After Laplace transform with respect to the variable t, equations (28) and (29) are reduced to the following ordinary differential equations

$$D(\mathrm{d}^2\bar{\psi}(x,s)/\mathrm{d}x^2) - s\bar{\psi}(x,s) + C^0 = 0 \qquad (36)$$

$$D(\mathrm{d}^2\bar{\varphi}(x,s)/\mathrm{d}x^2) - (s + k_f + k_b)\bar{\varphi}(x,s) = 0 \qquad (37)$$

and the boundary conditions are accordingly

$$\frac{\mathrm{d}\bar{\psi}(0,s)}{\mathrm{d}x} - \frac{\mathrm{d}\bar{\varphi}(0,s)}{\mathrm{d}x} = \frac{\lambda(1 + (k_b/k_f))}{s} \qquad (38)$$

$$\mathrm{d}\bar{\varphi}(0,s)/\mathrm{d}x = (k_b/k_f)(\mathrm{d}\bar{\psi}(0,s)/\mathrm{d}x) \qquad (39)$$

The solutions of equations (36) and (37) ($\bar{\psi}(x,s)$ and $\bar{\varphi}(x,s)$ are bound for $x \rightarrow \infty$) were given above in equations (17) and (18).

The integration constants M and N are evaluated by satisfying the boundary conditions (38) and (39). Thus

$$\bar{\psi}(x,s) = (C^0/s) - \lambda(D^{1/2}/s^{3/2}) \exp(-s^{1/2}x/D^{1/2}) \qquad (40)$$

$$\bar{\varphi}(x,s) = \lambda \frac{k_b}{k_f} \left(1/s\left(\frac{s + k_f + k_b}{D}\right)^{1/2}\right) \exp\left[-x\left(\frac{s + k_f + k_b}{D}\right)^{1/2}\right] \qquad (41)$$

By inverse transformation one finally obtains the functions $\psi(x,t)$ and $\varphi(x,t)$. The inverse transform of $\bar{\psi}(x,s)$, as given in equation (19), is obtained directly from tables.[13] The inverse transform of $\bar{\varphi}(x,s)$ is obtained by applying the convolution.[13] Thus

$$\varphi(x,t) = \lambda(k_b/k_f) \int_0^t (D/\pi\epsilon)^{1/2} \exp\left[-(k_f + k_b)\xi - (x^2/4\xi)\right]\mathrm{d}\xi \qquad (42)$$

For the evaluation of the integral in (42) see Horenstein.[21] By applying the result obtained by this author, equation (20) is readily derived.

As a final comment, it should be mentioned that the equation for the potential–time curve can be derived from the above results. If the reduction Ox to Red is irreversible, the potential during electrolysis is calculated by the same method as that exposed in the section entitled "Irreversible Electrode Processes." The concentration $C_{ox}(0,t)$ needed in this calculation is given in equation (21). If the process is reversible the potential is calculated from the Nernst formula. The concentration $C_{red}(0,t)$ needed in this calculation is determined from the flux of this substance (equal to $-D\partial C_{ox}(0,t)/\partial x$) at the electrode surface and by application of Duhamel's theorem.[22] This derivation is not given here for the sake of briefness, since it is the transition time which is of interest in the present case.

BATON ROUGE, LOUISIANA

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[21] W. Horenstein, *Quart. App. Math.*, **3**, 183 (1945).

[22] See for example H. S. Carslaw and J. C. Jaeger, "Conduction of Heat in Solids," Oxford University Press, London, 1947, p. 18.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

Determination of the Valence of a Heteropoly Anion: Dodecamolybdoceric(IV) Acid and its Salts. Structural Considerations

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RECEIVED DECEMBER 20, 1952

Solutions of pure 12-molybdoceric(IV) acid were prepared by the use of ion-exchange resin. Potentiometric titration confirmed the presence of eight replaceable hydrogen ions as indicated by the formulas of some of its salts. A new salt containing eight dimethylammonium groups was made from the free acid. A structural formula is suggested based on a central CeO_6 octahedron, which is consistent with the observed basicity.

Potentiometric titration of a solution of a free heteropoly acid offers a convenient method for determining approximate dissociation constants, and the number of replaceable hydrogen ions per molecule. The recent application of the ion-exchange method to the production of heteropoly acids from their recrystallized salts[2] has made it possible to prepare solutions of a number of these acids in a pure state. Heteropoly acids made by older methods could not be purified readily by recrystallization because of the high solubility characteristic of this class of compounds[3]; the presence of even small amounts of impurities, such as acids of low molecular weight, would introduce significant errors in the titrations because of the high molecular weight and polybasic nature of the heteropoly acids.

The purpose of the present work is to apply the method of potentiometric titration to a 12-molybdoheteropoly acid, and to one of its salts recently prepared in this Laboratory.

The dodecamolybdocerates(IV) were chosen for study because the free acid proved to be stable, and because the high basicity assigned to the anion by its discoverer seemed to offer interesting possibilities for discussing its structure.

Barbieri[4] has reported dodecamolybdocerates(IV) to which he assigned the following Miolati–Rosenheim formulas: $(NH_4)_8[Ce(Mo_2O_7)_6]\cdot 8H_2O$, $(NH_4)_6H_2[Ce(Mo_2O_7)_6]\cdot 10H_2O$, $Ag_8[Ce(Mo_2O_7)_6]$. Meinhard[5] has described the sodium salt: $4Na_2O$, $CeO_2\cdot 12MoO_3\cdot 6H_2O$, which may be formulated as $Na_8[Ce(Mo_2O_7)_6]\cdot 6H_2O$. All of these formulas indicate an octabasic anion.

Experimental

Yellow ammonium dodecamolybdocerate(IV) octahydrate, $(NH_4)_8[CeMo_{12}O_{42}]\cdot 8H_2O$, was prepared according to Barbieri[4] by adding 5% ammonium cerium(IV) nitrate solution to boiling 0.25 M ammonium paramolybdate solution. In order to obtain pure material the normal salt was converted to the light yellow acid salt, by saturating dilute sulfuric acid at 65° with the former, filtering, cooling, and adding a saturated ammonium nitrate solution. Light yellow crystals separated and were filtered and washed free of sulfate ion with saturated ammonium nitrate solution. The crystals were washed thoroughly with methyl alcohol, recrystallized from hot water, filtered and washed with methyl alcohol.

A warm solution of the light yellow crystals was converted to the free heteropoly acid by the ion-exchange method,[2] using Amberlite IR-200 (Rohm and Haas Company) which had been upflow regenerated and washed. The yellow

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[1] Chemistry Department, Boston University, Boston 15, Massachusetts.

[2] L. C. W. Baker, B. Loev and T. P. McCutcheon, THIS JOURNAL, **72**, 2374 (1950).

[3] See, for example, R. D. Hall, *ibid.*, **29**, 690 (1907).

[4] G. A. Barbieri, *Atti Accad. Lincei*, [5] **23**, 1, 805 (1914).

[5] A. Meinhard, "Zur Kenntnis der Heteropolymolybdate des Mangans und einiger vierwertiger Elemente," Berlin, 1928.

solution of the new acid gave no test with Nessler reagent. After regeneration of the resin, the used regenerant was concentrated. It contained much ammonium ion but no cerium or molybdenum. Analysis of aliquots of the acid solution showed the ionic cerium to molybdenum ratio to be 1.04:12. The concentration of the acid solution was determined by passing aliquots through the Jones reductor, running the effluent into ferric alum solution, and titrating with standard ceric sulfate in the presence of *o*-phenanthroline ferrous sulfate indicator.

An aliquot of suitable size was then titrated potentiometrically with 0.1135 M sodium hydroxide solution. Readings were taken when stirring for 4 minutes failed to produce a change of 0.01 pH unit. The results of this titration, giving graphically below, show that the acid has eight replaceable hydrogen ions per cerium atom, and that the dissociation constants for the first six of these lie close to values within the range 6×10^{-3} to 1×10^{-3}, while the last two are somewhat less acidic. The appearance of the solution remained unchanged until about ten equivalents of base had been added, whereupon precipitation of ceric hydroxide became evident.

Dimethylammonium dodecamolybdocerate(IV), a new compound, was prepared by adding the acid to a solution containing an excess of dimethylammonium chloride. A yellow crystalline precipitate separated, which was filtered and dissolved in warm water. This solution was added to another solution containing an excess of dimethylammonium chloride. The yellow crystals which separated were recrystallized from warm water, air-dried and analyzed. The compound is very slightly soluble in cold water.

Anal. Calcd. for $[(CH_3)_2NH_2]_8[CeMo_{12}O_{42}]\cdot 20H_2O$: N, 4.16; Ce, 5.21; Mo, 42.8; H_2O, 13.4. Found: N, 4.05; Ce, 5.13; Mo, 43.2; H_2O, 13.7 (by difference).

A solution of the analyzed sample of this salt was titrated potentiometrically with the results given graphically above. The curve indicates that the compound is not an acid salt. A similar curve was obtained by titration of a sample of the salt which had been prepared directly from the normal ammonium salt, instead of from the free acid.

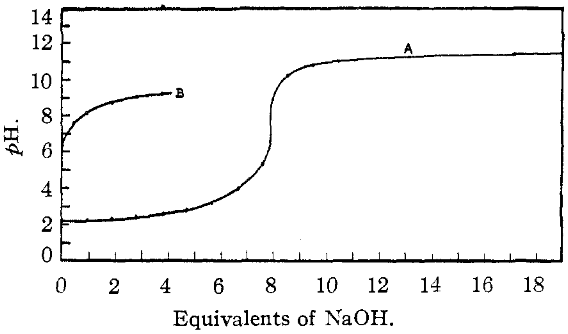

Fig. 1.—Titrations with 0.1135 M NaOH: A, 0.0017 M $H_8[CeMO_{12}O_{42}]$; B, $[(CH_3)_2NH_2]_8[CeMO_{12}O_{42}]$ solution of comparable concentration.

Discussion

The octabasic nature of dodecamolybdoceric(IV) acid, which is supported by the titrations described above, is also in agreement with the formula of its dimethylammonium salt and the salts reported by Barbieri[4] and Meinhard.[5] The acid salt formula, $(NH_4)_6H_2[CeMo_{12}O_{42}]\cdot 10H_2O$, of Barbieri for the light yellow crystals obtained from the deeper yellow normal salt in acid medium is also consistent with the observation that the dissociation constants of the first six hydrogen ions have nearly the same value, while the constants for the last two hydrogen ions are distinctly smaller.

The calculation of more precise values for the dissociation constants is not justified in the case of the acid under consideration, which has eight moderately strong replaceable hydrogen ions with constants quite close to the same value.[6]

Although these results confirm the basicity required by the Miolati–Rosenheim theory, the agreement probably should be regarded as fortuitous rather than significant in view of the formulas and structures established for a number of 12-heteropoly compounds by modern methods. Powder X-ray evidence has led Keggin[7] and others[8-12] to propose formulas of the type $H_{(8-n)}[XO_4Mo_{12}O_{36}]$, where n is the valence of X and X is phosphorus, arsenic, silicon, manganese or titanium, and $H_{(8-n)}[XO_4W_{12}O_{36}]$, where X is phosphorus, arsenic, silicon, boron or germanium. These views have been accepted widely.

In each of these cases a tetrahedral XO_4 group is in the center of the heteropoly anion, surrounded by twelve MoO_6 (or WO_6) octahedra which share corners with it while sharing corners and edges with each other in such a way that a total of forty oxygen atoms is utilized in the whole assemblage.

It seems clear that the Keggin formula does not fit the ceric compound. If a CeO_4 tetrahedron were at the center of the anion, its valence would be four $(8-n)$, which is at variance with all the experimental evidence cited above for an octabasic acid.

It is suggested, therefore, that the ceric ion is involved in sixfold rather than fourfold coördination with oxygen atoms, and that a symmetrical structure based on a central CeO_6 octahedron is possible which predicts the correct basicity. There are at least three different arrangements of the twelve MoO_6 octahedra about the central CeO_6 group which utilize the correct number of oxygen atoms.

One of these, which employs only edge and corner sharing of MoO_6 octahedra, is formed readily by joining two of Lindqvist's[13] paramolybdate ion structures in such a way that an octahedral pocket for the cerium atom remains in the center, and then eliminating the two MoO_6 octahedra which have all of their oxygen atoms shared. The other two are essentially similar to the Keggin structures; one involves six shared faces; the other distorted octahedra but no shared faces. In each case the formula of the acid would be: $H_8[CeO_6Mo_{12}O_{36}]$, and the general formulas for 12-heteropoly acids of this type: $H_{(12-n)}[XO_6Mo_{12}O_{36}]$ and $H_{(12-n)}[XO_6W_{12}O_{36}]$.

It will be recalled that the concept of a central octahedron has been suggested by Anderson[14] for 6-molybdoperiodates and similar compounds; in view of the evidence presented above, it seems reasonable to extend the idea to compounds of the 12-poly class. The coördination number six for cerium(IV) occurs in the well-known ammonium

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[6] S. Glasstone, "An Introduction to Electrochemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1949, pp. 403, 404.

[7] J. F. Keggin, *Nature*, **131**, 908 (1933).

[8] J. F. Keggin, *Proc. Roy. Soc* (*London*), **144**, 75 (A) (1934).

[9] J. L. Hoard, *Z. Krist.*, **84**, 217 (1933).

[10] R. Signer and H. Gross, *Helv. Chim. Acta*, **17**, 1076 (1934).

[11] J. W. Illingsworth and J. F. Keggin, *J. Chem. Soc.*, 575 (1935).

[12] J. R. deA. Santos, Dissert., Coimbra, 1947.

[13] I. Lindqvist, *Acta Cryst.*, **3**, 159 (1950); *Arkiv Kemi*, **2**, 325 (1950).

[14] J. S. Anderson, *Nature*, **140**, 850 (1937).

hexanitratocerate(IV). It is possible that other quadrivalent elements may have the same coördination number (6) in 12-heteropoly compounds. No X-ray studies appear to have been made with 12-heteropoly molybdo compounds of quadrivalent zirconium, thorium, germanium and tin, but salts with Miolati–Rosenheim formulas have been reported as

$(NH_4)_4H_4[Zr(Mo_2O_7)_6]\cdot 8H_2O$ $K_4H_4[Zr(Mo_2O_7)_6]\cdot 16H_2O$
$(CN_3H_6)_4H_4[Ge(Mo_2O_7)_6]$ $(NH_4)_8[Th(Mo_2O_7)_6]\cdot 15H_2O$
$(NH_4)_6H_2[Th(Mo_2O_7)_6]\cdot 11H_2O$ $Na_8[Th(Mo_2O_7)_6]\cdot 15H_2O$
$Na_6H_2[Th(Mo_2O_7)_6]\cdot 17H_2O$ $Ag_8[Th(Mo_2O_7)_6]$, $(NH_4)_8[Sn(Mo_2O_7)_6]\cdot 20H_2O$ and $(NH_4)_3H_5[Sn(Mo_2O_7)_6]\cdot 4H_2O$[15-18]

It seems probable that the coördination number is four in the zirconium and germanium compounds, and that they belong to the $H_{(8-n)}[XO_4Mo_{12}O_{36}]$ type. The thorium compounds, like those of cerium, appear to be derivatives of an octabasic acid, which may be formulated as $H_8[ThO_6Mo_{12}O_{36}]$. The case for the tin compounds is less clear and requires further study.

(15) G. A. Barbieri, *Atti Accad. Lincei*, [5] **22**, 781 (1913).

(16) C. G. Grossup, THIS JOURNAL, **52**, 5154 (1930).

(17) E. Pechard, *Compt. rend.*, **117**, 788 (1893).

(18) A. Rosenheim, *Z. anorg. Chem.*, **96**, 139 (1916).

PHILADELPHIA, PENNSYLVANIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF KANSAS]

The Reduction of Potassium Hexacyanomanganate(III) by Potassium in Liquid Ammonia

BY VALDEMAR J. CHRISTENSEN, JACOB KLEINBERG AND ARTHUR W. DAVIDSON

RECEIVED OCTOBER 17, 1952

The reduction of potassium hexacyanomanganate(III) by potassium in liquid ammonia results in the formation of a yellow product which is difficultly soluble in liquid ammonia and possesses strong reducing properties. The properties of the product, as determined by four different methods—reacting ratio studies, chemical analysis, reducing power determination and magnetic measurements—show it to contain manganese in a state which can only be characterized as intermediate between the unipositive and the zero oxidation state. If the product is regarded as containing both of these forms of manganese, they must be present in at least approximately the atomic ratio of 1:1. Its composition may be represented by the formula $K_5Mn(CN)_6\cdot K_6Mn(CN)_6\cdot 2NH_3$.

There is excellent evidence that unipositive manganese may exist in the form of cyanomanganate[1] complexes. Manchot and Gall[1] have demonstrated that potassium or sodium hexacyanomanganate(II) is reduced in an alkaline medium in an atmosphere of hydrogen by aluminum powder to give a yellow solution possessing strong reducing power. From such solutions these investigators isolated white solids containing the hexacyanomanganate(I) ion, $[Mn(CN)_6]^{-5}$. The evidence[1b] reported for the existence of the tricyanomanganate(I) ion is less convincing. Electrolytic reduction of the hexacyanomanganate(II) ion at a platinum cathode gives a white product which appears to contain unipositive manganese.[2,3] There remains, however, some question regarding the exact nature of this substance. Fernelius and Hood[4] have studied the reduction of potassium hexacyanomanganate(III) by potassium in liquid ammonia and have proposed that the orange product formed is $K_5Mn(CN)_6\cdot NH_3$. The present communication is also concerned with the reduction of potassium hexacyanomanganate(III) by potassium in liquid ammonia and describes the preparation of a yellow substance containing manganese in both the unipositive and the zero oxidation state, the composition of which may be represented by the formula $K_5Mn(CN)_6\cdot K_6Mn(CN)_6\cdot 2NH_3$.

Experimental

Materials.—The liquid ammonia was taken directly from commercial cylinders of the synthetic material. The potassium, obtained from the Mine Safety Appliances Company, was used without further purification. Potassium hexacyanomanganate(III) was prepared according to the method of Lower and Fernelius[5] and purified in the following manner. The impure crystals were placed in a large fritted-glass filter of medium porosity which was attached to a filter flask containing absolute ethanol. Just sufficient water was added to dissolve the crystals, and the solution was drawn into the ethanol by means of an aspirator. Any oxide formed by hydrolysis remained on the filter. As the aqueous solution came in contact with the ethanol, dark red crystals of potassium hexacyanomanganate(III) were formed. Two additional precipitations from ethanol gave a product of practically the theoretical manganese content.

Apparatus and Reduction Procedure.—The apparatus employed in the reductions is illustrated in Fig. 1. Individual sections of the apparatus were connected by means of flexible Tygon tubing. The reaction chamber was about 3.5 cm. in diameter and approximately 25 cm. high. Duplicate sampling bulbs A and B were inserted in the reaction chamber through ground glass joints. The ammonia delivery tube extended close to the bottom of the reaction chamber in order that the ammonia which was bubbled through during the course of the reaction might have a stirring effect on the reaction mixture. The presence at C of a large standard taper joint permitted the removal of the lower part of the reaction chamber for sampling purposes. The fritted-glass disk sealed into the bottom of the reaction chamber served, after withdrawal of the solvent into the filter trap by means of an aspirator, to hold the insoluble product formed in the reduction reactions.

Prior to each reduction the several pieces of the reaction chamber assembly were cleaned and dried in an oven at 110°. The apparatus was then completely assembled except for the sampling bulbs. The openings for the bulbs were stoppered with standard taper plugs and ammonia was passed through the system for at least one hour to sweep out the air and to dry the apparatus. The sampling bulbs were charged with weighed quantities of the reactants (the molar ratio of potassium to manganese(III) complex always being greater than 2.5:1), flushed with ammonia, and quickly inserted into the reaction chamber, a positive internal pres-

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[1] (a) W. Manchot and H. Gall, *Ber.*, **60B**, 191 (1927); (b) **61B**, 1135 (1928).

[2] G. Grube and W. Brause, *ibid.*, **60B**, 2773 (1927).

[3] W. D. Treadwell, O. Gübeli and D. Huber, *Helv. Chim. Acta*, **24**, 152 (1941).

[4] W. C. Fernelius, private communication.

[5] J. A. Lower and W. C. Fernelius, "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 213.