dra (positions 000). It must be assumed that the withdrawal of Na^+ (vacant sites remaining) causes the expansion of the lattice, but the process $W^{5+} \rightarrow W^{6+}$ ($W^{5+} + Na^+ = Na^\circ + W^{6+}$) or absorption of tungstic oxide causes the contraction of the lattice. Since there is enough space for the sodium ions, their removal causes only a slight expansion of the lattice, which is surpassed by the contraction involved by the W^{6+}. The lattice thus contracts with increasing tungstic oxide concentration C ($da/dC = -8.3 \times 10^{-4}$ Å. per weight % WO_3).

The small lithium ions (r = 0.6 Å.) contract the whole lattice appreciably, so that the radius of the oxygen ions is only 1.32 Å. When the lithium ions are removed from the lattice, the expansion becomes larger than the contraction. The solution of tungstic oxide in the bronze is associated with the formation of vacant sites (in the places of lithium ions) and the highly contracted lattice therefore expands ($da/dC = 4 \times 10^{-4}$ Å. per 1% WO_3 for the middle part of the curve, Fig. 1).

Figure 1 shows that a lithium tungsten bronze with a content less than 43% by weight of tungstic oxide would have a still smaller lattice constant. But this is evidently impossible, because the radius of the oxygen ions in this case must be smaller than 1.32 Å., which is already a very low value. The pure $LiWO_3$, therefore, cannot exist, at least not in the same lattice type.

The lithium ions can slip through the openings between the octahedra, having a width of 0.54 Å., because of their small size (r = 0.6 Å.). Therefore, the lithium tungsten bronzes are also ionic conductors already at 450°. Sodium ion (r = 0.95 Å.) cannot slip through and up to 450° the sodium bronze shows only electronic conductivity.

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Summary

It has been proven that the blue lithium tungsten bronze consists of $LiWO_3$, in which at least 42.6 ± 2% by weight tungsten(VI) oxide has been dissolved. Its composition may be represented by the formula $LiW^{V}O_3(W^{VI}O_3)_{0.77}$. The pure lithium tungsten bronze ($LiWO_3$) could not be obtained.

The bronze with 42.6% tungstic oxide is cubic (a = 3.7218 Å.) and possesses the perovskite ($CaTiO_3$) type structure.

The bronze can dissolve up to 68% tungstic oxide (at 900°) under expansion of the lattice, without changing the structure type. An anionic substitutional solid solution results.

The chemical behavior of the bronze can be explained on the basis of the reversible reaction $LiW^{V}O_3(W^{VI}O_3)_x \rightleftarrows Li^\circ + (1 + x)WO_3, x = 0.77$. Li can easily be bound by iodine or tungstic oxide.

The electric conductivity of the blue bronze (with 43% WO_3) in vacuum above 450° varies around 53 ohm^{-1}. At room temperature the conductivity is about 23 ohm^{-1}.

The temperature coefficient of conductivity is positive at lower temperatures. Conductivity is therefore ionic. Electronic conductivity may also exist.

The conductivity decreases with increasing concentration of tungsten(VI) oxide in the bronze.

The changes in conductivity caused by moist air are very similar to those of the sodium tungsten bronzes.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF SOUTHERN CALIFORNIA]

Exchange Studies with Complex Ions. I. The Exchange of Radiocyanide with Certain Heavy Metal Complex Cyanides[1]

BY ARTHUR W. ADAMSON, JOAN P. WELKER[2] AND MILTON VOLPE[3]

Early studies in the field of complex ions have yielded a degree of understanding of the descriptive chemistry and structural relationships of these compounds such that, in recent years, increased attention is being directed toward the more difficult problem of determining the mechanism of their formation and reaction. The group of complex cyanides constitute an important example of this point. These complex ions have been described in terms of methods of synthesis, composition, appearance and their simple reactions. The structure of a number of them has been established[4] and thermodynamic

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(1) Presented in part in the Symposium on Tracers at the San Francisco Meeting of the American Chemical Society, March–April, 1949.

(2) This paper is based on a portion of a thesis to be submitted by Joan P. Welker in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the University of Southern California.

(3) The work on potassium hexacyanoferrate(II) described in this paper is taken from a thesis to be presented by Milton Volpe to the Graduate School of the University of Southern California in partial fulfillment of the requirements for the degree of Master of Science.

(4) Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1945.

instability constants are available in several cases.[5] Much further information is needed concerning the kinetics of their dissociation into independently stable components and of the oxidation–reduction and other reactions in which they are involved.

Previous exchange studies, involving the heavy metal cyanide complexes, have been limited to the cobalt, iron and chromium compounds. Even then only the exchange of the central metal ion was investigated. Flagg[6] studied the exchange of Co^{+2} and $Co(CN)_6^{-3}$ and obtained negative results. Thompson[7] found that no metal ion exchange occurred in the four systems $Fe(CN)_6^{-3}$–Fe^{+3}, $Fe(CN)_6^{-3}$–Fe^{+2}, $Fe(CN)_6^{-4}$–Fe^{+3}, $Fe(CN)_6^{-4}$–Fe^{+2}. The exchange between $Fe(CN)_6^{-4}$ and $Fe(CN)_6^{-3}$ was reported[7,7a] to be complete in the time required for separation. Menker and Garner[8] investigated the system $Cr(CN)_6^{-3}$–Cr^{+3} and their results indicate that appreciable exchange occurred in solutions acidified with perchloric or acetic acid. No exchange was observed when hydrochloric acid was the acidifying agent.

The purpose of the present investigation has been to make a general survey of the exchange behavior of a number of complex cyanides. It was felt that more valuable results would be obtained if the exchange reactions were carried out with the coördinated group rather than with the central ion. Accordingly, experiments completed so far have centered about the exchange of radiocyanide ion with a series of complex cyanides.

Experimental Results

The complex cyanides chosen for this study are listed in Table I, and were selected as the more stable representatives of each coördination type. To permit an intercomparison of behavior, the exchange of each compound with C^{14}-labelled radiocyanide was measured under comparable conditions. The concentrations of complex ion and cyanide were approximately 0.05 *f*, respectively, the *p*H corresponded to the unadjusted or "natural" value of *ca.* 10 for the solution of the two substances. In addition, the effect on the exchange rates of varying the *p*H was determined in certain instances (*cf.* Table II).

The exchange experiments were carried out by mixing solutions of the complex ion and potassium radiocyanide and then chemically separating the two components. The loss of specific activity of the radiocyanide was then determined. The radiocyanide was converted to the zinc salt for the specific activity measurements, and the details of this procedure, as well as of the separation methods employed, are summarized in the Appendix. Also included in this section are the methods of synthesis and analysis of the complex compounds studied.

The results of this survey of exchange behavior are presented in terms of the percentage exchange, *E*, observed for various exchange times. In the present paper *E* is defined by the equation

$$E = 100(a/b)(y/x)$$

where *a* and *b* denote the moles of free cyanide and of cyanide in the complex, respectively, and *x* and *y* the amounts of radioactivity in the two forms after the elapse of the exchange time.

A summary of the exchange data is presented in Tables I and II. It is readily apparent that the di- and tetracyanides exchanged immeasurably rapidly and the hexacyanides (with the exception of potassium hexacyanomanganate (III)), very slowly at *p*H *ca.* 10. The exchange of the one octocyanide studied was found to be strongly photocatalyzed. These and other aspects of the exchange results for the various complexes are discussed in more detail under separate headings.

TABLE I

DATA ON THE EXCHANGE OF RADIOCYANIDE WITH COMPLEX CYANIDES AS MEASURED UNDER COMPARABLE CONDITIONS AT 25°

Compound	Concentrations, mole/liter Complex	Cyanide	*p*H	Exchange time[a]	Exchange, %
$K_2Ni(CN)_4$	0.0500	0.0500	10.1	*ca.* 3 min.	100
$K_2Pd(CN)_4$	.0500	.0500	*ca.* 10	*ca.* 3 min.	118[b]
$K_2Hg(CN)_4$[c]	.025	.024	*ca.* 10	*ca.* 5 min.	*ca.* 100
$Hg(CN)_2$[c]	.050	.048	*ca.* 10	*ca.* 15 sec.	115[b]
$K_3Mn(CN)_6$	.0625	.1063	*ca.* 11	*ca.* 2 min.	9.7
	.0625	.1063	*ca.* 11	*ca.* 4 min.	40.2
$K_3Cr(CN)_6$	.0500	.0500	10.5	*ca.* 3 min.	0.0
	.0500	.0500	10.5	66.7 hr.	0.9[d]
	.0500	.0500	10.5	189.2 hr.	2.6[d]
$K_4Fe(CN)_6$	.0852	.0568	11.8	Short	0.0
	.0852	.0568	11.6	118 hr.	0.7[d]
$K_3Fe(CN)_6$	.0500[e]	.0500[e]	10.5	*ca.* 6 min.	3.7
	.0500[e]	.0500[e]	*ca,* 10	115 hr.	1.0[f]
$K_3Co(CN)_6$	.0500	.0500	10.8	*ca.* 3 min.	0.7
	.0500	.0500	10.8	69.5 hr.	0.0
	.0500	.0500	10.8	190.5 hr.	0.0
$K_4Mo(CN)_8$	.0528	.0472	10.3	Short	0.7
	.0528	.0472	10.3	7.3 hr.	3.1
	.0528	.0472	10.3	142.8 hr.	12.4
	.0528	.0472	10.3	311.7 hr.	21.9
	.0528	.0472	10.3	143.5 hr.	0.0[f]
	.0528	.0472	10.3	264.0 hr.	0.0[f]
KCNO	.050	.050	*ca.* 10	43 hr.	0.0

[a] The short contact times are approximate due to uncertainties in estimating the time of settling of precipitates during centrifugation. [b] Only a single experimental determination made. [c] Two different separation procedures employed. [d] Such small per cent. exchange values are significant since they correspond to an appreciable decrease in specific activity of radiocyanide. [e] Initial concentrations, *i. e.* before occurrence of the oxidation–reduction reaction (*cf.* text). [f] Dark runs.

Di- and Tetracyanides.—The immeasurably fast exchange of these complexes at *p*H *ca.* 10 did not necessarily occur in solution since the possibility of rapid exchange induced during separation was not eliminated. To test this

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(5) Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1938.

(6) Flagg, THIS JOURNAL, **63**, 557 (1941).

(7) Thompson, *ibid.*, **70**, 1045 (1948).

(7a) Cobble and Adamson, *ibid.*, **72**, 2277 (1950).

(8) Menker and Garner, *ibid.*, **71**, 371 (1949).

TABLE II

EFFECT OF pH ON THE EXCHANGE RATES OF RADIOCYANIDE WITH CERTAIN COMPLEX CYANIDES AT 25°

Compound	Concentrations, moles/liter Complex	Cyanide[a]	pH[b]	Exchange time, hr.	Exchange, %
$K_3Cr(CN)_6$	0.0472	0.0472	3.3[c]	52.5	5.1
	.0472	.0472	2.4[c]	50.9	9.0
	.0472	.0472	2.3[c]	76.2	12.1[d]
	.0500	.0500	10.5	66.7	0.9
	.0493	.0493	11.7	50.3	0.7
$K_4Fe(CN)_6$	.0852	.0568	4.4[e]	82.0	6.8[d]
	.0852	.0568	4.4[e]	118	10.4
	.0852	.0568	7.0	101	0.6
	.0852	.0568	11.6	118	0.7
$K_3Co(CN)_6$	.0474	.0474	3.6	96.9	0.9
	.0481	.0481	7.5	96.9	2.2
	.0500	.0500	10.8	190.5	0.0
	.0495	.0495	11.8	97.3	3.2
$K_4Mo(CN)_8$	.0491	.0439	4.3	138.8	1.6[f]
	.0500	.0446	7.5	166.5	1.0[f]
	.0528	.0472	10.3	143.5	0.0[f]
	.0523	.0467	11.9	160.3	1.1[f]

[a] Despite the precautions taken, the cyanide concentrations for acid solutions may be in error due to escape of hydrogen cyanide. [b] Perchloric acid was the acidifying agent in all cases. [c] Initial pH values, *i. e.*, before excessive complex decomposition occurred. [d] Dark runs to illustrate the absence of photocatalysis. [e] During exchange the pH rose to *ca.* 4.9 (*cf.* text). [f] Dark runs.

point, somewhat different precipitation separation methods were employed in each case, and in one system, two different procedures were used. The results still indicated that exchange was complete in the approximate time required for separation. It is noteworthy that similar precipitation type separations did not catalyze the exchange of the hexacyanides. Thus, it is not unlikely that the observed rapid exchanges were truly solution phenomena.[8a]

Hexacyanides.—Potassium hexacyanomanganate(III) differs from all the other hexacyanides studied here in that it decomposes quite readily in aqueous solution to give hydrous oxides of manganese and free cyanide.[9] This process is inhibited by the addition of free cyanide. Such an effect must surely be due to the mass action repression of the dissociation, and the existence of such an equilibrium would account for the rapid exchange. To establish the kinetics of this exchange,[10] the effect on the exchange rate of varying the concentrations of complex and cyanide, respectively, must be determined. Preliminary experiments made at 0° indicated that the rate was slow enough at this temperature to permit such a study.

As the exchange of radiocyanide and potassium hexacyanochromate (III) was very slow at a pH of *ca.* 10, determinations were made at higher and lower pH's in an effort to increase the rate. No noticeable increase in rate was observed at $p\text{H} > 10$. Unfortunately, some complex decomposition occurred in the more acid solutions which not only diluted the radiocyanide and thus gave a spuriously low specific activity, but also liberated enough cyanide to neutralize the added perchloric acid and raise the pH to *ca.* 7. The rising pH also stopped further decomposition and probably also any exchange. For these reasons the results are qualitative but seem to indicate that the observed decrease in specific activity of the radiocyanide was only partly due to inactive cyanide formed by the decomposition of the complex. Some exchange might be occurring simultaneously.

These observations are of interest in view of the fact that Menker and Garner[8] have previously reported 55% exchange (by our definition) in seventy-two hours between 0.010 *f.* $Cr(ClO_4)_3$ and $K_3Cr(CN)_6$ in low concentration of perchloric acid (pH 3–4). The kinetics of neither of these exchange reactions is known and it therefore seems unwise to attempt at the present time any explanation of these apparently incompatible results.

Exchange in the potassium hexacyanoferrate(II)–cyanide system occurred only in acid solution and was not subject to photocatalysis. It was evident that some net chemical reaction accompanied the exchange. During each run the pH increased and a progressive change in color from yellow to yellow-brown took place. A simultaneous increase in free cyanide concentration did not occur so that complex decomposition was therefore not responsible for the observed lowering in specific activity.

No increase in exchange rate occurred in the pH range 12 to 7 though a marked increase in rate was observed at higher acidities, *e. g.*, pH *ca.* 4. Such an effect cannot be attributed to increasing hydrogen cyanide concentration as at pH 7 free cyanide already exists essentially as hydrogen cyanide. Apparently, either an undissociated acid form of the complex or some other type of aquo-substituted ion (*e. g.*, the formation of $Fe(CN)_5(H_2O)^{-3}$ is favored at low pH's)[11] is involved in the rate-determining step leading to exchange.

The observation that potassium radiocyanide and potassium hexacyanoferrate(III) do not exchange at pH *ca.* 10 is of special interest in view of the fact that in the presence of free cyanide, the complex is reduced to the hexacyanoferrate(II) ion, two moles of complex reacting per mole of cyanide, corresponding to the reaction

$$2Fe(CN)_6^{-3} + CN^- + 2OH^- = 2Fe(CN)_6^{-4} + CNO^- + H_2O$$

The velocity of the reaction depends in a complicated manner upon the concentrations of ferri-

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(8a) Long has recently confirmed our results with $K_2Ni(CN)_4$, using a solvent extraction separation method (private communication).

(9) Meyer, *Z. anorg. Chem.*, **81**, 394 (1913).

(10) *Cf.* Duffield and Calvin, THIS JOURNAL, **68**, 557 (1946).

(11) Williams, *J. Chem. Soc.*, **222** (1948).

cyanide, cyanide and hydrogen ions, but, under the exchange conditions, the reaction proceeded to completion in a few hours. Thus a major fraction of the hexacyanoferrate(III) ion was reduced to hexacyanoferrate(II) without bringing about any interchange of coördinated cyanide with the free cyanide in solution. The exchange of cyanide and cyanate, a product of the oxidation-reduction reaction, was also studied. As may be seen from the last entry in Table I, no detectable exchange occurred with contact times up to forty-three hours.

As potassium hexacyanocobaltate(III) showed no exchange with radiocyanide at *p*H *ca.* 11, several runs were made at *p*H's $\gtrless$ 11. The data indicate that a very small, if not negligible, exchange took place at *p*H's as low as 3.6. A similar result was found on raising the *p*H.

Octocyanide.—The exchange of potassium octocyanomolybdate (IV) and radiocyanide was found to be photocatalyzed at *p*H *ca.* 10. Additionally, it was learned that the dark exchange was negligible at both higher and lower *p*H's. The absorption spectrum of solutions of the complex was determined by means of a Beckman spectrophotometer in the wave length region 530 to 210 mμ. A single and rather diffuse peak was found at 370 mμ, and a much more intense band, also diffuse, but showing a double peak, in the region 290–250 mμ. The absorption obeys Beer's law in the concentration range 5×10^{-4} to 2×10^{-3} *f*. Extrapolation to obtain the amount of absorption in solutions 5×10^{-2} *f*. in complex indicated that in the exchange runs complete absorption of the incident light must have occurred even in the region of the less intense peak.

Discussion

It is of interest to consider what conclusions can be drawn concerning the mechanism of the exchange reactions which have been found to occur. The most obvious possibilities for exchange paths are (1) reversible, rapid dissociation of the complex, and (2) a substitution or inversion type process whereby one group leaves as the other enters. The corresponding kinetic expressions for the exchange rate, *c*,[12] are

$$(1) \quad c = k_1 \text{ (complex) } (1/a + 1/b)$$

$$(2) \quad c = k_2 \text{ (complex) (X) } (1/a + 1/b)$$

where *X* might be CN^-, H_2O, H_3O^+, etc., and k_1 and k_2 are specific rate constants. *a* and *b* have their previously designated significance. Either of these mechanisms would be possible in the case of the di- and tetracyanides studied. The experimental distinction between (1) and (2) cannot be made since the immeasurably rapid exchange precludes the necessary kinetic studies.

The case of the hexacyanides and the octocyanides may be treated with more certainty. It was found that, with the exception of potassium hexacyanomanganate(III), no exchange occurs in neutral or alkaline solution; with the additional exception of potassium hexacyanoferrate(II) and possibly of potassium hexacyanochromate(III), none takes place in solutions of *p*H as low as 2–4. In view of these results for neutral and alkaline solutions, the rate of dissociation must be very small for potassium hexacyanochromate(III), potassium hexacyanoferrate(II), potassium hexacyanoferrate (III), potassium hexacyanocobaltate(III), and potassium octocyanomolybdate(IV).

This conclusion is perhaps not the one to be expected *a priori*. Thus the great stability suggested by the dissociation constants available[5] for potassium hexacyanoferrate(II) and potassium hexacyanoferrate(III), (10^{-37} and 10^{-44}, respectively), is deceptive since the actual concentrations of iron and cyanide ions would be as high as *ca.* 10^{-6} *f* for solutions of complex of the order of concentration employed here. Moreover, by the simple dissociation picture, the equilibrium constant for the first step in the dissociation, *e. g.*, $Fe(CN)_6^{-3} = Fe(CN)_5^{-2} + CN^-$, should be more significant than that for the over-all process, $Fe(CN)_6^{-3} = 6CN^- + Fe^{+3}$. Normally the intermediates in a stepwise dissociation are expected to decrease in concentration, *i. e.*, $Fe(CN)_5^{-2} > Fe(CN)_4^{-1} > Fe(CN)_3$, etc., $> Fe^{+3}$. On this basis the equilibrium constant for the primary reaction should be at least as great as 10^{-12}. In view of the general rapidity of dissociation reactions, this constant is large enough to lead one to predict rapid exchange. The fact that none could be observed clearly shows the above argument to be specious, and it seems probable that the concentrations of intermediates such as those mentioned above must actually be very small. This can be explained on the grounds that loss of a cyanide group should make the octahedral hybridization less stable. It is significant, moreover, that comparatively few pentacoördinated metal complexes are known, and no pentacyanides are known for the metal ions studied here.

Another indication that dissociation is not in general the rate determining mechanism for exchange is the lack of correspondence of exchange rate and thermodynamic stability. In the following table this comparison is made for those cases where approximate stability constants are available.[5] The complex ions are listed in order of increasing concentration of the constituents (*i. e.* dissociation products) in 0.1 *f* solutions of complex (without added cyanide). This arrangement is felt to be of more significance than a tabulation according to increasing instability constants.

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[12] The value of *c* is obtainable from the first order exchange rate equation, $\ln y_\infty/(y_\infty - y) = ct$, where y_∞ and *y* are the specific activity of cyanide in the complex at infinite time and time, *t*, respectively. *c* is also related to the chemical rate at which free cyanide becomes complexed cyanide (or *vice versa*), by the expression: $c = 1R1(1/a + 1/b)$. $1R1$ is equivalent to a specific rate constant times some function of the reagents which is dependent on the reaction mechanism; *cf.* Duffield and Calvin, ref. 10.

TABLE III

COMPARISON OF EXCHANGE RATE AND DISSOCIATIVE STABILITY

Complex	Stability constants	Concn. (*f*) of constituents in a 0.1 *f* soln. of the complex	Exchange rate
$Hg(CN)_4^{-2}$	4×10^{-42}	*ca.* 10^{-6}	Immeasurably fast
$Fe(CN)_6^{-3}$	10^{-44}	*ca.* 10^{-6}	Negligible
$Fe(CN)_6^{-4}$	10^{-37}	*ca.* 10^{-5}	Negligible
$Ni(CN)_4^{-2}$	10^{-22}	*ca.* 10^{-4}	Immeasurably fast
$Mn(CN)_6^{-3}$	10^{-27}	*ca.* 10^{-4}	Measurable

TABLE IV

SELF-ABSORPTION CORRECTION DATA FOR $Zn(C^{14}N)_2$ PRECIPITATES

Mg./sq. cm. of $Zn(C^{14}N)_2$	Ratio of apparent to true activity in %
0.0	100
1.8	98.8
2.2	97.1
2.4	95.5
2.6	94.0
2.8	92.3
3.0	90.8

It appears from the above discussion that processes of type (1), *i. e.*, dissociation, are of dubious importance in accounting for the exchange behavior of the complex ions studied. However, processes of type (2), *i. e.*, substitution, would account for the present observations. In particular, the increase in exchange rate with decreasing *p*H in the case of potassium hexacyanochromate(III) and potassium hexacyanoferrate(II) could be explained in terms of a rate determining step involving replacement of a cyanide group by H_3O^+. Kinetic studies of these systems are in progress and, in the case of potassium hexacyanoferrate(II), preliminary results indicate the exchange rate to be approximately proportional to the first and one-third powers of the complex and hydrogen ion concentrations, respectively, and independent of the cyanide concentration.

An important consideration in a displacement reaction of this type is the ease, sterically, with which an additional group can enter the coördination sphere to form the activated state. It is interesting in this connection to note that the three tetracyanides studied exchanged immeasurably rapidly, whereas the hexacyanides and the octocyanide were slow. Apart from this general correlation between coördination number and exchange velocity, it does not appear possible to relate exchange stability to structural details. Thus no general relationships appear on considering the hexacyanides of chromium(III), manganese(III), iron(II) and (III), and cobalt(III). With respect to position in the periodic table, the manganese(III) complex exchanges unduly rapidly; with respect to electronic configuration, the isoelectronic iron(II) and cobalt(III) complexes behave very differently in acid solution.

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Appendix

Preparation of Radiocyanide Tracer.—At the time this research was initiated, radiocarbon C^{14} was available only in the form of barium carbonate.[13] The synthesis of potassium cyanide from this compound was accomplished by the method of Adamson.[14]

Counting Techniques.—To detect the weak beta radiation from C^{14}, mica end-window counter tubes of window thickness 2–3 mg./sq. cm. were used. These tubes were filled with the usual 10% alcohol, 90% argon mixture and connected to a standard amplifier and scaling circuit.

It was considered desirable to prepare the radioactive samples for counting in the form of uniform films, thin enough so that the self-absorption corrections were minimized. The procedure developed made use of zinc cyanide precipitates prepared as follows. The radiocyanide (either in solution or as an insoluble precipitate) to be analyzed was acidified with sulfuric acid and the liberated hydrogen radiocyanide swept by a stream of nitrogen through aqueous potassium hydroxide *until saturated*. Zinc nitrate solution was then added to the potassium cyanide solution so obtained, and the precipitate of zinc cyanide was washed twice with water (slightly acidified), then with alcohol. The precipitate was next slurried in alcohol and pipetted into a glass cylinder held firmly against an aluminum disc. The cylinder was ground on the bottom rim to prevent leakage. The alcohol was then evaporated off leaving a thin film of precipitate on the disc. The weight of the sample was determined by weighing the disc before and after adding the precipitate.

The usual method[15] was employed to evaluate the magnitude of the self-absorption correction. A number of samples of increasing thickness were prepared from a stock solution of potassium radiocyanide, and their activity plotted against the sample thickness. The ratio of apparent to true activity was then calculated from the progressive deviation of the curve from linearity, and values of this ratio are given in Table IV.

In measuring the activity of a solution, the activity of a sample prepared as described above was reduced to a specific activity (counts/mg.), and then corrected for self-absorption according to the sample thickness. In addition, the samples were corrected for coincidence using the experimentally determined value of 1.33% per 1000 counts/min. This correction factor was obtained according to the method of Moon.[16] In general the average mean deviation in duplicate specific activities was 1%.

Preparation and Purity of the Complex Salts: Potassium octocyanomolybdate(IV) dihydrate.—This compound was synthesized according to the directions of Willard and Thielke.[17] The preparation was analyzed for Mo(IV) content by acidifying a solution of the complex with sulfuric acid and titrating with a standard solution of potassium permanganate.[17] As the complex was only incompletely decomposed by prolonged boiling with concentrated sulfuric acid, analysis for the cyanide content was made by the method of Bellucci and Ricca.[18] A

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(13) The radioactive barium carbonate was obtained from the Oak Ridge National Laboratories, Oak Ridge, Tenn.

(14) Adamson, THIS JOURNAL, **69**, 2564 (1947).

(15) See Yankwich, Rollefson and Norris, *J. Chem. Phys.*, **14**, 131 (1946).

(16) Moon, *J. Sci. Instruments*, **14**, 189 (1937).

(17) Willard and Thielke, THIS JOURNAL, **57**, 2609 (1935).

(18) Bellucci and Ricca, *Atti congresso naz. chim. pura applicata*, 476 (1923); *C. A.*, **18**, 3334 (1924).

modification was introduced in that the period of digestion with mercuric oxide was lengthened to four hours.

Anal: Calcd. for $K_4Mo(CN)_8 \cdot 2H_2O$: Mo, 19.35; CN, 41.92. Found: Mo, 19.32; CN, 41.97.

Potassium Hexacyanomanganate(III).—This complex was prepared by the direct reaction of potassium cyanide with manganese(III) orthophosphate.[19] The complex was analyzed for cyanide content by decomposing it with dilute acid, distilling the liberated hydrogen cyanide into excess potassium hydroxide, and determining the resulting potassium cyanide by titration with standard silver nitrate.

Anal. Calcd. for $K_3Mn(CN)_6$: CN, 47.55. Found: CN, 43.16.

Magnetic susceptibility measurements[20] gave a value of 3.4 Bohr magnetons as compared to the theoretical value of 2.83, indicating the presence of a highly paramagnetic impurity such as manganese dioxide. The presence of about 8% of this oxide would account for the cyanide analysis and the magnetic data. Further purification was judged unnecessary at least for the preliminary exchange work.

Potassium Hexacyanochromate(III).—The method of Christensen[21] was used to prepare this complex. Analysis for the cyanide content was accomplished by decomposing the complex with dilute sulfuric acid and distilling the hydrogen cyanide evolved into an excess of potassium hydroxide. The potassium cyanide so formed was titrated with standard silver nitrate.

Anal. Calcd. for $K_3Cr(CN)_6$: CN, 47.3. Found: CN, 48.0.

Potassium Hexacyanoferrate(II) Trihydrate.—Reagent grade complex was recrystallized from hot aqueous solution. The first crystal crop was retained and air dried. The complex was analyzed for ferrous iron by the method of Müller and Diefenthäler[22] and the cyanide content was determined by Colman's method.[23]

Anal. Calcd. for $K_4Fe(CN)_6 \cdot 3H_2O$: Fe, 13.22; CN, 36.98. Found: Fe, 13.20; CN, 36.95.

Potassium Hexacyanoferrate(III).—Reagent grade complex was twice recrystallized from warm solution and the product dried at 60°. The preparation was analyzed for Fe(III) according to the directions of Müller and Diefenthäler.[22] Colman's method[23] was again used to determine the cyanide content.

Anal. Calcd. for $K_3Fe(CN)_6$: Fe, 16.98; CN, 47.45. Found: Fe, 16.98; CN, 47.48.

Potassium Hexacyanocobaltate(III).—This compound was prepared according to the method of Biltz and Biltz.[24] The cobalt content was determined as follows. Weighed samples were dissolved in water and treated with an excess of concentrated sulfuric acid. The solutions were evaporated to dryness, leached with water, and the cobalt precipitated by addition of a solution of α-nitroso-β-naphthol in acetic acid in accord with standard procedure.[25] A gravimetric potassium analysis was accomplished by decomposing the complex as described above, then precipitating the potassium by the addition of a solution of sodium cobaltinitrite in acetic acid.[26]

Anal. Calcd. for $K_3Co(CN)_6$: Co, 17.74; K, 35.3. Found: Co, 17.91; K, 35.8.

Potassium Tetracyanomercurate(II).—Solutions of this complex were prepared by the addition of stoichiometric amounts of potassium cyanide to solutions of reagent grade mercuric cyanide. It was not considered necessary to analyze the complex so formed.

Potassium Tetracyanonickelate(II) Monohydrate.—This compound was prepared by the direct reaction of potassium cyanide with nickel cyanide.[27] The nickel content was determined by treating an aqueous solution of the complex with concentrated hydrochloric acid. The solution was then evaporated to dryness, leached with water, and the nickel precipitated and weighed as nickel dimethylglyoxime.[28] The analysis for cyanide was accomplished by using the method of Bellucci and Ricca.[18]

Anal. Calcd. for $K_2Ni(CN)_4 \cdot H_2O$: Ni, 22.66; CN, 40.19. Found: Ni, 22.08; CN, 40.13.

The results of the two analyses indicated that the compound contained 2.6% potassium cyanide impurity, which was judged insufficient to interfere with the interpretation of the exchange data.

Potassium Tetracyanopalladate(II) Monohydrate.—This complex was synthesized by means of the reaction between palladium dicyanide and potassium cyanide solution.[29] The cyanide content was determined by the procedure of Bellucci and Ricca.[18]

Anal. Calcd. for $K_2Pd(CN)_4 \cdot H_2O$: CN, 33.90. Found: CN, 33.86.

Exchange Experiments.—The exchange studies were usually carried out by mixing 5 to 10 ml. volumes of solutions of the complex and of the radiocyanide tracer in a small, tapered centrifuge tube; this was then stoppered and placed in a thermostat regulated to 25 ± 0.3°. For short time runs thermostating was judged unnecessary; room temperature was approximately 24°. After an appropriate time interval, the tube was removed from the thermostat and the complex chemically separated from the radiocyanide. The specific activity of the radiocyanide fraction was then measured as described previously. The determinations of the extent of exchange in the dark were made in a similar manner except that the tubes were painted black on the outside.

Numerous experiments were made with acidified solutions and it was necessary to avoid excessive loss of hydrogen cyanide. Two procedures were used. The first consisted merely of placing the exchange solutions in a test tube and acidifying. The tubes were then corked and sealed with paraffin. The second and most satisfactory method involved sealing the flask containing the exchange solutions with a sponge rubber stopper of the type used to cap vaccine vials. Samples were withdrawn at intervals by inserting a hypodermic needle, attached to a calibrated syringe, through the self-sealing stopper. All samples were delivered, before further handling, into potassium hydroxide solution.

Separation Procedure.—For each system investigated it was necessary to devise methods of rapidly separating free cyanide from the complex cyanide without decomposing the complex ion. The determining criterion for the usefulness of a procedure was whether or not it induced exchange. This was established by rapidly mixing solutions of radiocyanide and of complex and immediately effecting the separation. To be satisfactory the specific activity of the separated radiocyanide should be the same as the initial value.

The salient features of the separation methods are given. Potassium octocyanomolybdate(IV) proved to be exceptional in that it was not decomposed by the addition of cold dilute acid. It was therefore possible to effect a separation of radiocyanide from the complex by acidifying the mixture with 0.2 *N* sulfuric acid, then sweeping out the liberated hydrogen cyanide by bubbling nitrogen gas through the solution for about three hours. The hydrogen cyanide was collected in a deficiency of potassium hydroxide and the specific activity determined as previously described.

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(19) Fernelius, "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 213.

(20) The magnetic analysis was carried out by Dr. S. S. Dharmatti.

(21) Christensen, *J. prakt. Chem.*, [2] **31**, 163 (1885).

(22) Müller and Diefenthäler, *Z. anorg. Chem.*, **67**, 418 (1910).

(23) Colman, *Analyst*, **33**, 267 (1908); **35**, 295 (1910).

(24) Biltz and Biltz, "Laboratory Methods of Inorganic Chemistry," 2nd ed., John Wiley and Sons, New York, N. Y., 1928, p. 146.

(25) Treadwell and Hall, "Analytical Chemistry," Vol. II, John Wiley and Sons, New York, N. Y., 1942, p. 199.

(26) Wilcox, *Ind. Eng. Chem., Anal. Ed.*, **9**, 136 (1937).

(27) Fernelius, *op. cit.*, p. 227.

(28) Willard and Diehl, "Advanced Quantitative Analysis," D. Van Nostrand Co., New York, N. Y., 1943, p. 385.

(29) Fernelius, *op. cit.*, p. 245.

In the case of potassium hexacyanomanganate(III), it was found that the cadmium salt of the complex could be completely precipitated by addition of a slight excess of cadmium sulfate solution. After centrifugation, the radiocyanide was precipitated as silver cyanide from the supernatant. The conversion to zinc cyanide was then made in the usual manner. This separation was found applicable to several other systems, namely, potassium hexacyanocobaltate(III), potassium hexacyanochromate(III), potassiumhexacyanoferrate(III), potassium hexacyanoferrate(II) and potassium tetracyanopalladate(II).

It was found possible to effect the separation of radiocyanide from solutions containing it and potassium tetracyanomercurate(II) by the direct precipitation of zinc radiocyanide and this method was first employed. As exchange appeared to take place instantaneously, it was considered desirable to devise a second procedure which would also be applicable to solutions containing mercuric cyanide rather than the ion, $Hg(CN)_4^{-2}$. A separation was achieved by precipitating silver radiocyanide from solution, then converting to zinc cyanide according to the usual procedure.

The separation of radiocyanide from potassium tetracyanonickelate(II) was accomplished by adding $0.05 f$ lead nitrate to precipitate lead radiocyanide. After centrifuging, the lead cyanide was freed from insoluble impurities (probably a trace of lead tetracyanonickelate(II)) by dissolving it in hot water and recentrifuging. The radiocyanide in the supernatant was then converted to zinc radiocyanide for the specific activity determination. The results indicated complete and instantaneous exchange and it therefore would have been desirable to have tested another separation procedure. To date, however, all attempts in this direction were unsuccessful.

Following the observation that cyanate was produced in solutions containing free cyanide and potassium hexacyanoferrate(III) (refer under "Experimental Results"), it was thought necessary to determine whether or not there was any exchange between cyanate and radiocyanide. The separation was accomplished by direct precipitation of zinc radiocyanide.

Summary

The exchange of radiocyanide with the following complexes was studied at *p*H *ca.* 10: potassium tetracyanonickelate(II), potassium tetracyanopalladate(II), potassium tetracyanomercurate(II), potassium hexacyanomanganate(III), potassium hexacyanochromate(III), potassium hexacyanoferrate(II) and (III), potassium hexacyanocobaltate(III), and potassium octocyanomolybdate(IV). Exchange was observed to be immeasurably rapid with the di- and tetracyanides, fast but measurable in the case of potassium hexacyanomanganate(III) and negligible for the other complexes. The exchange of potassium octocyanomolybdate(IV) was found to be strongly photocatalyzed. Exchange of potassium hexacyanoferrate(II), and possibly of potassium hexacyanochromate(III), was induced in acid solution, *i. e.*, at *p*H 2–4. This pattern of exchange data supports the viewpoint that over-all thermodynamic instability constants are misleading in predicting exchange. The postulate of decreasing exchange rate with increasing coördination number is in qualitative agreement with the results.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF YALE UNIVERSITY]

Determination and Significance of Polarographic Critical Micelle Concentrations

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The suppression of maxima, by the use of small quantities of gelatin, agar, various dyes, and other less commonly used materials, is well known in polarographic investigations. Kolthoff and Lingane[2] discuss the characteristics and elimination of maxima in polarography and point out the inadequacies in the adsorption theories[3,4] used to explain the phenomena. It has been shown that in practical work the suppressive action of gelatin on the diffusion current must be taken into account when using concentrations greater than about 0.01 per cent.[5,6] In the present investigation, it was found that even smaller quantities of gelatin and other colloidal agents can influence diffusion currents and half wave potentials.

In studying the significance of the polarographically determined critical micelle concentrations, cadmium, manganese(II), and copper(II) systems in neutral, acidic, and basic supporting electrolytes were investigated in the presence of non-reducible colloidal materials.

The polarographic micelle point (P.M.P.) is shown here to be identical with the classical critical micelle concentration (C.M.C.) as determined by an already accepted procedure,[7,8] namely, surface tension–concentration curves. Furthermore, this concentration seems to be equal to the concentration of colloidal agent just sufficient to suppress maxima, the maximum suppression point (M.S.P.).

Experimental

The polarographic apparatus and procedure used in this investigation has been described in detail elsewhere.[9] Determinations were made at 25.0 ± 0.1°. Special care was taken to ensure complete removal of adsorbed colloidal materials in the polarographic cell by washing thoroughly with alcohol and water between each polarographic deter-

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(1) Department of Chemistry, University of Portland, Portland, Oregon.

(2) Kolthoff and Lingane, "Polarography," Chap. 8, Interscience Publishers, New York, N. Y., 1946.

(3) Heyrovsky, "Actualités scientifiques et industrielles," No. 90, Paris, 1934.

(4) Ilkovic, *Collection Czechoslov. Chem. Commun.*, **8**, 13 (1936).

(5) Ilkovic, ref. 4, p. 122.

(6) Lingane, *Anal. Chem.*, **15**, 583 (1943).

(7) Early results: (a) Lottermoser and Puschel, *Kolloid Z.*, **63**, 175 (1933); (b) Powney and Addison, *Trans. Far. Soc.*, **33**, 1243 (1937).

(8) Miles and Shedlovsky, *J. Phys. Chem.*, **48**, 57 (1944).

(9) Meites and Meites, *Anal. Chem.*, in press.