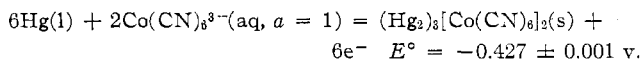
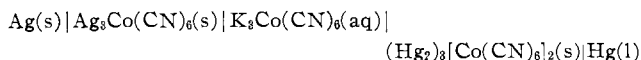


calomel electrode (-0.2680 v.),⁵ E_2° is the standard oxidation potential of the mercury-mercurous cobalticyanide electrode, $m\gamma_{\pm}$ refers to $K_3Co(CN)_6(aq)$, and $m'\gamma_{\pm}'$ refers to $KCl(aq)$. From the observed cell voltages, the above stated molalities, and the mean molal activity coefficients of $K_3Co(CN)_6$ ⁶ and KCl ,⁷ the standard oxidation potential of the mercury-mercurous cobalticyanide electrode is calculated to be



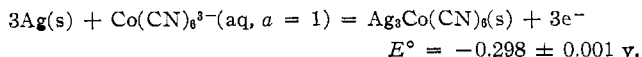
In the calculation of this E° the solid phase was assumed to be anhydrous salt, although it is probably the tetrahydrate. This introduces no significant uncertainty in E° , however, since the correction for the activity of water is within the experimental error.

Silver Cobalticyanide.—The potential of the silver-silver cobalticyanide electrode was determined in the cell



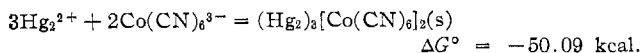
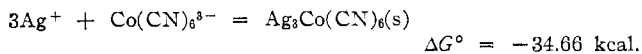
If the solid phases controlling the activities of Ag^+ and Hg_2^{2+} ions in solution are those represented in the cell diagram the observed cell voltage should be independent of the $K_3Co(CN)_6$ concentration and $E = E^\circ$. For $K_3Co(CN)_6$ molalities of 0.10, 0.20, and 0.50 the observed cell voltages were (silver negative): 0.130 ± 0.001 , 0.128 ± 0.001 , and 0.129 ± 0.001 v., respectively. This cell came to equilibrium in about 1 day and had a constant voltage for as long as it was followed (6–8 days in each case). The observed cell voltage was unaffected by the agitation of the electrode components.

Using the above-determined value of the mercury-mercurous cobalticyanide standard oxidation potential, the standard oxidation potential of the silver-silver cobalticyanide electrode is computed to be



Discussion

Taking the standard oxidation potential at 25° of the $Ag-Ag^+$ electrode as -0.799 v. and that of the $Hg-Hg_2^{2+}$ electrode as -0.789 v.,⁸ one computes



From these ΔG° values the solubility products of $Ag_3Co(CN)_6$ and $(Hg_2)_3[Co(CN)_6]_2(s)$ are computed to be 3.9×10^{-26} and 1.9×10^{-37} , respectively.

The previously reported value¹ for K_{sp} of $Ag_3Co(CN)_6$ is 8.6×10^{-21} . This value was obtained from potentiometric titration data in cells using salt bridges, a method which can introduce large uncertainties in the

data. The K_{sp} values differ, however, by more than can be accounted for by a liquid junction potential of even 0.05 v., and the K_{sp} obtained in the potentiometric investigation may have been adversely affected by failure to attain equilibrium as well, since it was found in this investigation that the silver-silver cobalticyanide electrode is slow to come to equilibrium.

CONTRIBUTION FROM THE JET PROPULSION LABORATORY,
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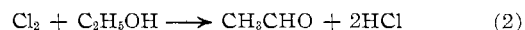
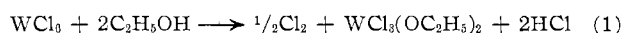
Chloride Alkoxides of Pentavalent Tungsten¹

BY OLGIERD J. KLEJNOT²

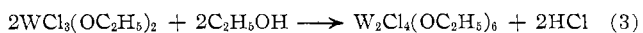
Received July 2, 1965

Studies aimed at syntheses of the unknown tungsten hexa- and pentaalkoxides have led to the first isolation of tungsten(V) chloride alkoxides (I–III). The reported green $W_2Cl_4(OC_2H_5)_6$ ³ obtained by reducing pentavalent solutions seems to be tetravalent with two ethanol ligands in place of two ethoxo ligands.

Dissolution of tungsten hexachloride in alcohols gave long-known yellow solutions,³ but the evolution of chlorine in methanol or ethanol has only been noted now



A violent reaction, which probably involves the aldehyde, occurs at high concentration of products. On evaporation the reaction solutions render paramagnetic, ink-blue trichloride dialkoxides, $WCl_3(OCH_3)_2$ (I) and $WCl_3(OC_2H_5)_2$ (II), whose blue solutions in alcohol give with hydrogen chloride a pale yellow color, reverting to blue on partial evaporation *in vacuo*. The trichloride dialkoxides react with moisture and oxygen. In alcohol they form soluble complexes with NaF, NaCl, and the methoxides of Li, Na, and K. Pure alcohol solutions, however, show at room temperature a slow limited solvolysis, up to a low concentration of HCl, with blue (methanol) or red (ethanol) color. From a solution of II, di- μ -chloro-dichlorohexaethoxoditungsten(V) (III) is slowly precipitated in 4–15% yield



Diamagnetic, red dimer III is inert to water, acids, and oxidizing agents, but is reactive toward bases. The dimeric formula and chemical evidence suggest a bioctahedral structure with two bridging chloro ligands and pentavalent tungsten atoms. The compound is

(1) Results of one phase of research supported by the National Aeronautics and Space Administration under Contract No. NAS7-100.

(2) Unified Science Associates, Inc., Pasadena, Calif. 91105.

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