H, 6.9; N, 19.2. Found: C, 40.1; H, 7.4; N, 19.3.

Reactivity of Complexes.—All the complexes were decomposed by air, very slowly in the solid state, but rapidly in solution. The molybdenum compounds were apparently less stable in this respect than the tungsten compounds, since the infrared spectra of solutions of the $L_2Mo(CO)_4$ complexes showed a new strong peak after the solutions had been exposed to air for a short time; similar bands were observed for the tungsten compounds only after exposure for 2–3 hr.

Infrared spectra were measured on Nujol mulls or solutions in various solvents using an SP 100 spectrophotometer.

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Crystal Field Effects in Coordination Compounds. A Calorimetric Study of Some Hexacyano Metal Complexes[1]

BY F. H. GUZZETTA[2] AND W. B. HADLEY

The heats of complexation of cyanide ion with V^{+2}, Cr^{+2}, Mn^{+2}, Fe^{+2}, Co^{+2}, Zn^{+2}, and Fe^{+3} have been determined by direct calorimetry. The large excess of cyanide ion and the temperature at which the reactions were carried out (25.4°) ensure the formation of the hexacyano complex with the obvious exceptions being the zinc and cobaltous ions. The heats of complexation for V^{+2}, Cr^{+2}, Mn^{+2}, Fe^{+2}, Co^{+2}, Zn^{+2}, and Fe^{+3} are 47.0, 63.2, 34.5, 73.7, 74.4, 27.7, and 68.0 kcal./mole, respectively. The thermal data have been interpreted in terms of the ligand field theory and Dq values for some divalent ions have been estimated.

Introduction

The majority of ligands for which formation constants with different metal ions have been determined belong to structural types in which oxygen atoms, oxy-gen and nitrogen atoms, or only nitrogen atoms are

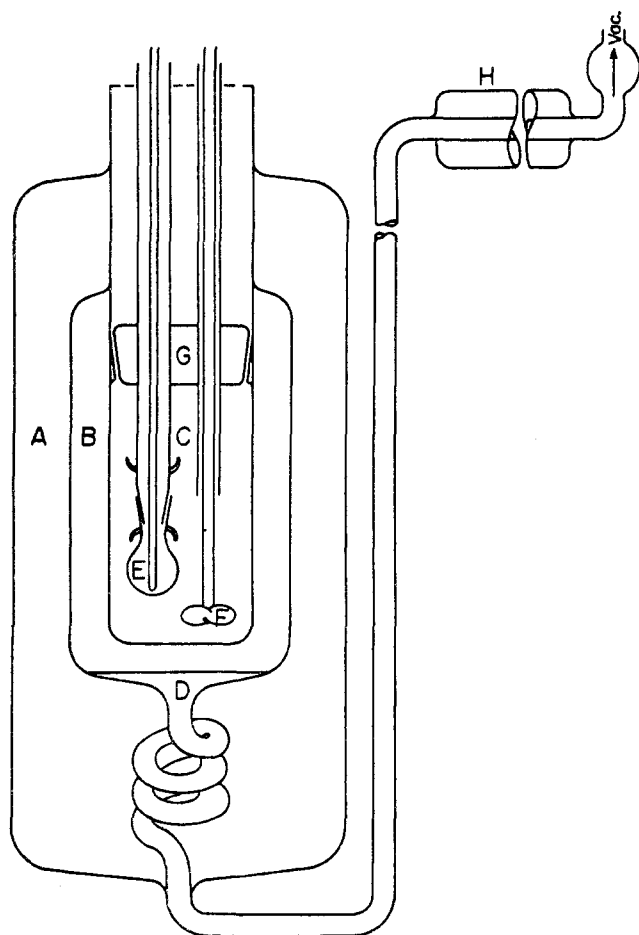(2) Knolls Atomic Power Laboratory, Schenectady, N. Y.

Fig. 1.—The calorimeter: A, silvered, evacuated dewar; B, solid–liquid mixture of *t*-butyl alcohol; C, reaction vessel; D, mercury; E, sample bulb; F, constant speed stirrer; G, evacuated, ground-glass stopper; H, dilatometer, capillary sealed in a 50-ml. buret.

bonded to the central metal ion.[3]   There is a lack of information on the stabilities of complexes in systems in which fluoride, bromide, nitrite, and cyanide ions are the ligands.

Various workers, using a variety of types of calorimeters, have accumulated direct values for heats of complexation,[4–13] although most of the work has been done on nitrogen donor atoms or nitrogen and oxygen donor atoms such as ammonia, ethylenediamine, trimethylenediamine, and the ethylediaminetetraacetate ion.   Schug and King[5] investigated the chromium(III)–chloride system, and Latimer and Jolly[6] made

(3) J. Bjerrum, G. Schwarzenbach, and L. G. Sillén, "Stability Constants of Metal Complexes with Solubility Products of Inorganic Substances, Part I, Organic Ligands (1957), and Part II, Inorganic Ligands (1958)," The Chemical Society, London.

(4) K. B. Yatsimirskii and P. M. Milyukov, *Zh. Neorgan. Khim.*, **2**, 1046 (1957); *Zh. Fiz. Khim.*, **31**, 842 (1957).

(5) K. Schug and E. L. King, *J. Am. Chem. Soc.*, **80**, 1089 (1958).

(6) W. M. Latimer and W. L. Jolly, *ibid.*, **75**, 1548 (1953).

(7) R. G. Charles, *ibid.*, **76**, 5854 (1954).

(8) F. Basolo and R. K. Murmann, *ibid.*, **76**, 211 (1954).

(9) W. S. Fyfe, *J. Chem. Soc.*, 2023 (1952).

(10) T. Davies, S. S. Singer, and L. A. K. Staveley, *ibid.*, 2304 (1954).

(11) I. Poulsen and J. Bjerrum, *Acta Chem. Scand.*, **9**, 1407 (1955).

(12) K. B. Yatsimirskii and L. B. Guskova, *Zh. Neorgan. Khim.*, **2**, 2039 (1957).

(13) K. B. Yatsimirskii and L. L. Pankova, *Zh. Obsch. Khim.*, **18**, 2051 (1948); **19**, 617, 623 (1949).

some measurements on the aluminum–fluoride system. Yatsimirskii and co-workers[12,13] have investigated thiosulfate complexes of cadmium and zinc and a few complexes of cobalt with ammonia and X, where X has been water, chloride, iodide, and nitrite.   The particular generality of the calorimetric technique has not been extensively utilized to obtain results not accessible from stability constant data.

In this paper, data are reported on the heats of complexation of cyanide ion with a series of divalent first row transition metal sulfates, and the ligand field splitting parameters of some hexacyano metal complexes are estimated.

Experimental

(A) **The Calorimeter.**—The calorimeter is similar to the Bunsen ice calorimeter[14] except that *t*-butyl alcohol is used rather than water.   Therefore, the calorimeter constant is dependent on the heat of fusion of *t*-butyl alcohol and the densities of the liquid and solid phases at 25.4°, the melting point of *t*-butyl alcohol.

The calorimeter was constructed from Pyrex tubing of various standard sizes (Fig. 1).   The reaction vessel (C), fitted with an evacuated ground-glass stopper (G), is surrounded by a solid–liquid mixture of *t*-butyl alcohol (B), which is entrapped by a mercury column (D) that is brought out of the calorimeter to a horizontally mounted dilatometer (H).   The reaction vessel and the *t*-butyl alcohol compartment are sealed inside an evacuated silvered vessel (A).   The contents of the reaction vessel are stirred by a glass stirrer (F) driven by a 130 r.p.m. constant-speed motor, and the sample holder (E) has a thin glass bottom to facilitate the addition of the transition metal ion to the potassium cyanide solution.

The calorimeter is in a constant temperature water bath, which is regulated such that the drift rate is minimized.   The drift rate is the rate of change of length of the mercury thread in the dilatometer when the calorimeter is at equilibrium.   The drift rate incorporates all heat leaks (into and out of the calorimeter) in addition to the heat added by the stirrer.

A "dummy dilatometer," a duplicate of the dilatometer, is mounted beside the dilatometer and extends into the water bath.   The changes in the "dummy dilatometer" readings compensate for room temperature variations and are subtracted algebraically from the dilatometer readings.

(B) **Preparation of the Metal Ion Solutions.**—Solutions (0.4 M) of $CoSO_4$, $MnSO_4$, and $FeSO_4$ were prepared from oxygen-free double-distilled water and recrystallized reagent grade commercial salts.   A pure iron wire was placed in the $FeSO_4$ solution and a nitrogen atmosphere was maintained to prevent oxidation.

$CrSO_4$ was prepared[15] from a solution of $Cr_2(SO_4)_3$ in 2 N H_2SO_4. The solution was reduced electrolytically, on a mercury electrode, at 0.02 amp./cm.² until the cathode solution was clear blue. After the solution had been completely reduced, it was transferred from the storage bulb to a container fitted with a "fritted disk." $CrSO_4$ was precipitated by addition of oxygen-free 95% ethyl alcohol.   The crystals were washed with alcohol, dissolved in oxygen-free, double-distilled water, recrystallized, and washed with alcohol.   A stream of "high purity" nitrogen, which had been bubbled through a $CrCl_2$ tower, swept away the excess alcohol and prevented oxidation.   The crystals were dissolved *in situ*, and the solution was analyzed.[16]   Then the volume was adjusted such that the final solution was approximately 0.4 M

(14) W. Swietoslawski, "Microcalorimetry," Reinhold Publishing Corp., New York, N. Y., 1946, pp. 53–70.

(15) A. Asmanov, *Z. anorg. allgem. Chem.*, **160**, 209 (1926).

(16) W. F. Hillebrand, G. E. F. Lundell, H. A. Bright, and J. I. Hoffman, "Applied Inorganic Analysis," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1953, pp. 527–530.
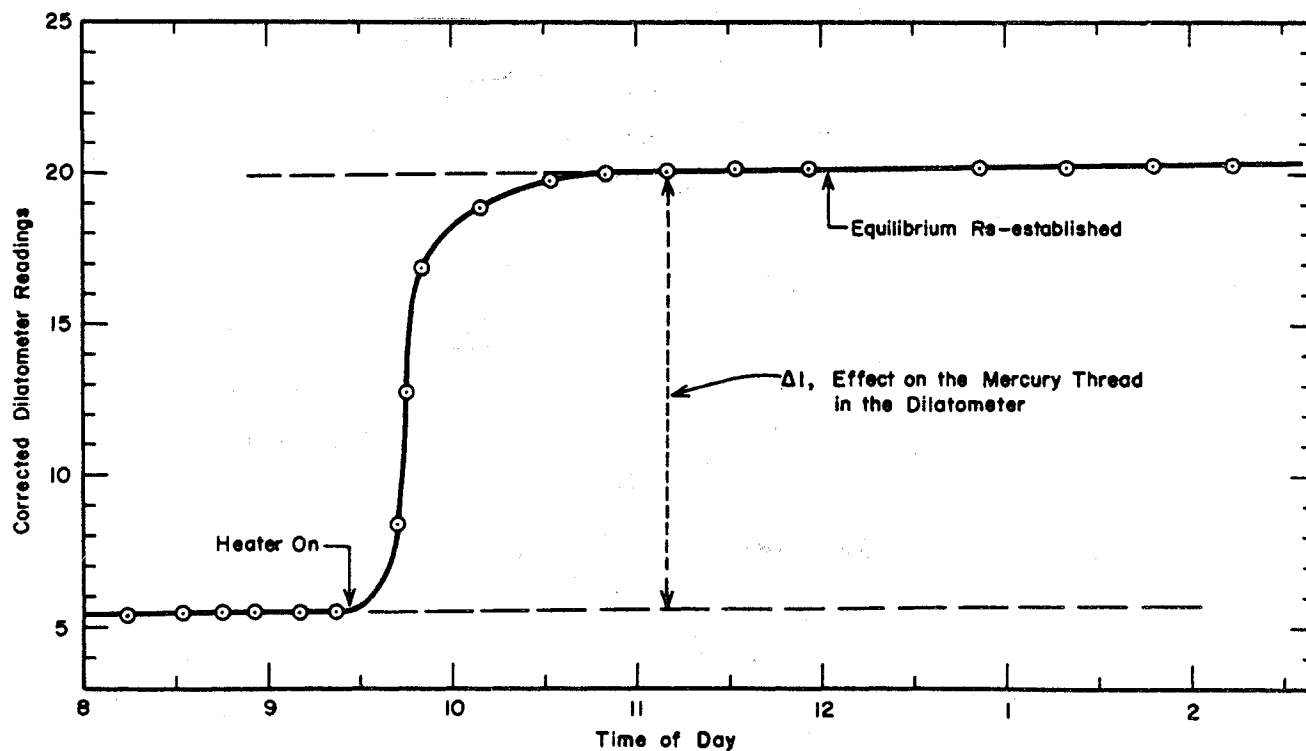
Fig. 2.—Calibration run no. 10. Corrected dilatometer readings *vs.* time of day.

with respect to chromium(II) ion, and the solution was analyzed again.

VSO$_4$ was prepared in a manner similar to that employed by Jones and Colvin.[17] Pure V$_2$O$_5$ (200 g.), concentrated H$_2$SO$_4$ (300 ml.), and H$_2$O (700 ml.) were placed in the cathode compartment of the nitrogen atmosphere preparation line. The solution in the cathode compartment, which was separated from the anode by an alundum diaphragm, was reduced on a mercury cathode at 0.10 amp./cm.^{2} until the solution was violet. A portion of the reduced solution was transferred to the filtration flask and filtered through the sintered glass disk, and the filtrate, which contained the VSO$_4$, was allowed to flow into a filter flask, which had been partially filled with absolute alcohol. The crystals obtained in this manner were washed several times with slightly acidic ethanol. The crystals were dried *in vacuo* for 1 hr. and stored under nitrogen, which had been passed through a chromous chloride tower. If VSO$_4$·7H$_2$O crystals are dissolved in water, the resulting solution is yellow rather than violet. However, if one dissolves these crystals in 0.05 *N* acid, the solution remains violet as long as oxidation does not take place. The yellow solution turns violet upon the addition of sulfuric acid. Therefore, the yellow color probably is due to hydrolysis rather than oxidation of the V^{+2} ion.

Reagent grade potassium chrome alum was recrystallized from an aqueous solution, separated from the mother liquor by filtration, dried in air for 15 min., and stored in a sealed bottle.

Potassium ferric alum was prepared by dissolving a stoichiometric amount of reagent grade Fe$_2$(SO$_4$)$_3$ and reagent grade K$_2$SO$_4$ in dilute H$_2$SO$_4$. The volume was reduced at approximately 100°, and the solution was chilled in an ice bath and stirred occasionally. The crystals were separated from the solution (while cold), washed with ice-water, and stored in a sealed bottle at −8°. The crystals, at −8°, are pale violet.

A 1.0 *M* stock solution of KCN was prepared from oxygen-free, double-distilled water and reagent grade KCN. This stock solution was used for all complexation reactions.

(C) The Calibration of the Calorimeter.—The calorimeter was calibrated by introducing a known amount of energy into the reaction vessel electrically. After the heat had been introduced, the length of the mercury thread in the dilatometer was tabulated

(17) G. Jones and J. H. Colvin, *J. Am. Chem. Soc.*, **66**, 1573 (1944).

with other data, *i.e.*, bath temperature, room temperature, time, atmospheric pressure, and the length of the mercury thread in the "dummy dilatometer." The corrected dilatometer readings were plotted *vs.* time (Fig. 2). The initial and final drift rates were extrapolated and the apparent effect on the mercury thread in the dilatometer (ΔL) was determined. The calorimeter constant, K, was calculated, and the enthalpy change for a reaction that had taken place in the calorimeter, Δh, could be calculated by using the simple expression $\Delta h = K\Delta L$.

In addition to calibration with an electrical heater, the calibration was checked by measuring the heat of dilution of sulfuric acid. The heat of dilution of sulfuric acid was repeated and the precision was within the experimental error. The precision of the data obtained in the electrical calibration was better than three parts per thousand.

Results

Measurement of Heats of Complexation.—In all the experiments where complexation with cyanide ion was studied, 250 ml. of 1.0 *M* KCN was placed in the reaction vessel and the transition metal ion source was placed in the small sample bulb. The source of transition metal ion was a known volume (∼4 ml.) of 0.4 *M* metal sulfate in the case of cobalt(II), iron(II), manganese(II), zinc(II), and chromium(II). Consequently, the cyanide to metal ion ratio was about 160 to 1.

Since vanadous sulfate hydrolyzed rapidly, it was necessary to measure three heats of reaction in the calorimeter, and by application of Hess's law, the desired heat was obtained.

(1)　　　　VSO$_4$·7H$_2$O(s) + H$_2$O ⟶

　　　　　　　　　　　　0.4 *M* (yellow soln.)

(2)　　　　0.4 *M* (yellow soln.) +

　　　　　　250 ml. 1 *M* KCN ⟶ products

(3)　　　　VSO$_4$·7H$_2$O(s) + H$_2$O (slightly acidic) ⟶

　　　　　　　　　　　　0.4 *M* (violet soln.)

$$\Delta H_1 + \Delta H_2 - \Delta H_3 = \Delta H_c$$

(1 + 2 − 3)   0.4 M (violet soln.) +

250 ml. 1 M KCN ⟶ products

During the experiments in the calorimeter, precautions were taken to avoid oxidation. The calorimeter was flushed with high purity nitrogen, which had been bubbled through a chromous chloride tower, and diffusion of air into the calorimeter was prevented by maintaining a nitrogen atmosphere over the entrances of the calorimeter.

The initial drift rate was established and the reaction was allowed to occur by breaking the small sample bulb. Dilatometer readings were recorded, as in the calibration runs, and plotted *vs.* time. ΔL, the effect on the dilatometer, was determined, and Δh, the enthalpy change for the reaction, was calculated.

The reactions of ferric alum and chromic alum with 1.0 M KCN were also studied. In these cases, the solid alum rather than a solution of the alum was placed in the small sample bulb.

The chromic alum, regardless of particle size, did not react to an appreciable extent with the 1.0 M KCN. In spite of attempts to catalyze the reaction with CrSO$_4$, practically no reaction of chromic alum with cyanide ion occurred; a large amount of unreacted
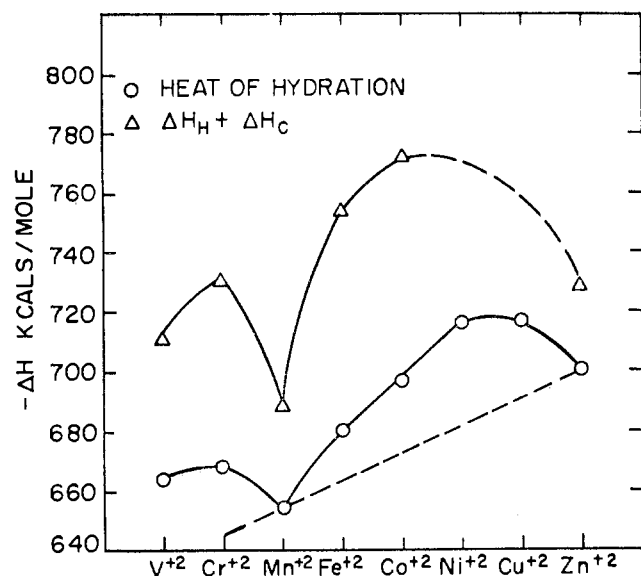

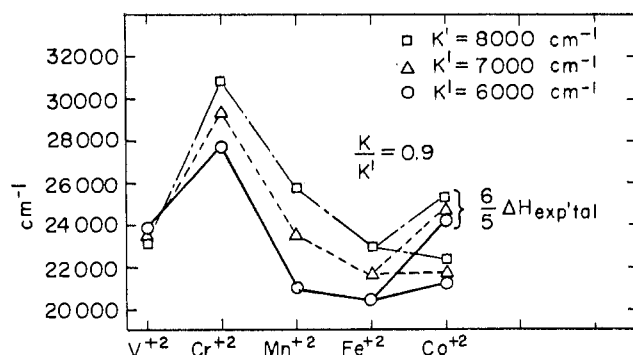Fig. 4.—Δ' *vs.* atomic number.

chromic alum was found in the reaction vessel after each attempt. Because of these difficulties, the heat of complexation for chromic alum with 1.0 M KCN was not determined.

The heats of complexation which were obtained are tabulated in Table I. The tabulated values represent the average of at least two or, in most cases, three runs.

Discussion

The instability constants for CoSO$_4$, FeSO$_4$, MnSO$_4$, and ZnSO$_4$ are approximately 5×10^{-3}. Consequently, the MSO$_4$ complexes do not dissociate much more than 10% in a 0.4 M solution. If the heat of dilution of MSO$_4$ from 0.4 M to infinite dilution were subtracted from the heat of complexation reported here, the resulting enthalpy change would correspond to the heat absorbed accompanying the replacement of water molecules by cyanide ions.

The one exception to this statement would be the reaction of CoSO$_4$ and KCN. The product of this particular reaction is not the hexacyano complex; it may be the pentacyanomonoaquo complex[18] or a dimer of the pentacyano complex. The species in solution has not been elucidated yet. The cyanide complexes of the other ions should be hexacoordinated,[19-22] the exception being the tetracyanozincate ion.

The heats of dilution of the metal sulfates have not all been reported, but the values for MnSO$_4$ and ZnSO$_4$ are approximately -0.72 kcal./mole. Since the heat of dilution is quite small compared to the measured heats of complexation and one may assume that the heats of dilution of the divalent metal sulfates are the same magnitude, 0.7 kcal./mole could be added to the measured heats of complexation for the computation of the heat of reaction for the replacement of water molecules by cyanide ions.

The cyanide ion has been thought to exert the strongest ligand field on a metal ion, thereby forming a very strong bond. The data presented here corroborate this contention. The heats of complexation
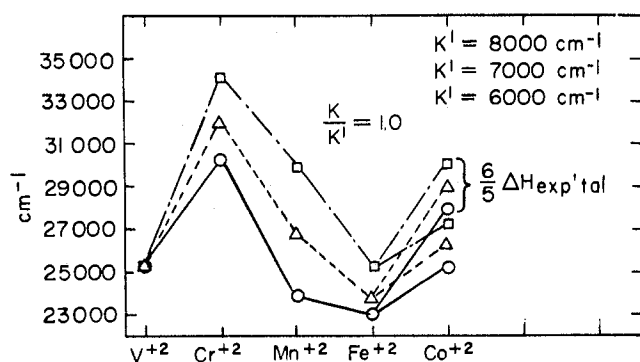

Fig. 3.—ΔH *vs.* atomic number.

TABLE I
HEATS OF COMPLEXATION

0.4 M metal ion sulfate	Av. ΔH_c, kcal./mole	Precision, %
V^{+2}	−47.0	±0.81
Cr^{+2}	−63.2	±0.47
Mn^{+2}	−34.5	±0.05
Fe^{+2}	−73.7	±0.54
Co^{+2a}	−74.4	±1.15
Zn^{+2}	−27.7	±0.45
Fe^{+3b}	−68.0	±0.23

a The product formed in this case may be [Co(CN)$_5$OH$_2$]$^{-3}$ or a dimer rather than [Co(CN)$_6$]$^{-4}$. *b* This ΔH_c corresponds to the reaction of KFe(SO$_4$)$_2$·12H$_2$O(s) with 1 M KCN at 25.4°.

(18) A. W. Adamson, *J. Am. Chem. Soc.*, **73**, 5710 (1951).
(19) S. Freedman and C. Kasper, *ibid.*, **52**, 1012 (1930).
(20) W. Kemula, S. Siekierski, and K. E. Siekierski, *Roczniki Chem.*, **29**, 966 (1955) (English summary).
(21) H. T. S. Britton and E. N. Dodd, *J. Chem. Soc.*, 1940 (1932).
(22) D. N. Hume and H. W. Stone, *J. Am. Chem. Soc.*, **63**, 1200 (1941).

Fig. 5.—Δ' vs. atomic number.

Fig. 6.—Δ' vs. atomic number.

with cyanide are as high as 12 kcal./mole/bond. The heats of complexation for ammination are usually about 4 kcal./mole/bond, and the heats of complexation with ethylenediaminetetraacetic acid are approximately 1.5 to 3 kcal./mole/bond.

It has been pointed out[23] that the ligands of an octahedral complex are capable of forming π-bonds by using empty p-π or d-π orbitals. In doing so, the t_{2g} orbitals are depressed with respect to the e_g orbitals. This effect is very important in cyanide complexes, where it lowers the energy of the t_{2g} orbitals of the metal and produces a very large value of Δ', the ligand field splitting parameter. (Unfortunately, the contribution to Δ' due to π-bonding cannot be separated from the other contributions.)

Since the nature of the ligand field changes in going from the hexaaquometal ion to the hexacyano complex, the magnitude of the ligand field splitting varies and this variation may manifest itself in the magnitude of the heat of complexation. For each electron in the t_{2g} energy level the amount of heat evolved should be $0.4\Delta'$ greater and for each electron in the e_g energy level the amount of energy evolved should be $0.6\Delta'$ smaller.

The cyanide complexes are expected to be low-spin complexes, and due to pairing energy considerations the d^5 configuration has been predicted to have a minimum in heat of complexation, as does the heat of hydration[24] (Fig. 3). The question arises—how much energy is required to pair electrons in the same orbital? A theory, which is somewhat quantitative, has been developed independently by Orgel[25] and Griffith.[24] The pairing energy is assumed to be approximately equal to the difference between the exchange energies of the two complexes. The exchange energy for the aquo complexes is approximately NK, where K is the mean exchange energy for one pair of electons and N is a coefficient which is determined by the electronic configuration of the central metal ion. For the cyanide complexes, the exchange energy is approximately $N'K'$, where K' is the mean exchange energy for one pair of electrons and N' is a coefficient which is determined by
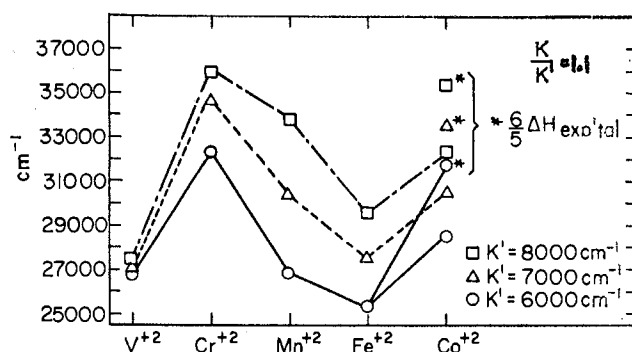
the electronic configuration of the metal ion. The pairing energy is then approximated as $NK - N'K'$.

Estimation of Δ'

Method I.—One can write the expressions for the heat of complexation, ΔH_n, where n is the number of d electrons in the divalent ion, and Δ_n is the value of the crystal field splitting parameter of the aqueous complexes.

$$\Delta H_3 = -1.2\Delta'_3 + 1.2\Delta_3 + \text{P.E.} \qquad \text{P.E.} = 3K - 3K'$$
$$\Delta H_4 = -1.6\Delta'_4 + 0.6\Delta_4 + \text{P.E.} \qquad \text{P.E.} = 6K - 3K'$$
$$\Delta H_5 = -2.0\Delta'_5 + \text{P.E.} \qquad \text{P.E.} = 10K - 4K'$$
$$\Delta H_6 = -2.4\Delta'_6 + 0.4\Delta_6 + \text{P.E.} \qquad \text{P.E.} = 10K - 6K'$$
$$\Delta H_7 = -1.8\Delta'_7 + 0.8\Delta_7 + \text{P.E.} \qquad \text{P.E.} = 11K - 9K'$$

The values of Δ_n are well known[26]: $\Delta_3 = 11,800$, $\Delta_4 = 14,000$, $\Delta_6 = 10,000$, $\Delta_7 = 9300$ cm.$^{-1}$. The values of ΔH_n are those reported in Table I, subject to the correction of 0.7 kcal./mole (the heat of dilution of the MSO_4): $\Delta H_3 = -16,200$, $\Delta H_4 = -21,900$, $\Delta H_5 = -11,800$, $\Delta H_6 = -25,500$, $\Delta H_7 = -25,800$, $\Delta H_{10} = -9440$ cm.$^{-1}$. Using the values above for ΔH_n and Δ_n, and solving for Δ'_n

$$\Delta'_3 = 25,300 \text{ cm.}^{-1} + K'(-2.5 + 2.5K/K')$$
$$\Delta'_4 = 18,900 \text{ cm.}^{-1} + K'(-1.875 + 3.75K/K')$$
$$\Delta'_5 = 5900 \text{ cm.}^{-1} + K'(-2.0 + 5K/K')$$
$$\Delta'_6 = 12,300 \text{ cm.}^{-1} + K'(-2.5 + 4.167K/K')$$
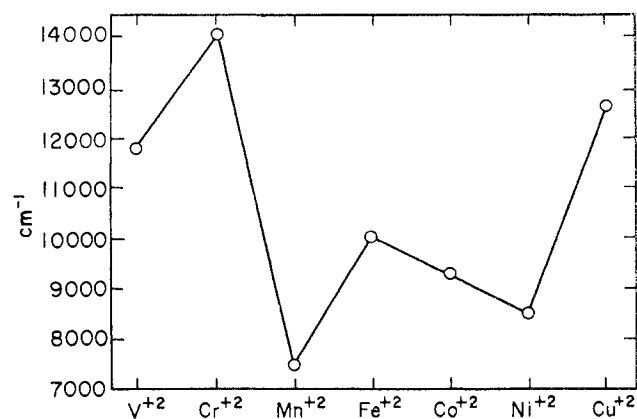$$\Delta'_7 = 18,500 \text{ cm.}^{-1} + K'(-5.0 + 6.111K/K')$$

If the ratio of K to K' is allowed to vary and if some value is given to K', the values of Δ'_n could be tabulated or graphically represented (Fig. 4, 5, 6).

The pairing energy of iron(II)[27] is approximately 24,000 to 26,000 cm.$^{-1}$, which indicates that K is approximately 7000 cm.$^{-1}$. Therefore, the value K' will be allowed to vary from 6000 to 8000 cm.$^{-1}$.

In Fig. 4, 5, and 6, two values of Δ' for cobalt(II) are plotted for each value of K' at a given ratio of K to K'. The higher result, in each case, is calculated by allowing the heat of complexation to be equal to $6/5$ times the experimentally determined heat of complexation. This is equivalent to assuming that each

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(24) J. S. Griffith, *J. Inorg. Nucl. Chem.*, **2**, 1, 229 (1956).
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Fig. 7.—Δ_{H_2O} vs. atomic number.

Ion	$-\Delta H_{lig}$, kcal./mole	Rel. ΔH_{lig}, kcal./mole	δH = C.F.S.E. $-$ P.E., kcal./mole	Δ' or $10Dq$, cm.$^{-1}$
V^{+2}	711	$+18$	-47.8	13,900
Cr^{+2}	731	-2	-58.4	25,500
Mn^{+2}	688	$+41$	-6.0	23,800
Fe^{+2}	754	-25	-62.6	24,400[a]
Co^{+2}	771	-42	-70.2	...
Zn^{+2}	729	0	0	...

[a] If the pairing energy for Fe^{+2} is 26,000 cm.$^{-1}$, the value of Δ' or $10Dq$ is 20,000 cm.$^{-1}$.

new cyanide metal bond is identical with respect to the heat of formation of the six stepwise bonds, if it were possible to prepare the hexacyanocobaltate(II) anion in this manner.

Another assumption in this treatment of the thermal data is that the K to K' ratio is independent of the change in atomic number. Attempts were made to include a spherical field term in the calculations, but the nature of the data did not lend itself to this treatment.

The shapes of the curve for Δ_{H_2O} vs. atomic number (Fig. 7) and the curve for Δ' vs. atomic number are similar. As an electron is added to the half-filled lower triplet, there is a large increase in the splitting parameters. As an electron is added to the half-filled upper doublet of the aquo complex or to the empty doublet of the cyano complex, another sharp increase in the splitting parameter is observed. Although this qualitative trend is interesting, attempts to make it quantitative were not successful.

Method II.—Orgel[28] has calculated the pairing energies of Cr^{+2}, Mn^{+2}, and Fe^{+2} in terms of Slater–Condon parameters. If these values are used with the heats of complexation, Δ' values could be calculated. The pairing energies are V^{+2}, 0; Cr^{+2}, 20,425; Mn^{+2}, 45,600; Fe^{+2}, 36,725 cm.$^{-1}$.

$16,200 = 1.2\Delta'_3 - 1.2(11,800)$	$\Delta'_3 = 25,300$ cm.$^{-1}$
$21,900 = 1.6\Delta'_4 - 0.6(14,000) - 20,425$	$\Delta'_4 = 31,700$ cm.$^{-1}$
$11,800 = 2\Delta'_5 - 45,600$	$\Delta'_5 = 28,700$ cm.$^{-1}$
$25,500 = 2.4\Delta'_6 - 0.4(10,000) - 36,725$	$\Delta'_6 = 27,600$ cm.$^{-1}$

These values agree fairly well with those obtained in method I when K equals K'.

Method III.—For comparison, the results in Table II have been obtained from the heats of ligation, which is the summation of the heat of hydration and the heat of complexation. The heats of ligation, in the absence

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of a ligand field, were assumed to have the same slope as the "corrected heats of hydration," *i.e.*, the straight line drawn through the heat of hydration of Mn^{+2} and Zn^{+2}.

The δH corrections in column 4 are necessary to make the heats of ligation lie on a straight line passing through the heat of ligation of Zn^{+2} with a slope equal to "the corrected heats of hydration" (Fig. 3). If these values are equal to the crystal field stabilization energy (C.F.S.E.) minus the pairing energy (P.E.), the value of $10Dq$ or Δ' could be calculated. The values of Δ' obtained in this manner compare favorably with those obtained by methods I and II.

Although methods I and II do not include any spherical corrections for estimating the Δ' values, the spherical corrections imposed on the heats of ligation in method III may be far too stringent. The estimates of Δ' for the various metal–cyanide complexes derived from the three methods should at least provide us with some data concerning the magnitude of the ligand field splitting.

Summary

As a result of this investigation, the heats of complexation of cyanide ion with V^{+2}, Cr^{+2}, Mn^{+2}, Fe^{+2}, Co^{+2}, and Fe^{+3} are known. By neglecting the spherical field contribution to the heats of complexation and by employing pairing energy approximations, an upper limit has been established for the Δ' values for the hexacyano complexes of some divalent ions. If the spherical field contribution to the heats of complexation were very small, these maximum values for Δ' would be accurate estimates. If the contributions to the heats of complexation due to spherical field changes are elucidated, or if the values of Δ' for this series of complexes are determined from their spectra, the ligand field theory could be applied to these data more rigorously.