TABLE II

CALCULATED PERCENTAGE COMPOSITION OF BASIC LEAD SALTS

Formula	Pb. %	NO_3. %	OH. %
$Pb(NO_3)_2 \cdot Pb(OH)_2$	72.4	21.7	5.9
$Pb(NO_3)_2 \cdot 5Pb(OH)_2$	80.9	8.1	11.1
$Pb(OH)_2$	85.9	0	14.1

through the $^1/_2$ equivalence point and that it corresponds to the empirical formula $Pb(NO_3)_2 \cdot Pb(OH)_2$ (Fig. 3). The analysis of the precipitates at the $^3/_4$, $^5/_6$ and 1 fractions of the equivalence point corresponds to the formula $Pb(NO_3)_2 \cdot 5Pb(OH)_2$. The precipitate at the $^2/_3$ equivalence point appears to be a mixture of the two precipitates noted above. The results of the analysis and solubility are in agreement with the data obtained by the conductometric and potentiometric titrations. The results do not confirm Berton's work.

Up to pH of 12, which is past the equivalence point there was no evidence that any appreciable amount of $Pb(OH)_2$, PbO, or the $PbO \cdot Pb(OH)_2$ complexes was formed. The pH ranges of existence of the two precipitates formed were

$Pb(NO_3)_2 \cdot Pb(OH)_2$	5.0–7.0
$Pb(NO_3)_2 \cdot 5Pb(OH)_2$	7.0->12

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

Complex Cyanide–Simple Cyanide Exchange Systems[1]

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The method of calculation of exchange data is discussed. The rate of exchange of free cyanide (labeled either with C^{14} or N^{15}) with the following complex cyanides is found to increase with decrease of pH: $K_4Fe(CN)_6$, $K_3Co(CN)_6$, $Na_3Fe(CN)_5(H_2O)$. The exchange reaction is found to be light-accelerated with the following complex cyanides: $K_4Fe(CN)_6$, $K_3Co(CN)_6$, $K_3Cr(CN)_6$, $Na_2Fe(CN)_5NO$, $Na_3Fe(CN)_5(H_2O)$. A relationship is found to exist between the rate of exchange of complex cyanides and the properties of their aqueous solutions on exposure to light, and to the lability of the cyanide ligand in ordinary chemical reactions. Exchange is found to be zero order with respect to the free cyanide concentration in the case of $K_4Fe(CN)_6$, $K_3Co(CN)_6$ and $K_3Cr(CN)_6$. All these effects are consistent with an exchange process proceeding by an aquation mechanism. A fairly satisfactory correlation of the rate of exchange with the electronic configuration of complex cyanides is observed.

Introduction

One of the main aims in isotopic exchange work is to attempt to correlate the essentially kinetic data obtained experimentally with the thermodynamic stability and electronic structure of the bond or bonds involved in the exchange process. Since complex metal cyanides all contain a common ligand, investigation of this class of compound should be profitable.

Previous work in the field of complex cyanide exchange reactions may be divided into three categories—those involving exchange of the central metal atom with metal ion,[3-6] those involving electron transfer between complex cyanides differing only in the oxidation state of the central metal atom[4,7,8] and those of Adamson, *et al.*, involving exchange of the cyanide ligand with cyanide ion or HCN.[8-10] A fourth category, which has not yet been investigated, would be the direct exchange of the cyanide ligands between ions of the same or different complexes.

Although slow exchange is reported in all the systems in the first category, it should be stressed that exchange between the pairs of ions in all these cases (except the $Fe(CN)_6^{-3}$–Fe^{+3} system) may actually be extremely rapid, since in all but one case, precipitates are formed on mixing solutions of the exchanging species. The value of the results is somewhat limited, and all that can be safely stated is that exchange is slow compared to the rate of precipitation of the compound formed, *i.e.*, $t_{1/2} >$ approx. 10^{-2} second.

The present investigation was carried out to expand the work of Adamson and co-workers in an endeavor to clarify the mechanism of the exchange in complex cyanide–simple cyanide systems, and to attempt to explain, qualitatively at least, the relationship between the observed rate of exchange and the pH, free cyanide concentration, and degree of illumination of the exchanging system.

Part I. Exchange Involving C^{14} Tagged Cyanide

Experimental

Preparation and Purity of the Complex Salts

Potassium hexacyanoferrate(II) trihydrate, potassium hexacyanoferrate(III), potassium hexacyanocobaltate(III), potassium octacyanomolybdate(IV) dihydrate, potassium hexacyanochromate(III) and potassium hexacyanomanganate(III) were prepared and analyzed as described in a previous publication.[11]

Sodium Aquopentacyanoferrate(II) Monohydrate.—This was prepared from sodium nitropentacyanoferrate(III)[12]

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[1] Based on portions of a thesis submitted by Alan G. MacDiarmid to the Graduate School of the University of Wisconsin, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Sidney Sussex College, Cambridge, England.

(3) J. F. Flagg, THIS JOURNAL, **63**, 557 (1941).

(4) R. C. Thompson, *ibid.*, **70**, 1045 (1948).

(5) H. E. Menker and C. S. Garner, *ibid.*, **71**, 371 (1949).

(6) F. A. Long, *ibid.*, **73**, 537 (1951).

(7) J. W. Cobble and A. W. Adamson, *ibid.*, **72**, 2276 (1950).

(8) A. W. Adamson, *ibid.*, **73**, 5710 (1951).

(9) A. W. Adamson, J. P. Welker and M. Volpe, *ibid.*, **72**, 4030 (1950).

(10) A. W. Adamson, J. P. Welker and W. B. Wright, *ibid.*, **73**, 4786 (1951.)

(11) A. G. MacDiarmid and N. F. Hall, *ibid.*, **75**, 5204 (1953).

(12) K. A. Hofmann, *Ann.*, **312**, 1 (1900).

and was purified by passing the crude substance through an alumina chromatographic column and eluting with water.

Anal.[13] Calcd. for $Na_3Fe(CN)_5(H_2O)\cdot H_2O$: Fe, 19.21; C, 20.62; N, 24.05; H, 1.37. Found: Fe, 18.94; C, 20.82; N, 23.85; H, 1.67.

Sodium Nitropentacyanoferrate(III).—The Merck Reagent Grade salt was used without further purification.

Potassium Hexacyanomanganate(II) Trihydrate.—This was prepared from manganous carbonate according to the method of Meyer.[14] A cyanide analysis was carried out by acidifying a solution of the complex, distilling the HCN liberated into excess potassium hydroxide and titrating the potassium cyanide formed with standard silver nitrate.

Anal. Calcd. for $K_4Mn(CN)_6\cdot 3H_2O$: CN, 37.0. Found: CN, 36.6.

Potassium Hexacyanochromate(II).—An attempt was made to prepare the pure solid compound by Christensen's[15] method; however, an analysis of the dry complex indicated that partial decomposition had taken place. It is noteworthy that owing to the instability of the compound in air, no analysis figures for it have ever appeared in the literature. Consequently, the hexacyanochromate(II) was prepared in solution by a method based on that of Hume and Stone[16] and the solid complex was not isolated or analyzed. Sufficient chromous acetate (prepared by a modification of the method in "Inorganic Syntheses"[17]) to give an approximately 0.05 *f* solution of hexacyanochromate(II) was dissolved in a slight excess of potassium cyanide solution at 0° in a centrifuge tube. The chromous acetate dissolved immediately to give the characteristic reddish-brown solution of hexacyanochromate(II). All work was carried out in an atmosphere of nitrogen.

Sodium Hexacyanovanadate(III).—This compound was prepared in solution by a slight modification of the method of Locke and Edwards.[18] A weighed amount of ammonium metavanadate, sufficient to make a 0.05 *f* solution of the complex cyanide, was treated with a little sodium hydroxide solution and boiled to drive off ammonia. The solution was then reduced with hydrochloric acid and alcohol, the resulting V(IV) solution being finally reduced to V(III) by sodium amalgam. This solution was then treated with excess solid sodium cyanide to give the characteristic wine-colored hexacyanovanadate(III) solution. The *total* cyanide content of the solution was then determined by acidifying a sample of the solution and distilling the hydrogen cyanide into excess potassium hydroxide followed by a back-titration. The solution was found to be 0.84 *f* in total cyanide, *i.e.*, ($V(CN)_6^{-3} + CN^-$). All reduced solutions of vanadium were handled in an atmosphere of nitrogen.

Potassium Argentocyanide.—A 0.100 *f* solution of the complex was prepared by mixing stoichiometric amounts of analytical reagent grade silver cyanide and potassium cyanide.

Potassium Tetracyanozincate.—A solution of potassium cyanide was treated with excess solid zinc cyanide. The excess zinc cyanide was filtered off and the total cyanide in solution was determined according to Williams.[19] The $K_2Zn(CN)_4$ was in this way found to be 0.0267 *f*.

Potassium Dicyanocuprate(I).—The complex was prepared by mixing stoichiometric amounts of cuprous cyanide (prepared by a modification of the method described by Barber[20]) and standard potassium cyanide solution. Some $Cu(CN)_3^{-2}$ ions are formed in solution and consequently all the cuprous cyanide does not dissolve. The undissolved cuprous cyanide was collected and weighed and the solution was then found to be 0.0368 *f* in Cu and 0.0916 *f* in CN, *i.e.*, it could be regarded as consisting of 0.0368 *f* $Cu(CN)_2^-$ in the presence of 0.0180 *f* free CN^-.

Exchange Procedure.—All exchange experiments were carried out, unless otherwise stated, by mixing equal quantities (5 ml.) of 0.050 *f* complex and approximately 0.05 *f* sodium radiocyanide solution. Unless stated to the contrary, the solutions were contained in glass-stoppered 10-ml. volumetric flasks during the period of exchange.

Acidification was carried out by the addition of one or two drops of perchloric acid. The *p*H of the solutions was determined by the use of a "one-drop" glass electrode in conjunction with a line-operated Beckman *p*H meter. Experiments in the light were conducted in the bright, diffuse daylight of the laboratory. In these experiments, the time given includes that during the night. The actual time of exposure to diffuse daylight would, therefore, be approximately half this. Exchange experiments in the dark took place in a flask painted black on the outside which was placed in a dark cupboard.

All exchange experiments were carried out at room temperatures, *i.e.*, approximately 24°. Thermostating was judged to be unnecessary as the results were compared with other experiments being carried out *at the same time*, but under different conditions of illumination, *p*H, etc.

Separation and Counting Procedure.—The sodium radiocyanide was prepared from $BaC^{14}O_3$[21] as described in a previous publication.[22]

In the exchange experiments, unless stated to the contrary, the activity of the free cyanide only was measured. It was separated from the complex cyanide and counted as an "infinitely thick" film of silver cyanide. Two different procedures were used. Both were a combination and modification of Adamson, Welker and Volpe's[9] and Long's[6] methods, and enabled a separation to be performed and a film to be prepared for counting both rapidly and reproducibly.

After precipitating and removing the complex as the cadmium salt, the simple cyanide was precipitated with silver nitrate in a solution buffered with acetic acid and sodium acetate. This precipitate was washed with water and acetone and then slurried with acetone (10 ml.). The slurry was then transferred to a 1.4-cm. circle of filter paper on which was pressed a 1.2-cm. glass chimney. The excess acetone was removed by other layers of filter paper below. The film was counted under an end window tube through a hole in a 2-mm. lead plate.

The following complex cyanide–simple cyanide exchange systems require particular mention.

Aquopentacyanoferrate(II).—The exchange reaction was not carried out for periods of more than one hour, because, as shown in a previous publication,[11] all the aquo(II) salt will have disappeared at the end of one hour under the conditions of the experiment. Since a chemical reaction takes place between the aquo salt and free cyanide, it was necessary to add excess free cyanide to the system to make up for cyanide removed during the reaction.

Hexacyanoferrate(III).—Since hexacyanoferrate(III) oxidizes free cyanide and is itself reduced to hexacyanoferrate(II), it was necessary to add excess free cyanide to the solutions of the complex. The final mixture of hexacyanoferrate(II), hexacyanoferrate(III), cyanate and cyanide was separated in the following manner. The complex cyanides were precipitated from the cyanide and cyanate by cadmium sulfate solution and the precipitate was immediately removed by centrifuging. The cyanide was separated from the cyanate by precipitation as nickel cyanide, and was then dissolved in warm, dilute perchloric acid in a stoppered 10-ml. volumetric flask followed by precipitation as silver cyanide in the usual way.

Hexacyanomanganate(III).—Since the complex is rapidly hydrolyzed by water it was necessary for stabilization to dissolve the solid salt in inert potassium cyanide solution.

Hexacyanomanganate(II).—This complex is also rapidly hydrolyzed by water. Consequently, sufficient solid salt was dissolved in 2 *f* inert potassium cyanide solution to make the final solution 0.100 *f* in the complex. It was necessary to use a greater concentration of the complex in these experiments so that the decrease in specific activity of the cyanide might be more accurately measured in the presence of so much free cyanide.

The complex is oxidized very readily by air. Consequently, all solutions were prepared and all exchange experi-

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[13] All carbon, hydrogen and nitrogen analyses in this investigation were kindly carried out by the Micro-Analytical Laboratory of the Department of Chemistry, University of Wisconsin.

[14] J. Meyer, *Z. anorg. Chem.*, **81**, 385 (1913).

[15] O. T. Christensen, *J. prakt. Chem.*, **139**, 163 (1885).

[16] D. N. Hume and H. W. Stone, THIS JOURNAL, **63**, 1200 (1941).

[17] H. S. Booth, "Inorganic Syntheses," Vol. I, McGraw-Hill Book Co., Inc., New York, N. Y., 1939, p. 122.

[18] J. Locke and G. H. Edwards, *Am. Chem. J.*, **20**, 594 (1898).

[19] H. E. Williams, "Cyanogen Compounds," Edward Arnold and Co., London, 1948, page 163.

[20] H. J. Barber, *J. Chem. Soc.*, 79 (1943).

[21] The $BaC^{14}O_3$ was obtained from the Isotopes Division of the United States Atomic Energy Commission.

[22] A. G. MacDiarmid and N. F. Hall, THIS JOURNAL, **75**, 4850 (1953).

Experimental Results

Expt. no.	Compound	Cyanide concn. *f*	Initial *p*H	Final *p*H	Time	Illumination	Exchange, %	$t_{1/2}^{a}$
1	$K_4Fe(CN)_6$	0.051	10.4	..	0.5 hr.	Dark	−0.8	......
2		.045	10.2	..	20 sec.	Diff.	0.4	......
3		.045	3.5	..	20 sec.	Diff.	1.1	......
4		.045	3.5	3.8	71 hr.	Diff.	86.4	24.6 hr.
5		.045	3.5	3.6	75.5 hr.	Dark	62.5	53.4 hr.
6		.045	10.2	10.3	74.5 hr.	Diff.	79.4	32.7 hr.
7		.045	10.2	10.2	77.0 hr.	Dark	−0.3	∞
8		.045	10.2	10.2	3.5 hr.	Sun	99.6	0.0^{b} hr.
9		.045	3.5	4.0	3.5 hr.	Sun	99.0	0.0^{b} hr.
10		.045	10.2	10.2	0.5 hr.	Sun	40.6	0.7^{b} hr.
11	$Na_3Fe(CN)_5(H_2O)$	.045	10.1	10.1	1.0 hr.	Dark	1.8^{i}	37.7 hr.
12		.049	3.6	3.2	1.0 hr.	Dark	72.6^{i}	0.5 hr.
13		.049	10.4	10.3	1.0 hr.	Diff.	3.7^{i}	18.8 hr.
14		.049	3.3	3.0	1.0 hr.	Diff.	71.0^{i}	0.5 hr.
15	$Na_2Fe(CN)_5NO$	.051	10.4	..	*ca.* 0.2 hr.	Diff.	1.9	*ca.* 6 hr.
16		.051	2.9	..	*ca.* 0.25 hr.	Diff.	5.9	*ca.* 3 hr.
17		.051	2.6	..	*ca.* 16 hr.	Diff.	12.1	*ca.* 87 hr.
18		.051	10.4	..	*ca.* 19 hr.	Diff.	12.8	*ca.* 95 hr.
19		.051	3.0	..	163 hr.	Diff.	21.5	466 hr.
20		.051	2.3	..	172.5 hr.	Dark	11.1	1015 hr.
21		.051	4.1	..	169.5 hr.	Diff.	20.9	500 hr.
22		.051	5.5	..	176.0 hr.	Dark	22.6	476 hr.
23		.051	10.4	..	187.75 hr.	Diff.	71.8	103 hr.
24		.051	10.3	..	191.0 hr.	Dark	62.8	134 hr.
25	$K_3Co(CN)_6$	.044	10.3	..	3 min.	Diff.	0.8	∞
26		.044	2.0	2.0	72.25 hr.	Diff.	25.7	167 hr.
27		.044	10.3	10.2	73.25 hr.	Diff.	10.7	439 hr.
28		.044	10.3	10.3	74.25 hr.	Dark	0.0	∞
29		.044	2.0	2.0	75.25 hr.	Dark	1.9	2509 hr.
30		.044	10.2	10.0	1.5 hr.	Sun	27.0	3.3 hr.
31	$K_3Fe(CN)_6$	.044	10.0	9.1	16 hr.	Dark	$3.7^{c,i}$	265 hr.
32		.044	10.0	..	2 min.	Dark	-0.1^{i}	∞
33		.044	10.0	9.2	18 hr.	Dark	0.0^{i}	∞
34	$K_3Cr(CN)_6{}^{d}$	.0528	10.4	..	2 min.	Diff.	3.6	......
35		.0528	10.4	..	2 min.	Diff.	4.9	......
36		.0528	10.4	10.0	1 hr.	Sun	46.5	1.1 hr.
37		.0528	10.4	9.8	71.25 hr.	Diff.	46.7	79 hr.
38		.0528	10.4	10.3	72.25 hr.	Dark	5.0	986 hr.
39	$K_3Mn(CN)_6{}^{d}$	.0528	10.6	10.6	5 min.	Diff.	100.1^{e}	0
40		.0528	10.6	..	4 min.	Dark	99.5^{e}	0
41	$K_4Mn(CN)_6{}^{d}$	.0528	11.8	..	5 min.	Diff.	$40.2^{e,h}$	6.8 min.
42		.0528	11.8	..	1 hr.	Diff.	$103.0^{e,h}$	......
43		.0528	11.8	..	6 min.	Dark	$51.5^{e,h}$	5.7 min.
44		.0528	11.8	..	6 min.	Sun	$46.0^{e,h}$	6.7 min.
45	$K_4Cr(CN)_6{}^{d}$	.0528	11.3	..	5 min.	Diff.	102.8^{g}	0
46		.0528	11.3	..	35–40 sec.	Diff.	100.8^{g}	0
47	$Na_3V(CN)_6{}^{d}$	.0528	9.0	..	5 min.	Diff.	$115^{e,f}$	0
48		.0528	9.0	..	1 min.	Diff.	$110^{e,f}$	0
49	$KAg(CN)_2{}^{d}$	.0528	10.3	..	2 min.	Diff.	102.5	0
50	$K_2Zn(CN)_4{}^{d}$	.0528	10.3	..	2 min.	Diff.	99.4	0
51	$KCu(CN)_2{}^{d}$	.0528	9.8	..	2 min.	Diff.	101.5	0

[a] $t_{1/2}$ calculated by means of equations 1.9 and 1.12.[23] [b] Temperature of solution rose approximately 3° while in the sun. [c] The cyanide film was slightly thinner than that necessary for infinite thickness and consequently this result may be a little high. [d] Experiments were not carried out at low *p*H values since the complex decomposes in acid solutions. [e] Exchange figures corrected for free cyanide used in preparing solutions of complex. [f] The large dilution of the radiocyanide by the inert free cyanide used for stabilizing the solution of the complex lowered the specific activity of the free cyanide to a point where the accuracy of counting was impaired. [g] Exchange values are calculated on the basis of total cyanide in solution. Since the results show that exchange is immeasurably rapid, there is no point in determining the exact concentration of free cyanide in the solution of the complex. [h] Accuracy of results: approximately ± 8%. [i] Per cent. exchange calculated using the initial concentration of free cyanide in the exchange system.

ments were carried out in an atmosphere of nitrogen. The solid complex was weighed into a 15-ml. centrifuge tube which was then sealed with a tightly fitting serum bottle stopper. Two hypodermic needles were inserted through the stopper and a stream of nitrogen passed through to expel oxygen. The 2 *f* potassium cyanide solution and the radio-

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(23) A. C. Wahl and N. A. Bonner, "Radioactivity Applied to Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1951, equations 1.9, 1.12, pp. 9–11.

cyanide solution were injected into the tube by means of one of the needles. A hypodermic syringe was also employed for removing samples of the solution for *p*H measurements and also for the addition of the cadmium nitrate solution used in precipitating the complex.

The only source of illumination for all manipulations in the "dark" experiments was an ordinary photographic red lamp.

Hexacyanochromate(II) and Hexacyanovanadate(III).—To avoid air oxidation, the same experimental procedure as that used for the hexacyanomanganate(II) was employed.

Argentocyanide and Tetracyanozincate.—The complexes were precipitated from the exchange solution as the somewhat insoluble cadmium salt. This *cadmium* salt was then decomposed by 10 ml. of acetic acid–acetate buffer solution and the cyanide precipitated as silver cyanide in the usual way.

Dicyanocuprate(I).—Separation of the $Cu(CN)_2^-$ ion from the free cyanide could not be achieved. However, cuprous cyanide could be precipitated from the exchange solution by acidifying with 1 *N* nitric acid. The cyanide solution remaining was treated with the acetic acid–acetate buffer solution and then with silver nitrate to obtain the silver cyanide for counting. The separation is by no means ideal, since it involves the decomposition of the complex ion.

Calculation of Exchange Values

It is unfortunate that two different equations are sometimes used for calculating the per cent. exchange values from the experimental data. These methods of calculation give widely different exchange values for the same experimental data except at 0 and 100% exchange. This can prove most misleading when comparing exchange values given by authors using different methods of calculation, unless it is clearly recognized that the methods used are different. It is even more confusing when neither the activity values of the samples nor the method of calculation is given.

For example, Adamson, Welker and Volpe[9] in their paper on the exchange of simple cyanides with complex cyanides, used the method of calculation shown below

$$E = \frac{a}{b} \times \frac{y}{x}\,100 \qquad (1)$$

where

E = per cent. exchange
a = moles of free cyanide
b = moles of cyanide in complex
x = amount of radioactivity in the free cyanide after time t
y = amount of radioactivity in the complex after time t

The value of the per cent. exchange using the more common method of calculation is given by the equation

$$P = \frac{Z - x}{Z - \frac{a}{a + b}Z}\,100 \qquad (2)$$

where

P = per cent. exchange
Z = initial activity of the cyanide = $x + y$

Therefore

$$P = E\,\frac{100\,(a + b)}{100a + Eb} \qquad (3)$$

For example, in a particular experiment with $Cr(CN)_6^{-3}$ a 2.6% exchange was obtained using equation 1.[9] This could, perhaps, be reasonably considered as indicating zero exchange; however, a value of 15.7% was obtained for *P* by use of equation 3, thus indicating definitely that exchange had taken place.

On converting Adamson, Welker and Volpe's[9] results for the hexacyanoferrate(III) exchange system by means of equation 3 from *E* values to *P* values, it becomes apparent that the exchange reaction is strongly light-accelerated. This effect was not so obvious by their method of calculation.

Time	Illumination	Exchange, % (Adamson, *et al.*)	Exchange, % (converted)
ca. 6 min.	...	3.7	21.2
115 hr.	Dark	1.0	6.6

All percentage exchange results in the present research were calculated by means of equation 2.

Effect of *p*H on Exchange Rate.—i. With the following complexes no change in rate of exchange with *p*H is observed[9,10]: $K_3Mn(CN)_6$, $K_4Mo(CN)_8$. ii. With the following complexes the rate of exchange increased with decrease of *p*H: $K_4Fe(CN)_6$,[9] $K_3Cr(CN)_6$ (Adamson, Welker and Volpe state that these results are not trustworthy owing to decomposition of the complex in acid solution), $K_3Co(CN)_6$ (*cf.* expt. 26–29), $Na_3Fe(CN)_5(H_2O)$ (*cf.* expt. 11–14). iii. With the following complex the rate of exchange decreased with decrease of *p*H: $Na_2Fe(CN)_5NO$ (*cf.* expt. 20, 22, 24).

Effect of Light on Exchange Rate.—i. The following complexes exhibited light-acceleration of their rate of exchange with free cyanide: $K_4Mo(CN)_8$,[9] $K_4Fe(CN)_6$ (*cf.* expt. 4–10), $K_3Co(CN)_6$ (*cf.* expt. 26–30), $K_3Cr(CN)_6$ (*cf.* expt. 36–38), $Na_2Fe(CN)_5NO$ (*cf.* expt. 19, 20, 23, 24), $Na_3Fe(CN)_5(H_2O)$[24] (a small effect noted only in alkaline conditions (*cf.* expt. 11 and 13), $K_3Fe(CN)_6$[9,25] (this effect became clear on recalculating the results of Adamson, Welker and Volpe,[9] as illustrated earlier). ii. The following complexes showed no measurable light acceleration of their exchange with free cyanide: $K_3Mn(CN)_6$,[10] $K_4Mn(CN)_6$.

Rate of Exchange.—Slow or measurable: $K_4Mo(CN)_8$,[9] $K_4Fe(CN)_6$, $K_3Fe(CN)_6$, $K_3Cr(CN)_6$, $K_3CO(CN)_6$, $K_3Mn(CN)_6$,[9] $K_4Mn(CN)_6$, $Na_2Fe(CN)_5NO$, $Na_3Fe(CN)_5{\cdot}(H_2O)$. Immeasurably rapid: $K_2Ni(CN)_4$,[9,6] $K_2Pd(CN)_4$,[9] $K_4Cr(CN)_6$, $Na_3V(CN)_5$, $K_2Zn(CN)_4$, $K_2Cu(CN)_3$, $KAg(CN)_2$, $K_3Co(CN)_5(H_2O)$.[8]

Part II. Exchange Involving N^{15} Labeled Cyanide

Experimental

Preparation and Purity of Compounds. Potassium Hexacyanoferrate(II), Potassium Hexacyanocobaltate(III), the solid complexes were from the same samples as those used in previous experiments.

Tetracyanonickelate(II).—This was prepared from nickel cyanide and potassium cyanide.[26]

Exchange Procedure.—The same procedure was used as for the C^{14} labeled experiments. The $Ni(CN)_4^{-2}$ was separated from free cyanide by the ether extraction method of Long.[6] The free cyanide was precipitated as silver cyanide

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[24] These results must be accepted with caution since $Fe(CN)_6^{-4}$ is being formed throughout the time that exchange is taking place and the photo-acceleration effect may actually be due to the hexacyanoferrate(II) so formed. However, this does not seem very likely since, if this were so, one would expect to get the same effects as shown by the hexacyanoferrate(II) system. As can be seen, this is not the case, as no light acceleration effect is noted in acid solution.

[25] This effect may be due either in whole or in part to the hexacyanoferrate(II) which is formed during exchange and which has been shown in this research to be light-accelerated.

[26] W. C. Fernelius, "Inorganic Syntheses," Vol II, McGraw-Hill Book Company, Inc., New York, N. Y., 1946, p. 227.

which was then converted to nitrogen gas for use in the mass spectrometer. In order to keep the exchange systems free from any nitrogen-containing ion, cadmium sulfate was always used instead of cadmium nitrate for precipitating the complex, and silver acetate was used instead of silver nitrate for precipitating the free cyanide.

N^{15} Determination.—The $NaCN^{15}$ was prepared from potassium phthalimide containing N^{15} as described in a previous publication.[22] The atom-per cent. excess N^{15} in the free cyanide only was determined.[27,28] The silver cyanide was converted to nitrogen gas in the following manner. The precipitated cyanide was dried by means of alcohol and ether, and then mixed with 5 ml. of concentrated hydrochloric acid in a test-tube with a loosely fitting stopper. This was placed in a beaker of water which was brought to boiling over a period of 20 minutes and then held at this temperature for five minutes. The cyanide was thus hydrolyzed to ammonia. The resulting solution was then made alkaline and the ammonia distilled into excess sulfuric acid. Trial runs on silver cyanide gave 80-90% yields of ammonia. The resulting ammonium sulfate was converted to nitrogen by treatment with alkaline hypobromite solution.[29]

Results.—These experiments gave exchange values which were the same as those obtained in the C^{14}-tagged cyanide experiments carried out in Part I, and in previously published results of C^{14} experiments with $Ni(CN)_4^{-2}$.[6,9]

Part III. Kinetic Studies

Experimental

Complex Cyanides.—The complexes were from the same samples as those used for previous experiments.

Method.—Since the exchange reactions were all immeasurably slow in the dark, it was necessary to conduct the experiments in bright, diffuse daylight. The concentration of the complex cyanide in all the exchange systems was 0.025 *f*. The experiments were conducted in pairs, the concentration of free cyanide in one experiment being twice what it was in the other. Each pair of experiments was carried out at the same time, so that any variation in illumination or temperature conditions would be the same for each system. For the sake of convenience, the system in any pair of experiments which contains the higher concentration of free cyanide is termed the "concentrated" solution, the other system being the "dilute" solution.

Initially the *p*H of the "dilute" solutions was always slightly less than that of the "concentrated" solutions, and so to eliminate any change in rate due to hydrogen ion dependence, the *p*H of the "dilute" solutions was adjusted as closely as possible to the *p*H of the "concentrated" solutions by the addition of two or three drops of potassium hydroxide solution. Buffer solutions were not used since it was thought desirable to keep the systems as free from foreign ions as possible.

The rate of the exchange reaction, R, was obtained from this relationship

$$R = -\frac{AB}{(A + B)t}\ln(1 - F) \qquad (4)$$

where

A = concn. of free cyanide in moles/l.
B = concentration of cyanide in complex in moles/l.
F = fraction of exchange
t = time of exchange

Results.—The results are given as $R_{\text{conc}}/R_{\text{dil}}$. If the exchange reaction is zero order with respect to the free cyanide, then this ratio would ideally be unity; if it were first order it would be two, etc.

Compound	Time, hr.	Initial *p*H	Concn. of free CN, *f*		Rate × 10^6, moles/hr./l.	$\frac{R_{\text{conc}}}{R_{\text{dil}}}$
$K_4Fe(CN)_6$	14	10.22	0.0132	0.153	144	1.00
	14	10.35	.0264	.086	144	
	1.05	10.20	.0132	.040	470	0.94
	1.0	10.23	.0264	.020	444	
	12	10.38	.0124	.073	74.7	1.16
	12	10.36	.0248	.047	86.1	
$K_3Cr(CN)_6$	72	10.40	.0124	.443	93.0	1.04
	72	10.34	.0248	.278	96.2	
$K_3Co(CN)_6$	80	10.43	.0124	.119	18.1	1.06
	80	10.41	.0248	.070	19.2	

Since the fraction of exchange in most of these experiments is small, the experimental error in counting is fairly high. However, the results serve as reasonable evidence for a zero-order dependence of the rate of exchange on the free cyanide concentration in all the systems investigated.

Discussion

Induced Exchange.—It can be seen that no exchange induced by the separation procedure occurs with the complexes which exchange slowly since zero exchange was obtained in several cases. It also seems fairly reasonable to assume that exchange was not induced by the separation procedure in those compounds which exchanged very rapidly, since the same method of separation was used. This is also substantiated by the fact that although two different methods of separation (precipitation[9] and ether extraction[6] were used with the tetracyanonickelate(II), immeasurably rapid exchange was observed in both cases).

N^{15}-Labeled Experiments.—Since the results of experiments in which the carbon and the nitrogen of the cyanide were alternatively tagged are identical it becomes apparent that the cyanide group as a whole is exchanged between the simple and complex cyanide and that it is not just the C or the N of the CN group which exchanges. There is therefore no trace of severing of the C-N bond during exchange.

Mechanism of Exchange.—It is proposed that exchange between complex cyanides and simple cyanide ion or HCN, at least in the presence of light, takes place by an "aquation" mechanism, as distinct from a process in which a cyanide is associated to the complex to form an activated ion of one higher coördination number, followed subsequently by a dissociation, *i.e.*, it is proposed that the exchange mechanism follows the lines of the equations

$$\text{ia}\quad M(CN)_x^{-y} + H_2O \longrightarrow M(CN)_{x-1}(H_2O)^{1-y} + CN^- \quad \text{Slow}$$

or

$$\text{ib}\quad M(CN)_x^{-y} + H_3O^+ \longrightarrow M(CN)_{x-1}(H_2O)^{1-y} \quad HCN \quad \text{Slow}$$

followed by

$$\text{iia}\quad M(CN)_x^{-y}(H_2O)^{1-y} + C^*N^- \longrightarrow M(CN)_{x-1}(C^*N^-)^{-y} \quad \text{Rapid}$$

or

$$\text{iib}\quad M(CN)_{x-1}(H_2O)^{1-y} + HC^*N \longrightarrow M(CN)_{x-1}(C^*N)^{-y} + H_3O^+ \quad \text{Rapid}$$

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[27] The authors wish to thank Dr. R. H. Burris and Mr. D. Wilson for instruction and help in the use of the mass spectrometer in the Biochemistry Department of the University of Wisconsin.

[28] Thirty-two atom per cent. N^{15} potassium phthalimide obtained from Eastman Kodak Company, Rochester 4, New York.

[29] D. Rittenberg, A. S. Keston, F. Rosebury and R. Schoenheimer, *J. Biol. Chem.*, **127**, 292 (1939).

as distinct from

$$M(CN)_x^{-y} + C^*N^- \longrightarrow M(CN)_x(C^*N)^{-y-1}$$

followed by

$$M(CN)_x(C^*N)^{-y-1} \longrightarrow M(CN)_{x-1}(C^*N)^{-y} + CN^-$$

Furthermore, it is proposed that the exchange is basically a combination of two simple chemical reactions. This is particularly true for those complexes which exchange at a slow or fairly rapid rate. In fact, the proposed stable, intermediate complex, the aquo complex, can be obtained as a chemically pure substance in several cases.[12,30] This type of exchange might therefore be termed "apparent" exchange since it is caused by two orthodox chemical reactions occurring simultaneously as distinct from "true" exchange which involves direct interchange.

The mechanism in systems which exchange immeasurably rapidly may also be simply explained by an aquation process. All complex cyanides, regardless of their thermodynamic stability, are slightly dissociated into free cyanide, *e.g.*, the type of equilibrium below occurs to some extent even though the over-all equilibrium constant (10^{-22})[31] is very small. The fact that a complex is only slightly dissociated at equilibrium is of no importance whatsoever. The *rate* at which the equilibrium below can be attained is the all important factor, and since this is rapid, isotopic exchange should also be rapid.

$$Ni(CN)_4^{-2} + H_2O \rightleftarrows Ni(CN)_3(H_2O)^{-1} + CN^-$$

The fact that $Ni(CN)_4^{-2}$ is very stable (NiS cannot be precipitated from $Ni(CN)_4^{-2}$)[32] should not be *expected* to affect the rate at which it exchanges.

The six following observed effects in the exchange of complex cyanides with the simple cyanide ion or HCN are qualitatively consistent with an exchange process which proceeds by an aquation mechanism. Of the seventeen complexes investigated, there appears to be only one exception, and this only in one respect, *viz.*, the rate of exchange of nitropentacyanoferrate(III) decreases with decrease of *p*H.

i. The rate of the exchange reaction is zero order with respect to the concentration of free cyanide in the exchange system. This is to be expected if the rate of exchange is governed by a step involving the slow dissociation of the complex cyanide.

ii. A decrease in *p*H increases the rate of exchange (with one exception, *viz.*, nitropentacyanoferrate(III)). This is to be expected if equation ia or ib is true.

iii. Those complexes which exhibit an increase of dissociation with illumination also exhibit light acceleration of their exchange reactions. (It has been shown in an earlier publication[11] that the rate of dissociation of $Fe(CN)_6^{-4}$, $Fe(CN)_6^{-3}$, $Co(CN)_6^{-3}$ and $Mo(CN)_8^{-4}$ is increased by light.) This is consistent with the proposal that the rate of the slow, rate-controlling ionization step is increased, and hence the over-all rate of exchange is increased.

iv. The following complex ions exhibit slow exchange with cyanide: $Mo(CN)_8^{-4}$, $Fe(CN_6^{-4}$, $Fe(CN)_6^{-3}$, $Co(CN)_6^{-3}$, $Cr(CN)_6^{-3}$, $Fe(CN)_5(H_2O)^{-3}$, $Fe(CN)_5(NO)^{-2}$. If exchange takes place by an aquation mechanism, then these complexes should be *expected* to exchange slowly at room temperatures since their rate of formation from, and ionization to, their constituent ions is small.

v. The following complex ions exhibit comparatively rapid exchange with cyanide: $Mn(CN)_6^{-3}$, $Mn(CN)_6^{-4}$. From the manner of formation of these complexes,[15,33] and from their ease of decomposition in solutions which do not contain free cyanide, their rates of substitution (and exchange) would be expected to be greater than those complexes in the preceding category.

vi. The following complex ions exhibit immeasurably rapid exchange with cyanide: $Ni(CN)_4^{-2}$, $Pd(CN)_4^{-2}$, $Zn(CN)_4^{-2}$, $Cu(CN)_3^{-2}$, $Ag(CN)_2^{-1}$, $Cr(CN)_6^{-4}$, $V(CN)_6^{-3}$, $Co(CN)_5(H_2O)^{-3}$. This is consistent with the known lability of their cyanide ligands in ordinary chemical reactions.

As has been pointed out by Adamson, Welker and Volpe[9] over-all thermodynamic instability constants are misleading in predicting exchange. The fundamental point is that the thermodynamic stability of a complex should not necessarily be *expected* to show a relationship with its rate of exchange. It may be argued that the rate of exchange of a complex should increase with decrease of thermodynamic stability, since the chance of a bond gaining sufficient energy to break will then be proportionally increased. This is, of course, only the case if the activation energy for the breaking of the bond is the same for all complexes. It is proposed that the rate of exchange is governed by the magnitude of the activation energy necessary to break the bond, which is in turn governed mainly by the electronic structure of the complex ion, as suggested by Taube.[34]

An example may serve to illustrate the point. Both $Fe(CN)_6^{-4}$ and $Ag(CN)_2^-$ are very stable thermodynamically with respect to their constituent ions (dissociation constants of 10^{-37},[9] and 10^{-21},[35] respectively). However, the former complex exchanges slowly and the latter exchanges immeasurably rapidly. It is proposed that the energy of activation for the dissociation of the $Fe(CN)_6^{-4}$ is much greater than for the $Ag(CN)_2^-$. The argument used is as follows: $Fe(CN)_6^{-4}$ is diamagnetic and will therefore have the electronic configuration of $3d^2\ 3d^2\ 3d^2\ 3D^2\ 3D^2\ 4S^2\ 4S^2\ 4P^2\ 4P^2\ 4P^2$. Any disruption of this stable d^2sp^3 configuration will require considerable energy.[34] The $Ag(CN)_2^-$ ion probably has the following configuration $4d^2\ 4d^2\ 4d^2\ 4d^2\ 4d^2\ 5S^2\ 5P^2$ (or $4d^2\ 4d^2\ 4d^2\ 4d^2\ 4d^2\ 5S^2\ 5P^2\ 5P^2\ 5P^2$ if the ion is aquated). A disruption of the sp configuration should not require much energy since the hybridization does not involve any of the stable 4d orbitals of the silver atom.[34]

The type of bonding in the $Fe(CN)_6^{-4}$ may then

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[30] K. A. Hofmann, *Ann.*, **312**, 18 (1900).

[31] W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1938.

[32] H. E. Williams, ref. 19, p. 141

[33] W. C. Fernelius, ref. 26, p. 213.

[34] H. Taube, *Chem. Revs.*, **50**, 69 (1952).

[35] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1948, p. 478.

be termed "inert inner orbital" bonding and that in the $Ag(CN)_2^-$ (labile) "outer orbital" bonding, as suggested by Taube.[34] These terms appear to be more descriptive and less confusing than the conventional terms of "covalent" and "ionic" bonding.

A similar argument applies for the following complexes, all of which are of the "inert inner orbital" bonding type. All these complexes exchange slowly or at a measurable rate, *viz.:* $Fe(CN)_6^{-4}$, $Fe(CN)_6^{-3}$, $Cr(CN)_6^{-3}$, $Co(CN)_6^{-3}$, $Fe(CN)_5(H_2O)^{-3}$, $Fe(CN)_5NO^{-2}$, $Mo(CN)_8^{-4}$, $Mn(CN)_6^{-3}$, $Mn(CN)_6^{-4}$.

In the group of fast-exchanging complexes one has only the comparatively low energy "outer orbital" bonding. All these complexes exchange rapidly, *viz.:* $Ag(CN)_2^-$, $Pd(CN)_4^{-2}$, $Cu(CN)_2^-$, $Zn(CN)_4^{-2}$, $Ni(CN)_4^{-2}$.

It should be mentioned that although $K_2Ni(CN)_4$ and $K_2Ni(CN)_4 \cdot H_2O$ are diamagnetic in the solid state, the complex may very likely be paramagnetic in solution. This is suggested by the fact that solid anhydrous $Ni(CN)_2$ (which has a similar structure to the tetracyanonickelate(II) ion) has only an extremely small paramagnetic susceptibility while $Ni(CN)_2 \cdot 4H_2O$ has a susceptibility corresponding to one unpaired electron.[36] The $Ni(CN)_4(H_2O)_2^{-2}$ ion so formed would therefore have a low energy outer orbital bonding as shown below and one would therefore expect rapid exchange, $3d^2$ $3d^2$ $3d^2$ $3d^1$ $3d^1$ $4S^2$ $4P^2$ $4P^2$ $4P^2$ $4D^2$ $4D^2$. A similar argument probably applies for $Pd(CN)_4^{-2}$.

The three complex ions $V(CN)_6^{-3}$, $Co(CN)_5^{-3}$ and $Cr(CN)_6^{-4}$ demand special consideration. $V(CN)_6^{-3}$ has the "labile inner orbital" bonding described by Taube and exhibits rapid exchange. Since the electronic configuration of the Co(II) complex cyanide is very uncertain,[8] its bonding will not be discussed.

Since $Cr(CN)_6^{-4}$ has an "inert inner orbital" type of bonding, one would expect the complex to exchange at a measurable rate. However, exchange takes place very rapidly. Of the sixteen complexes investigated, this appears to be the only exception when correlating rate of exchange with electronic configuration. Nevertheless, it is possible that it is not really so exceptional since all "inert inner orbital" bonded complexes having the same electronic configuration as $Cr(CN)_6^{-4}$ tend to be the most labile members of the "inert inner orbital" type of complex.

It will be noticed from the above discussion that magnetic susceptibility itself is not used as a criterion of the lability of a compound in exchange. For instance, both $Fe(CN)_6^{-4}$ and $Ag(CN)_2^-$ are diamagnetic and yet the former compound exchanges very slowly and the latter very rapidly. Also, both $Cr(CN)_6^{-3}$ and $V(CN)_6^{-3}$ are paramagnetic and yet the former exchanges very slowly and the latter very rapidly.

In the light of three of the experiments carried out in this research, it is possible to verify one of Taube's[34] predictions on exchange rates. He stated that hexacyanochromate(II) should exchange more rapidly than hexacyanoferrate(II) and hexacyanomanganate(II). This is now shown to be the case. He also stated that all substitution reactions of V(III) appear to be extremely rapid. Exchange with $V(CN)_6^{-3}$, a substitution reaction, is shown to take place immeasurably rapidly and is, therefore, consistent with other work on V(III) complexes.

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(36) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1948, p. 119.

(37) A. G. MacDiarmid.