

TABLE III
RESOLUTION THROUGH ELECTRON TRANSFER IN THE SYSTEM [Co(PDТА)]²⁻-[Co(PDТА)]⁻
T = 100°; pH 2.0

[Co(PDТА)] ⁻ , a	[Co(PDТА)] ²⁻ , b	Expt.	Calcd.	% Resolution ^a	k (M ⁻¹ hr. ⁻¹) ^b
Racemic, 0.02 M	D-L, 0.04 M	...	-0.202	84	1.9
Racemic, 0.02 M	D-L, 0.02 M	-0.138	- .138	75	2.2
D-L, 0.02 M	Racemic, 0.02 M	- .133	- .138	75	2.2
D-L, 0.02 M	Racemic, 0.03 M	- .119	- .116	70	2.1

^a Per cent. resolution is the ratio of the calculated concentration of the more abundant isomer in the equilibrium mixture to the concentration of the initial racemate. ^b Each value of k is the average of more than two experiments.

tribution might vary anywhere from about 51% (D-L)—49% (L-L) to something like 99+ % (D-L)—1% (L-L), since the kinetic equations will be obeyed so long as the rotation is instantly proportional to the concentration of the cobalt(II) complex.

From the nature of the steric interaction of the methyl group with the remainder of the ligand, an increase in the size of the metal ion should increase this repulsion, for this would fold back the methylene hydrogen atoms into the methyl group. One therefore expects the methyl group to be at least as selective for ions bigger than cobalt(III) as it is for that ion. Since the results given here prove the cobalt(III) complex to exist at equilibrium as 99+ % D-L (or L-D) isomer and since cobalt(II) is larger than cobalt(III), it is only reasonable to conclude that the cobalt(II) complex is essentially all (99+ %) of the single preferred configuration.

From the foregoing, a novel method of resolution may be suggested for certain very special systems. In systems retaining configuration, these configurations (d and l) are distributed statistically between the exchanging species as a result of electron transfer (just as an isotopic tracer is).

In consequence, an excess of an optically active ion will confer a high degree of resolution on the second ion (originally racemic) at equilibrium. This has been demonstrated (Table III) by following such solutions to their equilibrium rotations, which may be calculated from equation 8

$$\alpha_{\infty} = \frac{b}{(a+b)} \{[\alpha]_{II}b - [\alpha]_{III}a\} \quad (8)$$

where a and b are as previously defined and $[\alpha]_{II}$ and $[\alpha]_{III}$ are the rotations of one molar solutions of the divalent and trivalent complexes. In all cases the experimental and predicted values for the equilibrium rotation agree closely. Other novel resolution methods based on equilibria have been demonstrated among complexes.^{12,13}

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(12) F. P. Dwyer, M. F. O'Dwyer and E. C. Gyrfas, *Nature*, **167**, 336 (1951); F. P. Dwyer and E. C. Gyrfas, *ibid.*, **168**, 29 (1951).

(13) D. H. Busch, *J. Am. Chem. Soc.*, **77**, 2747 (1955).

[CONTRIBUTION FROM THE DIVISION OF PHYSICAL CHEMISTRY OF THE CHEMICAL RESEARCH LABORATORIES, AUSTRALIAN COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANIZATION, MELBOURNE, AUSTRALIA]

The Liquid Phase Hydrogenation of Cyanocobaltate(II)

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Solutions containing $[\text{Co}^{\text{II}}(\text{CN})_5]^{3-}$ react reversibly with molecular hydrogen to give a colorless hydride ion of probable structure $[\text{Co}^{\text{III}}(\text{CN})_5\text{H}]^{3-}$, which has considerable stability in alkaline water or methanol, or in the solid state. The same product results from reduction of $[\text{Co}^{\text{II}}(\text{CN})_5]^{3-}$ electrolytically or by means of NaBH_4 . It is formed also in the first step in the aging of $[\text{Co}^{\text{II}}(\text{CN})_5]^{3-}$, which proves to be disproportionation to hydride and $[\text{Co}^{\text{III}}(\text{CN})_5\text{OH}]^{3-}$ rather than a simple dimerization as formerly believed. Since cations accelerate both disproportionation and H_2 uptake, the influence of added salt on the latter reaction is not readily analyzed but is probably a combination of cation promotion and a general salt-effect diminished by loss of reactant by disproportionation. Cs^+ provides a clear example of excellent promotion of gas uptake vitiated by excessive stimulation of disproportionation. K^+ is the best compromise promoter in the series of alkali metal ions. Use of methanol in place of water as solvent increases the rate of H_2 uptake 4-fold (taking into account a 10-fold increase in gas solubility). Descriptions are given of the sequence of reactions which follow mixing of CoCl_2 and KCN solutions and of the spectra of essentially pure solutions of $[\text{Co}^{\text{II}}(\text{CN})_5]^{3-}$ and $[\text{Co}^{\text{III}}(\text{CN})_5\text{H}]^{3-}$. The hydride has a single absorption band in the visible and ultraviolet regions, situated at 305 μ . The H_2 evolution and exchange reactions, which have been observed in mixtures of CoCl_2 and KCN by previous investigators, can be explained in terms of $[\text{Co}^{\text{III}}(\text{CN})_5\text{H}]^{3-}$ as the source of the liberated gas.

Introduction

Cobaltous chloride added to excess aqueous KCN yields a greenish solution containing the pentacyanocobaltate(II) ion¹⁻³ which can be re-

(1) M. A. Descamps, *Compt. rend.*, **67**, 330 (1868).
(2) D. N. Hume and I. M. Kolthoff, *J. Am. Chem. Soc.*, **71**, 867 (1949).

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

duced by various means to an ion whose color and absorption spectrum have not previously been determined correctly because of masking by other compounds present. Treadwell and Huber,⁴ as well as later investigators, have regarded the ion as a complex of Co^{I} , the expected product of a 1-electron reduction of $[\text{Co}^{\text{II}}(\text{CN})_5]^{3-}$.

(4) W. D. Treadwell and D. Huber, *Helv. Chim. Acta*, **26**, 10 (1943).

TABLE I
VISIBLE AND ULTRAVIOLET SPECTRA OF CYANO-COMPLEXES OF Co^{II} AND Co^{III} AT 25°

Complex	Solvent	Wave length (λ m μ) and molar extinction coefficient (ϵ)						
		λ	ϵ	λ	ϵ	λ	ϵ	λ
$[\text{Co}^{\text{II}}(\text{CN})_5]^{3-}$	Water	231	(263)	280	316	428	618	967
		6800	~ 1000	5300	530	49	7	298
$[\text{Co}^{\text{II}}(\text{CN})_5]^{3-}$	Dry methanol	232	(263)	279.5	317	430 ^a	620 ^a	965 ^a
		5800	~ 1000	4800	580	49	~ 7	290
$[\text{Co}^{\text{II}}(\text{CN})_5]^{3-}$	Dimethyl sulfoxide	296		356	396		1110	
		>2600		>330	>300		>200	
$[\text{Co}^{\text{III}}(\text{CN})_5\text{H}]^{3-}$	Water			305				
				610				
$[\text{Co}^{\text{III}}(\text{CN})_5\text{OH}]^{3-}$	Water	235		380				
		~ 7000		360				

* The solubility in methanol is insufficient to permit accurate determination of λ and ϵ in the visible region of the spectrum.

That molecular hydrogen could be used for the reduction appears to have been first noticed by Iguchi.⁵ The reaction has since been studied by us⁶⁻⁹ and by several other groups¹⁰⁻¹² with the object of determining the nature of the active molecular species and how it combines with H_2 . The rapidity of gas uptake, even at 0° , suggested that the structure was uncommonly well adapted to the "activation" of H_2 ; knowledge of the molecular structure of reactant and product might therefore lead to a better understanding of hydrogenation catalysis.^{7,8,10,13,14}

In the present paper we wish to describe experimental work mentioned in previous communications^{6,7,9} and whose publication has been delayed by difficulties of interpretation. Recently we have succeeded in obtaining a clean spectrum of the hydrogenated product, which permits a re-assessment of our earlier results and those of Mills, Weller and Wheeler.¹¹ It provides also the key to understanding the exchange reaction described by Mills, *et al.*, and the hydrogen evolution reaction discussed by King and Winfield.⁹ Meanwhile the demonstration by nuclear magnetic resonance measurements¹² that the reduced complex does indeed contain a hydrogen atom has resolved the major doubt regarding its structure.

Results

Aging in vacuo.—By working in dilute aqueous solution, taking considerable care to exclude reactive gases, it is possible to mix CoCl_2 and KCN in a Thunberg tube to obtain a solution whose absorption spectrum is essentially that of the pentacyanocobaltate(II) ion (Table I and Fig. 1). There is negligible contribution from ions other than $[\text{Co}^{\text{II}}(\text{CN})_5]^{3-}$ and CN^- as judged by the constancy

(5) M. Iguchi, *J. Chem. Soc. (Japan)*, **63**, 534 (1942).

(6) N. K. King and M. E. Winfield, *Biochem. Biophys. Acta*, **18**, 431 (1955).

(7) M. E. Winfield, *Revs. Pure Appl. Chem. (Australia)*, **5**, 217 (1955).

(8) J. Bayston, N. K. King and M. E. Winfield, "Advances in Catalysis," Vol. IX, Academic Press, Inc., New York, N. Y., 1957, p. 312.

(9) N. K. King and M. E. Winfield, *J. Am. Chem. Soc.*, **80**, 2060 (1958).

(10) S. W. Weller and G. A. Mills, "Advances in Catalysis," Vol. VIII, Academic Press, Inc., New York, N. Y., 1956, p. 163.

(11) G. A. Mills, S. Weller and A. Wheeler, *J. Phys. Chem.*, **63**, 403 (1959).

(12) W. P. Griffith and G. Wilkinson, *J. Chem. Soc.*, 2757 (1959).

(13) J. Halpern, *Quart. Revs. Chem. Soc.*, **10**, 463 (1956).

(14) J. Halpern, "Advances in Catalysis," Vol. XI, Academic Press, Inc., New York, N. Y., 1959, p. 301.

of extinction coefficients when the cobalt concentration is varied through the range 0.0003 to 0.0072 M .

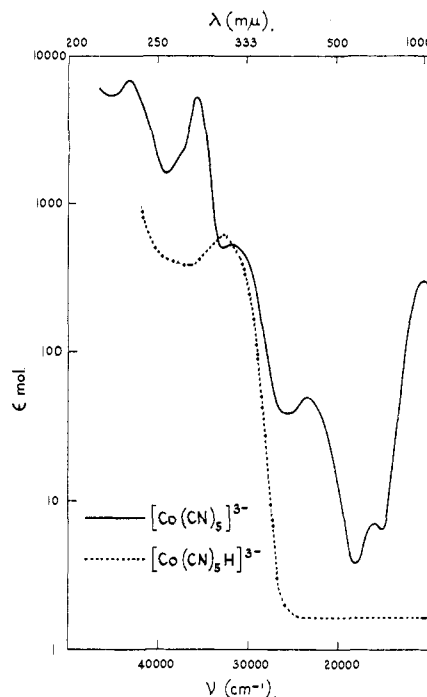


Fig. 1.—Absorption spectra of $[\text{Co}^{\text{II}}(\text{CN})_5]^{3-}$ and of $[\text{Co}^{\text{III}}(\text{CN})_5\text{H}]^{3-}$ in water at 25° . The hydride solution was obtained by reducing $[\text{Co}^{\text{II}}(\text{CN})_5]^{3-}$ with NaBH_4 until a negligible amount of the Co^{II} complex remained.

Under the conditions mentioned above and at 25° the $[\text{Co}^{\text{II}}(\text{CN})_5]^{3-}$ ion is remarkably stable. The aging process¹¹ is so slow that at a cobalt concentration of 0.0024 M and with a cyanide to cobalt ratio (R) of 10, the complex declines in concentration only 1% in two days. We may therefore assume that all of the change that occurs in a few hours when H_2 is admitted is due to reaction with H_2 , with a negligible loss of $[\text{Co}^{\text{II}}(\text{CN})_5]^{3-}$ by aging.

We have already mentioned⁹ that the 967 $m\mu$ band can be used as an accurate measure of the $[\text{Co}^{\text{II}}(\text{CN})_5]^{3-}$ concentration. It lies remote from the bands of other complexes likely to be present. Of the remaining $[\text{Co}^{\text{II}}(\text{CN})_5]^{3-}$ bands only the one at 280 $m\mu$ is useful quantitatively, and then only

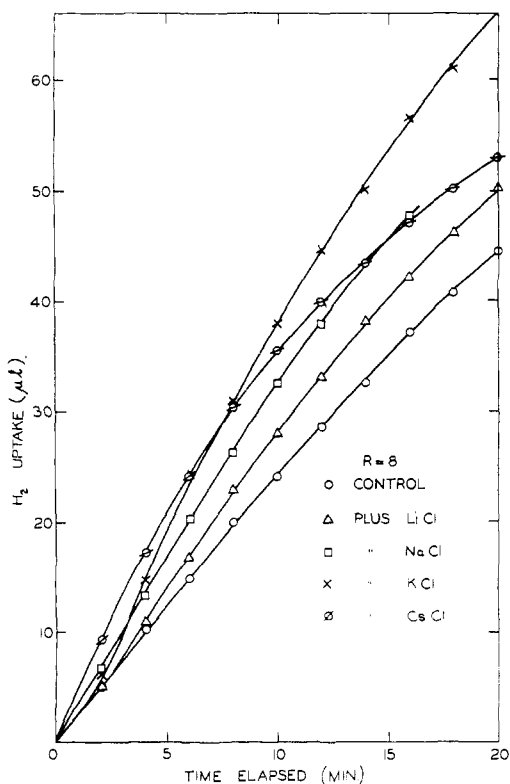


Fig. 2.—Homogeneous H_2 uptake by mixtures of aqueous $CoCl_2$ and KCN in the presence of alkali metal ions. R (mole ratio CN/Co) = 8.0; 20 micromoles Co in 2.8 ml. total vol.; 1 atm. H_2 ; 1° ; 90 micromoles of added salt.

in exceptional circumstances. The $316\text{ m}\mu$ peak is particularly susceptible to the presence of impurities, a trace of O_2 for example being sufficient to obliterate the peak leaving an indeterminate shoulder.

Hydrogenation with H_2 .—When $[Co^{II}(CN)_5]^{3-}$ is prepared in the presence of 1 atm. of H_2 , and in the above-mentioned concentration range 0.0003 to 0.0072 M , the $967\text{ m}\mu$ peak falls rapidly at first, then gradually for several days, the change being accompanied by formation of a colorless complex which absorbs at $305\text{ m}\mu$ (Table I and Fig. 1). There is no other product detectable spectrophotometrically. Since rise of the $305\text{ m}\mu$ peak is accompanied by decline of the nearby $316\text{ m}\mu$ band of $[Co^{II}(CN)_5]^{3-}$ and since traces of O_2 can result in the appearance of two complexes which absorb at 310 and $311\text{ m}\mu$, some care is required in carrying out the experiment.

Analysis of the spectra obtained after hydrogenation appears to have reached equilibrium indicates that almost all of the $[Co^{II}(CN)_5]^{3-}$ is finally converted to the $305\text{ m}\mu$ complex, which we shall write as $[Co^{III}(CN)_5H]^{3-}$, *i.e.*, a cobaltic complex in which one of the ligands is the hydride ion H^- . The structure is discussed later.

Manometric Determination of H_2 Uptake.—Iguchi⁸ obtained an uptake of 0.8 hydrogen atom per atom of cobalt, and Mills, Weller and Wheeler¹¹ have found values near 0.95 under favorable circumstances. Thus the experimentally determined stoichiometry is close to that expected from

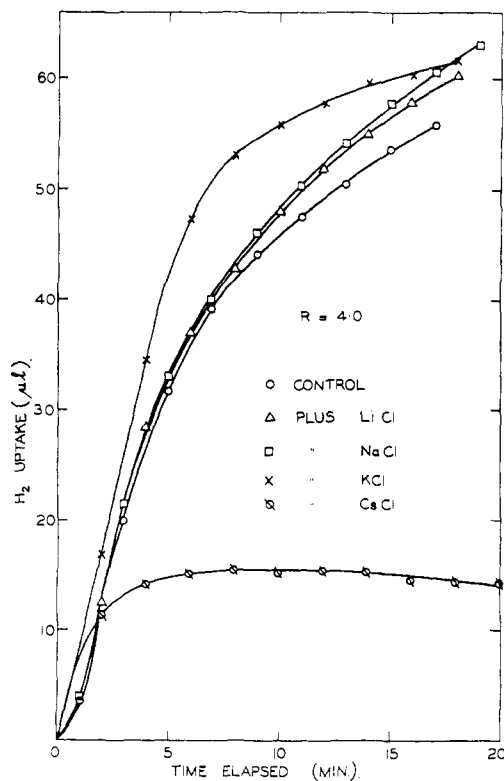
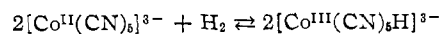


Fig. 3.—Heterogeneous reaction with H_2 showing the effect of alkali metal ions. $R = 4.0$; other conditions as in Fig. 2.

the equation



if the reaction were to go to completion. With dilute solutions in the presence of 1 atm. of H_2 a few % of $[Co^{II}(CN)_5]^{3-}$ remain at equilibrium.

Since the rate of aging, and its extent, are temperature dependent, the experimentally observed activation energy and frequency factor for H_2 uptake are of uncertain significance. Values obtained at $R = 4$ over the range $1-10^\circ$ are 6 kcal./mole, and 5×10^3 l./hr./mole of cobalt, respectively.

The order of effectiveness of alkali-metal cations in accelerating H_2 uptake is $Cs^+ > K^+ > Na^+ > Li^+$ as shown in Fig. 2. After a brief period the rate in the presence of Cs^+ declines due to considerable loss of cobaltocyanide ion by disproportionation (discussed later). A sustained high rate of reaction with H_2 can be achieved by using KCl as promoter. It was demonstrated later that Rb^+ lies between Cs^+ and K^+ in promoting H_2 uptake and also in producing the absorption peak at $380-390\text{ m}\mu$ which in our previous paper⁹ we have related to the H_2 evolution reaction.

Qualitatively the salt effect is the same in the presence of precipitated cobaltous dicyanide, at an R value of 4 (Fig. 3). Here however the apparent rate in the presence of Cs^+ tapers off sharply due to H_2 evolution, which after 10 min. exceeds H_2 uptake.

Reversibility of Hydrogenation.—If after reaction with H_2 the residual gas is pumped off, the $967\text{ m}\mu$ band can be observed to increase (after allowing

for loss of water during pumping). Complete recovery of the original cobaltous complex is not possible.

A solution of $[\text{Co}^{\text{II}}(\text{CN})_6]^{3-}$ allowed to stand for several days in H_2 at 0° will, when warmed to 25° , evolve H_2 with simultaneous increase in absorption at $967 \text{ m}\mu$.

An alternative demonstration can be made by adding ethanol.¹² The experiment is convincing if the cobaltous complex is treated with NaBH_4 rather than H_2 , thus achieving virtually complete conversion to $[\text{Co}^{\text{III}}(\text{CN})_5\text{H}]^{3-}$. On addition of ethanol there is a copious evolution of H_2 accompanied by precipitation of considerable $\text{K}_6\text{Co}_2(\text{CN})_{10}$.

Reversal can also be observed on turning off the current during electrolytic reduction of $[\text{Co}^{\text{II}}(\text{CN})_6]^{3-}$.

Reduction by Sodium Borohydride.—When NaBH_4 is used in place of H_2 the reaction is more rapid and complete, again yielding the $305 \text{ m}\mu$ complex (Fig. 1) with no other products readily detectable in the spectrophotometer.

Electrolytic Reduction.—The result is similar to that obtained with H_2 , although it is much more difficult to achieve a clean spectrum. Thus the Co^{I} complex claimed by Treadwell and Huber⁴ to be the reduction product is our $305 \text{ m}\mu$ complex, which we believe to be $[\text{Co}^{\text{III}}(\text{CN})_5\text{H}]^{3-}$.

"Self-Reduction."—Formation of the $305 \text{ m}\mu$ complex in solutions containing $[\text{Co}^{\text{II}}(\text{CN})_6]^{3-}$, without the addition of reducing agent, may be observed in certain circumstances, for example when CsCl is added. It is then accompanied by a rise at $375\text{--}390 \text{ m}\mu$, shown later to be due to a complex whose absorption peak is at $380 \text{ m}\mu$ and whose structure is $[\text{Co}^{\text{III}}(\text{CN})_5\text{OH}]^{3-}$ or $[\text{Co}^{\text{III}}(\text{CN})_5\text{OH}_2]^{2-}$.

It can be demonstrated spectrophotometrically that two moles of the $967 \text{ m}\mu$ complex yield one of the $305 \text{ m}\mu$ and one of the $380 \text{ m}\mu$ compound, assuming all three to be monomeric. Thus the simple disproportionation mechanism for the loss of paramagnetism¹¹ on aging proves to be correct. The view previously held by Mills, Weller and Wheeler¹¹ and by us that dimerization was responsible was based on inability to detect the products of disproportionation. We were unable to distinguish the $305 \text{ m}\mu$ band of $[\text{Co}^{\text{III}}(\text{CN})_5\text{H}]^{3-}$ from the $316 \text{ m}\mu$ band of $[\text{Co}^{\text{II}}(\text{CN})_6]^{3-}$ and the $310 \text{ m}\mu$ band of $[\text{Co}^{\text{III}}(\text{CN})_6]^{3-}$, while Mills, *et al.*, failed to observe the band near $380 \text{ m}\mu$. The latter is clearly visible if the region is scanned continuously during the experiment. Mills, *et al.*, may have used more dilute solutions for their spectrophotometry than for their paramagnetic studies, or the $380 \text{ m}\mu$ complex may have already been converted to $[\text{Co}^{\text{III}}(\text{CN})_6]^{3-}$ before the spectrum was examined.

Absorption Spectrum of $\text{K}_6\text{Co}_2(\text{CN})_{10}$.—The purple crystalline diamagnetic³ form of potassium pentacyanocobaltate(II) has a visible absorption band at $532 \text{ m}\mu$ when a crystal is examined in air.¹⁵ With the wave length shifted a little toward the red the peak is also readily detected in tricresyl-

phosphate or Nujol mulls. In the ultraviolet region the absorption of $\text{K}_6\text{Co}_2(\text{CN})_{10}$ is not clearly distinguishable from that of the products of disproportionation and oxidation at the surface of the crystal.

Methanol as Solvent.—On mixing CoCl_2 and KCN solutions in methanol which contains a little water (A.R. methanol without further drying), the absorption spectrum resembles that obtained in water, with the following exceptions:

(i) The 230 , 316 and $967 \text{ m}\mu$ bands are displaced $2 \text{ m}\mu$ to higher wave lengths.

(ii) There is appreciable disproportionation, as in water containing CsCl .

(iii) The reduced product of the disproportionation is less soluble than the $380 \text{ m}\mu$ complex and tends to precipitate out. In the absence of oxygen it can be separated and dissolved in water with no change in wave length of the absorption band ($305 \text{ m}\mu$).

(iv) A weak band at $510\text{--}530 \text{ m}\mu$ is readily detectable for several minutes after mixing, at 2° . At room temperature it is far less apparent. The band is also seen when pure $\text{K}_6\text{Co}_2(\text{CN})_{10}$ is dissolved in methanol at low temperatures. It is a reasonable assumption that the ion responsible for the absorption is $[\text{Co}_2(\text{CN})_{10}]^{6-}$.

Although $[\text{Co}^{\text{II}}(\text{CN})_6]^{3-}$ is much less soluble in A.R. methanol than it is in water, the solubility is adequate for determination of absorption spectra and rates of H_2 uptake and evolution. When the reagents and solvent are dried further, the solubility becomes quite small (about 0.00025 mole/l.). It is of interest that in the driest solutions which we are able to achieve there is negligible shift in wave length of the absorption bands compared with those seen in pure water (Table I). There is little disproportionation (about 6% per day in 0.00024 M solution at room temperature), and its slow progress seems to be accompanied by decreasing solubility of $[\text{Co}^{\text{II}}(\text{CN})_6]^{3-}$, suggesting that the disproportionation is removing the last traces of water from the solvent. Since no new absorption bands are seen, it is unlikely that both of the ions $[\text{Co}^{\text{II}}(\text{CN})_6]^{3-}$ and $[\text{Co}^{\text{II}}(\text{CN})_5\text{OH}_2]^{3-}$ can exist in solution.

Hydrogenation in Methanol.—Uptake of H_2 in A.R. methanol is accompanied by increased absorption at $305 \text{ m}\mu$, as in water, so that the product is again assumed to be $[\text{Co}^{\text{III}}(\text{CN})_5\text{H}]^{3-}$.

Manometric measurements show that the rate of reaction is much greater than in water: for example, 46 times greater at 21° in 1 atm. of H_2 , with $R = 16$ and a cobalt concentration of 0.005 M . Allowing for the 10 -fold greater solubility of H_2 in methanol, we may conclude that the concentration of the reactive cobalt species is 4 times higher in methanol or that the active species is 4 times more reactive due to an enhanced salt effect. It is clear from the remarks in the previous section that the proportion of cobalt present as $[\text{Co}^{\text{II}}(\text{CN})_6]^{3-}$ is less in methanol.

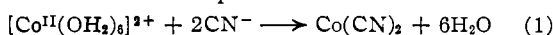
The initial rates of gas uptake at a given value of R are proportional to approximately the second power of the total cobalt concentration, as in water.³

(15) Measurement carried out by Dr. J. Ferguson, of the Division of Chemical Physics, Australian Commonwealth Scientific and Industrial Research Organization, using a microspectrophotometer.

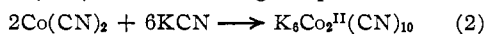
Although the results in methanol are suggestive that $[\text{Co}_2(\text{CN})_{10}]^{6-}$ is the ion which reacts with H_2 , experiments in which the height of the 530 $m\mu$ band was determined as a function of time showed no correlation between $[\text{Co}_2(\text{CN})_{10}]^{6-}$ concentration and rate of H_2 uptake. No ions which might conceivably react with H_2 were consistently found in greater concentration in methanol than in water.

Dimethyl Sulfoxide as Solvent.—The pentacyanocobaltate(II) ion has a distinctly different absorption spectrum in dimethyl sulfoxide, indicating reaction with the solvent. At first the principal product is a 1110 $m\mu$ complex which has an intense band at 296 $m\mu$ (Table I). It ages rapidly, reacts weakly with H_2 and strongly with O_2 .

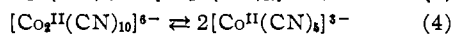
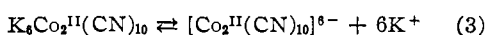
Aging Reactions in Water in the Absence of Reactive Gas.—At high cobalt concentrations ($>0.1 M$) the aging is rapid¹⁶ and results in loss of most of the $[\text{Co}^{\text{II}}(\text{CN})_5]^{3-}$ as indicated by decline of the 967 $m\mu$ band. Visual and spectrophotometric observations indicate that the sequence of events initiated when strong solutions of CoCl_2 and KCN are mixed proceeds as



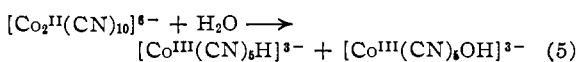
At the surface of the precipitated dicyanide¹⁷ the $\text{Co}(\text{CN})_2$ appears to be converted for a brief period to $\text{K}_6\text{Co}_2^{\text{II}}(\text{CN})_{10}$, thus coloring the particles red⁹



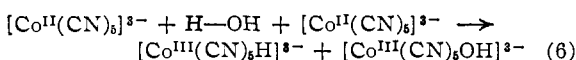
The $\text{K}_6\text{Co}_2^{\text{II}}(\text{CN})_{10}$ then dissolves in the surrounding water to give the dissociated dimeric ion, which rapidly monomerizes



Particularly in strong solutions it is likely that disproportionation occurs partly by the direct route *via* the dimer

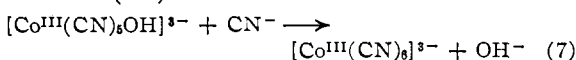


and the remainder *via* the monomer



a reaction for which close approach of the two negatively charged ions without formation of the Co-Co bond is probably adequate.

The next phase of the aging process is the irreversible formation of the very stable hexacyanocobaltate(III) ion

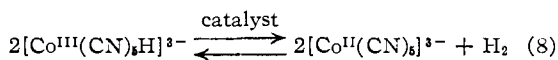


It is unexpectedly slow, suggesting that appreciable activation is required for addition of the sixth cyanide group.

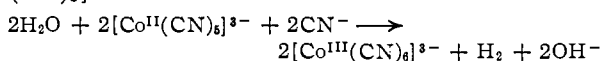
A tendency for the reduced product of disproportionation to generate an equilibrium concentration of H_2 becomes evident if a catalyst is present or the solution heated⁹

(16) This had been shown earlier by Mills, Weller and Wheeler¹¹ by following the decline in paramagnetism.

(17) In the early literature it is regarded as a hydrated salt which may exist in either of the two forms $\text{Co}(\text{CN})_2 \cdot 2\text{H}_2\text{O}$ or $\text{Co}(\text{CN})_2 \cdot 3\text{H}_2\text{O}$. Since it is undoubtedly a complex and contains Co^{II} , it is either $\text{Co}^{\text{II}}[\text{Co}^{\text{II}}(\text{CN})_4] \cdot n\text{H}_2\text{O}$ or a complex in which the ratio of cyanide to cobalt is not exactly 2. A new analysis is desirable.



Since the liberated Co^{II} complex can recycle *via* reactions 6-8, the net result is the one which has been so often observed when solutions of $[\text{Co}^{\text{II}}(\text{CN})_5]^{3-}$ have been heated



When the solutions are cool and free from precipitate, little or no H_2 is generated and the final stage of aging yields polymers which may take the form of threads or globules of colorless jelly. Since the products have negligible absorption in the visible or near ultraviolet regions, the reaction is difficult to follow spectrophotometrically.

Poor mixing of solutions, causing a local deficiency of cyanide, can result in precipitation of the green complex regarded by Descamps¹ as $\text{K}_2\text{Co}[\text{Co}(\text{CN})_4]$ and by Griffith and Wilkinson¹² as $\text{Co}_3[\text{Co}_2(\text{CN})_{10}]$. Since as we have already reported⁹ the amount of green complex formed is proportional to the amount of alkali added but not to the concentration of KCl , neither formula is convincing. It is possible that the green compound analyzed by the above authors was the one which forms on aging.

At temperatures below 3° we have observed a black precipitate, cobalt metal or cobalt oxide, which disappears when the temperature is raised a few degrees.

If aging in dilute solution is found to exceed a few % loss of $[\text{Co}^{\text{II}}(\text{CN})_5]^{3-}$ per day, it can be assumed that added salt or impurities is responsible. Oxygen is the most common cause. The absorption spectra of the products of oxygenation and subsequent oxidation will be discussed in a later paper.

Significance of the Salt Effect.—Mills, Weller and Wheeler¹¹ have pointed out the strong influence of added salt on the observable kinetics of homogeneous H_2 uptake, so strong that we may write approximately

$$r = k[\text{K}^+][\text{Co}] \quad (9)$$

up to values of $[\text{K}^+]/[\text{Co}]$ in the neighborhood of 25 (Fig. 4, ref. 8). Here r is the reaction rate, $[\text{K}^+]$ the total potassium ion concentration and $[\text{Co}]$ the concentration of $[\text{Co}^{\text{II}}(\text{CN})_5]^{3-}$ (equal at the beginning of the experiment to the total cobalt concentration). When the only source of K^+ is KCN , R has the value $[\text{K}^+]/[\text{Co}]$ and expression 9 becomes

$$r = kR[\text{Co}]^2$$

Thus our earlier finding,⁸ that r is proportional to $[\text{Co}]^2$ when $[\text{Co}]$ is varied while R is held constant, should be interpreted to mean that the rate is first order in $[\text{Co}^{\text{II}}(\text{CN})_5]^{3-}$, at least in the dilute solutions which we employed.

In the same paper⁸ we interpreted the observed kinetics to support $[\text{Co}^{\text{II}}(\text{CN})_6]^{4-}$, present in very small amounts in equilibrium with $[\text{Co}^{\text{II}}(\text{CN})_5]^{3-}$, as the ion which reacts with H_2 . The absorption band thought due to the hexacyanide ion has since proved to be that of a product of disproportionation. A comprehensive search has shown that if $[\text{Co}^{\text{II}}(\text{CN})_6]^{4-}$ can exist in solution it is at concen-

trations below the limit of detection by spectrophotometric means, even in the presence of methanol or CsCl. In addition Mills, Weller and Wheeler¹¹ have shown that added salt in the form of KCl is about as effective as excess KCN in accelerating H₂ uptake, thus confirming the irrelevance of [Co^{II}(CN)₅]⁴⁻ to the reaction mechanism.

The above statement regarding the equivalence of KCl and KCN as promoters requires amplification. By taking appropriate rates from the curves given in Fig. 4 of Bayston, King and Winfield⁸ and in Fig. 2 of the present paper, it can be estimated that KCN is about 15% more effective than KCl. The discrepancy is accounted for as follows: (i) KCN increases the pH of solutions of [Co^{II}(CN)₅]³⁻, and KOH is known⁵ to be 10–20% more effective than KCl in accelerating H₂ uptake; (ii) spectrophotometric measurements (unpublished) show that KCN induces less disproportionation than KCl.

It will be noticed in Figs. 2 and 3 that the variations in promoter effectiveness through the scale of cations from Li⁺ to Cs⁺ do not match with those which have been observed in H₂ evolution and in the disproportionation reaction by which it is preceded.⁹ In particular the anomalously large effect of Cs⁺ on disproportionation does not find a parallel in H₂ uptake, suggesting that a different property of the cation is utilized (perhaps hydration number in disproportionation and ionic radius in H₂ uptake).

Structure of the Reduced Complex.—The product of electrolytic reduction⁴ of [Co^{II}(CN)₅]³⁻ has usually been considered to be a Co^I complex, probably [Co^I(CN)₅]⁴⁻, since five cyanide ligands would confer on the cobalt the electronic structure of the inert gases. We have regarded it instead as a hydride of Co^{III} since it can be formed by reaction of [Co^{II}(CN)₅]³⁻ with H₂ without apparent liberation of protons.⁸ It can be shown that the complex persists in the presence of considerable KOH and therefore does not behave as an acid. Griffith and Wilkinson¹² have recently shown by nuclear magnetic resonance measurements that the complex does contain hydrogen.

The stoichiometry of its formation is good evidence that the complex has one more reducing equivalent per cobalt atom than [Co^{II}(CN)₅]³⁻. Thus if it is monomeric and the cobalt atom has the inert gas electronic structure, it should be written [Co^{III}(CN)₅H]³⁻. To be consistent with the accepted nomenclature of coordination chemistry, it is necessary to write the cobalt atom as formally Co^{III} rather than Co^I, since the ligand is by convention regarded as contributing two electrons to the sigma bond to the metal irrespective of the location of the electrons before addition of the ligand. Also we may argue that since [Co^{II}(CN)₅]³⁻ is a stronger¹⁸ reducing agent than H₂, it will reduce hydrogen to hydride ion while itself becoming oxidized to Co^{III}.

Owston, Partridge and Rowe's¹⁹ recent work on the structure of Pt(C₂H₅)₃P₂HBr is in harmony with the concept of a hydride ion occupying a nor-

mal ligand position. The absorption spectrum of the reduced cobalt complex (Fig. 1), with its single band, situated in the near ultraviolet region, is better explained in terms of an octahedral than a 5- or 4-coordinate structure.

That it contains not more than 5 cyanides per cobalt can be shown by the lack of precipitation when the hydride is formed in high yield in an R = 5 solution. Proof that there are no less than five cyanide ligands is still lacking. As evidence against a lesser number may be cited the very small activation energy of H₂ uptake. If the reaction required dissociation of a cyanide ligand, an activation energy of 20–50 kcal./mole of [Co^{II}(CN)₅]³⁻ would be expected.

Structure of the Oxidized Complex.—Spectrophotometrically and chemically the more oxidized of the two disproportionation products appears to be identical with the 380 mμ complex which has been prepared by several investigators^{20,21} by different methods and regarded as [Co^{III}(CN)₅OH]³⁻. It can be formed also by irradiation²² of pure aqueous K₃Co(CN)₆ and shown to contain five cyanide groups per cobalt atom, with OH or H₂O as the only possible ligands for the sixth position, providing that the complex is monomeric. We have chosen to write it as the hydroxo-complex since the pH in most of our experiments is 10 or more.

The absorption spectrum given in Table I is that of the purified complex prepared either by irradiation of [Co^{III}(CN)₅]³⁻ or oxidation of [Co^{II}(CN)₅]³⁻, followed by column chromatography.²² In the presence of 20% ethanol the 380 mμ peak is shifted to 382 mμ and in absolute alcohol to 388 mμ. When the complex is formed in dilute solution by disproportionation of [Co^{II}(CN)₅]³⁻, induced by added CsCl, the band is at 382–390 mμ. The displacement from 380 mμ may be explained by overlapping of the 428 mμ band of residual [Co^{II}(CN)₅]³⁻.

It should be noted that the pH behavior of mixtures of CoCl₂ and KCN⁹ will depend largely on the proton affinity of [Co^{III}(CN)₅OH]³⁻ and the rate at which the hydroxo-group can be replaced by $\bar{C}N$, a rate which will determine also the rate of the H₂ evolution whose kinetics we described in an earlier paper.⁹

Conclusions

Whereas aqueous solutions of the pentacyanocobaltate(III) compounds have a simple absorption spectrum with only two or even one clear band between 200 and 1000 mμ, the pentacyanocobaltate(II) ion has six definite bands and a probable shoulder. In methanol and in glycerol²² the spectrum is altered little while in dimethyl sulfoxide the bands are displaced considerably toward the red. After taking care to exclude water the methanolic solutions exhibit negligibly different absorption from that in pure water; on the other hand the solubility decreases as the water content

(20) P. R. Ray and N. K. Dutt, *Z. anorg. allgem. Chem.*, **234**, 65 (1937).

(21) L. C. Smith, J. Kleinberg and E. Griswold, *J. Am. Chem. Soc.*, **75**, 449 (1953).

(22) Unpublished results.

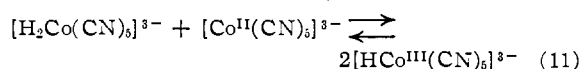
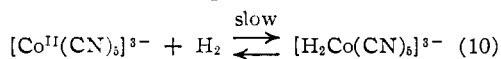
(18) G. Grube, *Z. Elektrochem.*, **32**, 561 (1926).

(19) P. G. Owston, J. M. Partridge and J. M. Rowe, *Acta Cryst.*, **13**, 246 (1960).

is diminished. Although these observations are in better harmony with the structure $[\text{Co}^{\text{II}}(\text{CN})_5]^{3-}$ than $[\text{Co}^{\text{II}}(\text{CN})_5\text{OH}_2]^{3-}$ the 5-coördinate structure cannot be considered proved.²³

When solutions containing the ion are allowed to age, the more reduced of the two products which appear is the same as that obtained by hydrogenation using H_2 or NaBH_4 , but the yield per $[\text{Co}^{\text{II}}(\text{CN})_5]^{3-}$ ion consumed is one-half as great. Early investigators described the reduction product, which they believed to contain Co^{I} , as reddish brown or yellow.²⁴ It proves to be colorless, very soluble in water, slightly soluble in methanol, stable in solution or the solid state provided that oxidants are excluded and much slower than $[\text{Co}^{\text{II}}(\text{CN})_5]^{3-}$ to react with O_2 . The assumption that it is a hydride of Co^{III} is in fair accord with the experimental evidence.

Combination of H_2 with $[\text{Co}^{\text{II}}(\text{CN})_5]^{3-}$ to yield $[\text{Co}^{\text{III}}(\text{CN})_5\text{H}]^{3-}$ is truly reversible, although complete recovery of the starting materials is unattainable. The evidence assembled to date on the mechanism of the reaction in dilute solution is most simply explained in terms of a slow first step, which is first order in cobalt, followed by a rapid second-order reaction, *e.g.*



The product in equation 10 is regarded as a short-lived free-radical, as in the uptake of oxygen or acetylene²² by $[\text{Co}^{\text{II}}(\text{CN})_5]^{3-}$. Although the Debye-Hückel limiting law governing the activity coefficients of the reactants will result in acceleration by added salt, the effect is expected to be weak when one of the two reactants is a neutral molecule. To explain the large acceleration by cations and the approximate validity of expression 9 we suggest that the reactive ions in equations 10 and 11 are $[\text{KCo}(\text{CN})_5]^{2-}$ and $[\text{KH}_2\text{Co}(\text{CN})_5]^{2-}$, respectively.²⁵

The H_2 -evolving complex discussed in a previous paper⁹ is now assumed to be $[\text{Co}^{\text{III}}(\text{CN})_5\text{H}]^{3-}$ formed by disproportionation in the presence of cations. The irreversible nature of the net H_2 evolution is due to the irreversible formation of $[\text{Co}^{\text{III}}(\text{CN})_5]^{3-}$ *via* $[\text{Co}^{\text{III}}(\text{CN})_5\text{OH}]^{3-}$, and the slowness of the final step in formation of the hexacyanide ion introduces the need for elevated temperatures.

The exchange reaction described by Mills, *et al.*,¹¹ depends upon the reversibility of D_2 uptake by $[\text{Co}^{\text{II}}(\text{CN})_5]^{3-}$ and requires that the deuteride ion of $[\text{Co}^{\text{III}}(\text{CN})_5\text{D}]^{3-}$ exchange with hydrogen of the solvent. Thus although a deuteron cannot be dissociated from the complex to give $[\text{Co}^{\text{I}}(\text{CN})_5]^{4-}$,

(23) Some arguments in its favor have been given by Adamson² and some in favor of the aquo complex by Griffith and Wilkinson.¹²

(24) In the presence of O_2 colored complexes will be found to obscure the result. The yellow color is due to the 380 $m\mu$ complex, the reddish brown to mixtures of $[\text{Co}^{\text{II}}(\text{CN})_5]^{3-}$ with the red peroxo compound.

(25) For a discussion of the participation of cations as part of the activated complex and of the relative insignificance of the Brönsted effect under these conditions, see A. R. Olson and T. R. Simonson, *J. Chem. Phys.*, **17**, 1167 (1949).

the D^- ligand can be replaced by H^- by an $\text{S}_{\text{N}}2$ mechanism. The reason for the roughly equal rates of exchange in fresh, aged and reduced solutions¹¹ lies in the compensatory effects of their different content of the ions $[\text{Co}^{\text{II}}(\text{CN})_5]^{3-}$, $[\text{Co}^{\text{III}}(\text{CN})_5\text{D}]^{3-}$ and $[\text{Co}^{\text{III}}(\text{CN})_5\text{H}]^{3-}$, these being the reactants in the three equilibria which comprise the exchange cycle. A contributory factor is the higher $p\text{H}$ in aged solutions.

Experimental

The manometric technique and the chemical reagents have already been described.^{8,9} In the spectrophotometric studies the following procedure is adhered to: KCN solution is pipetted into the main compartment of a quartz Thunberg tube and CoCl_2 solution into the sidearm. After alternate pumping and shaking for 10 min. at room temperature, the tube is flushed with O_2 -free gas and again shaken. It is then alternately pumped for 1 min. and shaken for 3 min. until the amount of water lost by evaporation is 0.4 g., as found by weighing. Accurate correction can thus be made for the change in reagent concentration due to pumping. When methanol is used as solvent the amount pumped off is 1.4 g. To prevent leakage over a period of several days, it is necessary to regrind the joints of the Thunberg tubes with some precision. Precautions are taken to minimize contamination of the solutions with silicone grease used to lubricate the joints.

Two scrubbers in series, containing aqueous 0.1 *M* $[\text{Co}^{\text{II}}(\text{CN})_5]^{3-}$ ($R = 6$), are used to remove reactive impurities from gases used for flushing and filling the Thunberg tubes. The method proves to be satisfactory for H_2 as well as N_2 and argon, since after saturating with H_2 the equilibrium concentration of $[\text{Co}^{\text{II}}(\text{CN})_5]^{3-}$ is sufficient to take care of impurities.

Particularly when NaBH_4 is used as reductant the success of an experiment depends upon freedom from nucleating agents in the Thunberg tube. When the tube is cleaned with considerable care no bubbles form in the solution after mixing the reagents and smooth absorption curves are obtained.

Reaction of CoCl_2 with the KCN is initiated by gently rocking the Thunberg tube back and forth 7 times in 14 sec., after which it is rapidly returned to the constant-temperature cell of the recording spectrophotometer in which it previously has been held for 20 min. to attain thermal equilibrium. Condensation on the optical surfaces is overcome by streams of filtered dry air brought to correct temperature by a heat exchanger cooled by the brine which is circulated through the cold cell.

A.R. grade solvents are used in most of the experiments in non-aqueous media, and therefore a little water must be assumed present. In attempting to use completely anhydrous reagents, they are dispensed in a dry-box containing P_2O_5 . The KCN is dried beforehand over P_2O_5 , the methanol by refluxing and distilling over magnesium methylate²⁶ and the $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ by converting to $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ over P_2O_5 at room temperature and then pumping at 200° until the remainder of the water is removed.

When determining extinction coefficients accurate correction is made for differences in optical properties of the sample and reference tubes. The latter contains the appropriate solvent with the addition of enough KCN to make the concentration of free cyanide the same in both tubes. It is unnecessary to have equal chloride ion concentrations. A difference in temperature between the two cells causes an error at 967 $m\mu$, where water itself has an absorption band. Values of ϵ for the 967 $m\mu$ peak of the cobaltocyanide ion can be reproduced to better than 1%, with correspondingly less exact results for peaks close to their neighbors. For example the 305 $m\mu$ band of $[\text{Co}^{\text{III}}(\text{CN})_5\text{H}]^{3-}$ is usually overlapped by the 316 $m\mu$ band of residual $[\text{Co}^{\text{II}}(\text{CN})_5]^{3-}$ and in faulty experiments by the 310 $m\mu$ bands of $[\text{Co}^{\text{III}}(\text{CN})_5]^{3-}$ and $[(\text{CN})_5\text{Co} \cdot \text{O}_2 \cdot \text{Co}(\text{CN})_5]^{6-}$. By reducing virtually all of the $[\text{Co}^{\text{II}}(\text{CN})_5]^{3-}$ with NaBH_4 (as in Fig. 1), values for ϵ_{965} can be obtained which are re-

(26) A. I. Vogel, "Practical Organic Chemistry," Longmans, Green and Co., London, 1951, p. 168.

producibile to about 2%. Suitable amounts of borohydride are 4 mg. in 5 ml. of 0.0024 M $[\text{Co}^{1+}(\text{CN})_6]^{3-}$ or 1 mg. in 5 ml. of 0.0003 M .

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kinetics. In the spectrophotometry we received valuable assistance from several members of the Division of Chemical Physics of C.S.I.R.O., including Dr. J. B. Willis, Dr. N. S. Ham, and Dr. R. N. Beale who carried out the exploratory absorption measurements.

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS]

Specific Interaction between Np(V) and U(VI) in Aqueous Perchloric Acid Media¹

BY J. C. SULLIVAN, J. C. HINDMAN AND A. J. ZIELEN

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Spectrophotometric, potentiometric and proton relaxation measurements provide evidence for a specific interaction between the oxygenated cations Np(V) and U(VI) in an aqueous acidic media. A value of $K = 0.690 \pm 0.013$ has been calculated for the reaction $\text{NpO}_2^+ + \text{UO}_2^{++} = [\text{NpO}_2^+ \cdot \text{UO}_2^{++}]$ at 25° in perchlorate media, from the spectrophotometric and potentiometric measurements. The reaction also has been studied spectrophotometrically in aqueous chloride media. The improved value of 1.13638 ± 0.00016 abs. v. was determined for the formal potential of the Np(V-VI) couple in 1 M perchloric acid at 25°.

Introduction

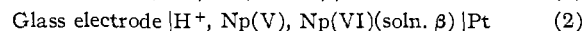
In the course of a study on the kinetics of the reduction of Np(VI) by U(IV),² spectrophotometric observations indicated that there was an interaction between Np(V) and U(VI) ions in an aqueous perchloric acid media. Such an unusual association reaction, *i.e.*, between two different cations in an acidic non-complexing medium, warranted a more detailed investigation. The results of such a study, in which both spectrophotometric and potentiometric methods have been used to establish the existence of a definite complex, are presented in this communication.

Experimental

Reagent Preparation.—Hydrochloric acid solutions were prepared by diluting constant boiling hydrochloric acid with triply distilled water. Sodium chloride solutions were prepared by dissolving recrystallized and dried sodium chloride in triply distilled water. The solution of Np(V) in hydrochloric acid was prepared by dissolving neptunium(V) hydroxide in hydrochloric acid. Conventional radiometric and analytical techniques were used to standardize the solutions. The preparation and standardization of the other reagents employed have been described in a previous publication.²

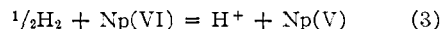
Spectrophotometric Measurements.—Two or five cm. silica absorption cells were filled with a measured volume of a solution containing the sodium or magnesium and uranyl salts plus the appropriate acid. The ionic strength was adjusted to 3.00. Absorption measurements were made from 10,800–9100 Å. with a Carey Model 14 Spectrophotometer. An aliquot of Np(V) solution then was introduced into the cell and the measurements repeated. Measurements on each cell were run in duplicate, and three different cells were used for each uranyl concentration. The average precision was ± 0.003 in the optical density. All measurements were made at 25.0°. No change could be detected in the spectra over a period of ten days.

Potentiometric Measurements.—Potential measurements were made on the independent cell pairs



Except for substitution where necessary in solution α of inert ions of charge +1 and +2, corresponding pairs of cell solutions α and β were formally identical. The e.m.f. of (1)

thus served as a calibration of the glass electrode. Assuming that this calibration potential is the same in solution β , addition of the two potentials (to be referred to as E_α and E_β) yields junction free e.m.f. values corresponding to the reaction



A single Beckman type 39177 glass electrode was used for all measurements. Lightly platinized hydrogen electrodes of the type described by Bates³ were freshly prepared for each determination of E_α . A short spiral of shiny 30 mil platinum wire sealed in soft glass tubing was employed to measure E_β ; this electrode was stored in concentrated nitric acid when not in use. Cell potentials were read to 0.01 mv. using a Leeds and Northrup K-2 potentiometer (with a recently calibrated standard cell) and a Cary Model 31-V Vibrating Reed Electrometer as a null point detector.

The cell proper consisted of a stubby test-tube 28 × 90 mm., which fitted snugly into a cup-shaped glass jacket through which water thermostatted at $25.00 \pm 0.01^\circ$ was pumped. A rubber stopper provided support for the electrodes and gas bubbling tubes. Convenient stirring of the cell solution was obtained by resting the entire assembly on top of a magnetic stirrer.

Electro-grade hydrogen was passed through a commercial catalytic purifier, then through a series of several scrubbing towers: dilute sodium hydroxide, dilute perchloric acid, distilled water and finally a sample of solution α immersed in the thermostated water-bath source for the cell jacket. All measurements were carried out in a constant temperature room, $25 \pm 1^\circ$.

Figure 1 illustrates both the data from a typical run (first entry of Table III) and the procedure employed to obtain the final E_α and E_β values. For each cell pair potential E_α was measured first, the hydrogen electrode requiring from 30 min. to 2 hr. to attain equilibrium. This effect is indicated in Fig. 1 and, of more importance, the continued slow drift in cell potential due to the instability of the glass electrode. From day to day this potential drift varied erratically both in magnitude and direction, but over a period of several hours the change usually could be approximated as linear with time.

After establishment of a satisfactory drift rate for E_α , the glass electrode was carefully rinsed and dried; and the entire procedure was repeated with a fresh tube containing solution β and the appropriately altered electrode assembly for the measurement of E_β . In this change over the sign of the glass electrode is reversed, which ideally should also reverse the slope but not the magnitude of the E_β drift. Addition of the values for E_α and E_β at a common time then yields the potential corresponding to equation 3. In practice any difference in the two drift rates was averaged by use of the

(1) Work performed under the auspices of the U. S. Atomic Energy Commission.

(2) J. C. Sullivan, A. J. Zielen and J. C. Hindman, *J. Am. Chem. Soc.*, **82**, 5288 (1960).

(3) R. G. Bates, "Electrometric pH Determination," John Wiley and Sons, Inc., New York, N. Y., 1954, pp. 166-167.