33. *The Oxidation–Reduction Potential of Sexa- and Quinque-valent Molybdenum Ions.*

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Sexa- and quinque-valent molybdenum ions in 8—6 and 4—2N-hydrochloric acid are found to possess the formulæ $MoO_2^{\cdot\cdot}$ and $MoO^{\cdot\cdot\cdot}$ within the former range and $(MoO^{\cdot\cdot})_2$ and $(MoO^{\cdot\cdot\cdot})_2$ within the latter. The formulæ refer, however, only to the cationic forms which are present in equilibria with other, anionic ones. Between both acid ranges there exist probably mixtures of the respective ionic species. By evaluating the redox potentials of the systems within both acid ranges and plotting them against $\sqrt{u}$, curves are obtained the extrapolation of which to zero ionic strength is found unjustifiable. It is therefore safer to consider as practically useful values a series of formal potentials each of which pertains to a definite acid concentration.

(I) *The Formulæ of Sexa- and Quinque-valent Molybdenum Ions in Acid Solutions.*—In studying the mechanism of the electrolytic reduction of acid molybdates, Foerster and Fricke (*Z. physikal. Chem.*, 1930, **146**, 81, 173) determined the redox potentials of sexa- and quinque-valent molybdenum ions in 2, 4, and 8N-hydrochloric acid. They suggested a formula for the molybdenum ion in each state of oxidation and accordingly represented the half-cell reaction by: $MoO_2^{\cdot\cdot} + 2H^{\cdot} = MoO^{\cdot\cdot\cdot} + H_2O + e$, irrespective of the acidity of the solutions. The observed potentials were found, however, to differ considerably from the calculated ones, especially in 2 and 4N-acid. This was attributed to a profound effect of the acid on molybdenum ions in solution which manifests itself further in the colour change from green to brown as the solutions pass from 8 to 2N-acid. Now, although it may be probable that the formulæ assigned by Foerster and Fricke are valid in one range of acidity, yet it is desirable to obtain insight into the changes in constitution which accompany the change in colour. As is shown elsewhere (Tourky, Farah, and El Shamy, *Analyst*, 1948, **73**, 258), quinquevalent molybdenum is suited for use as volumetric reagent, and this required the evaluation of the redox potential of the system Mo^{VI}–Mo^{V} on a sound basis.

Wieland and Knöl (*Z. anorg. Chem.*, 1905, **44**, 181) prepared compounds to which they assigned formulæ such as $MoCl_4(OCs)_2$, $MoOCl_3(ORb),H_2O$, and $Mo_6O_{11}Cl_{14},K_2O,6H_2O$. By tracing the formation of the corresponding acids in concentrated hydrochloric acid solutions by transport-number experiments it could be ascertained that molybdenum did not move in any appreciable quantity in the current, indicating that it formed part of the anionic radical(s) of an acid or acids whose ionisation was suppressed in presence of hydrochloric acid. As such, sexavalent molybdenum may be incapable of reduction unless it is transformed partly into the cationic form(s) which may therefore be assumed to be present in equilibrium by a reaction such as: $MoO_2Cl_4 + xH_2O \rightleftharpoons MoO_2(H_2O)_x + 4Cl^-$.

Analogous equilibria may prevail with respect to quinquevalent molybdenum ions (Foerster and Fricke, *loc. cit.*). We have now determined the equation for the molybdenum half-cell reaction, and established the most probable formulæ for the sexa- and quinque-valent molybdenum ions at different acidities, adopting a procedure similar to that used by Carpenter (*J. Amer. Chem. Soc.*, 1934, **56**, 1847) for finding the constitution of the vanadium ions.

Owing to the ease with which molybdenum-blue is formed on reduction in solutions less than 2N in hydrochloric acid content, only more concentrated acid solutions were employed. This necessitated the use of a saturated calomel electrode as the other half-cell. The saturated potassium chloride bridge was assumed to reduce the liquid-junction potential to a minimum.

In each mixture the concentrations of any two constituents were kept constant while the third was varied.

EXPERIMENTAL.

Molybdic acid of " AnalaR " grade was dissolved in pure concentrated hydrochloric acid. The molybdenum content of the solution was determined by precipitation as sulphide and weighing as oxide. The chloride ion was determined gravimetrically as silver chloride after distilling measured portions with concentrated sulphuric acid and receiving the evolved hydrogen chloride in redistilled water.

Quinquevalent molybdenum was obtained by electrolytic reduction of solutions containing molybdic acid in 2 or 8N-hydrochloric acid according to the method of Chelesotti (*Z. Elektrochem.*, 1906, **12**, 197), the reduction cell being essentially that proposed by Foerster and Fricke (*loc. cit.*). The reduction product was accurately checked by titration against standard ceric sulphate.

Solutions containing sexa- and quinque-valent molybdenum ions were made by mixing together the appropriate amounts of each solution, and the composition checked by analysis. From a determination of the total chloride and subtraction of the amount supposed to be combined, the amount of free hydrochloric acid was computed. Measurements were made on solutions approximately 6—8 or 2—4N with regard to free hydrochloric acid. In all cases the molybdenum-ion concentrations were kept low relative to the acid.

The oxidation–reduction cell used was a modified form of that used by Hart and Partington (*J.*, 1940, 1532). The measurements were performed in a thermostat adjusted at 30° ± 0·02°, a very sensitive mirror galvanometer and a platinum–iridium meter bridge being used. The readings for each cell were taken during 24 hours. Equilibrium was usually attained after a few hours and the final results did not diverge on the average by more than 0·5 mv.

Results and Discussion.—By assuming that sexa- and quinque-valent molybdenum ions can be represented by $MoO_2^{\cdot\cdot}$ and $MoO^{\cdot\cdot\cdot}$ respectively and by letting x and y represent the number of molybdenum and oxygen atoms in the former ion and z the number of molybdenum atoms in the latter, the formula of the respective ions will be $Mo_xO_y^{6x-2y}$ and $Mo_zO_z^{3z}$. The cell reaction can then be represented by

$$Mo_xO_y^{6x-2y} + (2y - 2x)H^{\cdot} = \frac{x}{z} Mo_zO_z^{3z} + (y - x)\ H_2O$$

from which it follows that

$$E = E_0 - \frac{RT}{Fn} \ln \frac{[Mo_zO_z^{3z}]^{1/z}}{[Mo_xOy^{(6x-2y)}]^{1/x}\ [H^{\cdot}]^{(2y-2x)/x}}$$

the expression for water being regarded as a constant term.

Not knowing the activity coefficients of the molybdenum ions, we shall use concentrations instead of activities. Now, by keeping the concentrations of any two solutes constant and varying the third in a series of cells, we obtain three relations in which the term E_0 will include the contribution of the first two solutes. Such relations can be represented as follows :

Case I. $E = E_{0_1} + (0{\cdot}0601/x) \log [MoO_2^{\cdot\cdot}]$
Case II. $E = E_{0_2} + [0{\cdot}0601(2y—2x)/x] \log [H^{\cdot}]$
Case III. $E = E_{0_3} + (0{\cdot}0601/z) \log [MoO^{\cdot\cdot\cdot}]$

If E is plotted in each case as a function of the variable concentrations, approximately straight lines should result, from the slopes of which x, y, and z could be determined. Measurements were made corresponding to the three cases above, each in three series. The concentrations of the fixed and the variable constituents, together with the e.m.f. values measured and the values of x, y, or z as evaluated from the plots (of the e.m.f. against the logarithm of the concentrations of the variable constituents), which were always straight lines, are shown in the Table.

Where the normalities of hydrochloric acid varied between 6 and 8N, it was necessary to insert activities (as obtained from Lewis and Randall, " Thermodynamics ", p. 336) instead of concentrations for that acid; otherwise values for y were obtained which were quite improbable. In solutions with more dilute acid, the replacement of concentrations by activities did not materially affect the results. In the 2—4N-acid solutions, it was found that x, y, and z have nearly double the values found for them in the 6—8N-acid solutions.

Foerster (*loc. cit.*) inferred that Mo^{VI} became on reduction dark emerald-green in 8N-hydrochloric acid, and yellow or dark brown in 4—2N-solutions. At acid concentrations lower than 2N, molybdenum-blue was formed. It is clear from the change in colour of the reduced products within the acid ranges 8—6 and 4—2N that a change in the molecular composition takes place. Since x, y, and z in the 4—2N-acid have double their values in the 8—6N-solutions, it is legitimate to assume that within the former range we have double rather than single molecules. It is probable that in the absence of concentrated hydrochloric acid to favour the formation of the anionic form(s), cations are abundantly formed which associate, however, in solution, forming the double molecules. The cell reaction in 8—6N-acid may now be represented by $MoO_2^{\cdot\cdot} + 2H^{\cdot} = MoO^{\cdot\cdot\cdot} + H_2O + e$, whereas in 4—2N-acid it may be $(MoO_2^{\cdot\cdot})_2 + 4H^{\cdot} = (MoO^{\cdot\cdot\cdot})_2 + 2H_2O + 2e$, which does not, however, imply that portions of the ions are not present in the anionic forms.

Series I. (A) HCl = 8·150M, Mo^{V} = 0·1364M.

[Mo^{VI}]	0·1267	0·1436	0·1477	0·1730	0·1857	0·1940
E.m.f.	0·4859	0·4892	0·4898	0·4939	0·4957	0·4968

Mean slope = 0·0571; x = 1·02.

(B) Mo^{V} = 0·151M, Mo^{VI} = 0·151M.

[H$^{\cdot}$]	8·207	7·959	7·768	7·576	7·385	7·194
E.m.f.	0·4735	0·4664	0·4604	0·4544	0·4484	0·4421

Mean slope = 0·1704; y = 2·42.

(C) HCl = 8·150M, Mo^{VI} = 0·1962M.

[Mo^{V}]	0·1364	0·1063	0·0871	0·0735	·00631	0·0532
E.m.f.	0·4926	0·4990	0·5040	0·5084	0·5124	0·5169

Mean slope = 0·0598; z = 1·00.

Series II. (A) HCl = 7·998M, Mo^{V} = 0·0032M.

[Mo^{VI}]	0·0032	0·0061	0·0091	0·0124	0·0149	0·0179
E.m.f.	0·4656	0·4828	0·4933	0·5018	0·5067	0·5116

Mean slope = 0·0615; x = 0·98.

(B) Mo^{V} = Mo^{VI} = 0·0032M.

[H$^{\cdot}$]	7·998	7·615	7·233	6·850	6·468	6·086
E.m.f.	0·4468	0·4372	0·4269	0·4162	0·4051	0·3932

Mean slope = 0·1440; y = 2·21.

(C) HCl = 7·998M, Mo^{VI} = 0·0099M.

[Mo^{V}]	0·0029	0·0058	0·0090	0·0119	0·0150	0·0197
E.m.f.	0·4838	0·4669	0·4564	0·4496	0·4440	0·4375

Mean slope = 0·0554; z = 1·08.

Series III. (A) HCl = 3·00M, Mo^{V} = 0·0001M.

[Mo^{VI}]	0·0034	0·0063	0·0093	0·0122	0·0152	0·0181
E.m.f.	0·2907	0·2990	0·3041	0·3078	0·3107	0·3132

Mean slope = 0·0309; x = 1·94.

(B) Mo^{V} = Mo^{VI} = 0·0032M.

[H$^{\cdot}$]	2·00	2·40	2·80	3·30	3·60	4·00
E.m.f.	0·2720	0·2820	0·2908	0·3003	0·3052	0·3113

Mean slope = 0·1305; y = 4·18 if x = 2.

(C) HCl = 3·122M, of Mo^{VI} = 0·009M.

[Mo^{V}]	0·0031	0·0062	0·0093	0·0125	0·0156	0·0187
E.m.f.	0·3152	0·3063	0·3012	0·2976	0·2947	0·2924

Mean slope = 0·0293; z = 2·05.

(II) *The Oxidation–Reduction Potential of Sexa- and Quinque-valent Molybdenum Ions.*—On account of the presence of quinque-valent molybdenum in two forms within the acid ranges 8—6 and 4—2N-hydrochloric acid, it is probable that the system Mo^{VI}–Mo^{V} will possess two redox potentials. In order to evaluate these potentials, series of cells were made in which the concentration ratio of sexa- and quinque-valent molybdenum ions and of hydrochloric acid were maintained constant but their actual concentrations were varied. In the following table representative results of measurements of cells where the acid concentrations were either 8—6 or 4—2N are shown. The quinque- and sexa-valent molybdenum concentrations were equal to each other in each cell and were much lower than those of the acid.

HCl, N	8·16	7·92	7·32	7·00	6·70	6·12
Mo^{VI} (Mo^{V}) × 10^{4}	197·94	118·77	63·34	31·67	15·84	4·75
E.m.f.	0·4670	0·4547	0·4301	0·4184	0·4082	0·3909

HCl, N.	3·60	3·30	3·00	2·70	2·40	2·10
Mo^{VI} (Mo^{V}) × 10^{4}	128·27	102·61	76·96	51·31	25·65	5·15
E.m.f.	0·3426	0·3316	0·3194	0·3072	0·2955	0·2835

Results.—The cell reaction giving rise to the e.m.f. can be written as follows:

$$MoO_2^{\cdot\cdot} + 2H^{\cdot} + Cl' + Hg = MoO^{\cdot\cdot\cdot} + H_2O + HgCl$$

The relation connecting the e.m.f. of the cell and the activities is represented by the equation

$$E = E_0' + (RT/nF)\ln\frac{[\mathrm{MoO_2}^{\cdot\cdot}]\,[\mathrm{H}^{\cdot}]^2[\mathrm{Cl}']}{[\mathrm{MoO}^{\cdot\cdot\cdot}]} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

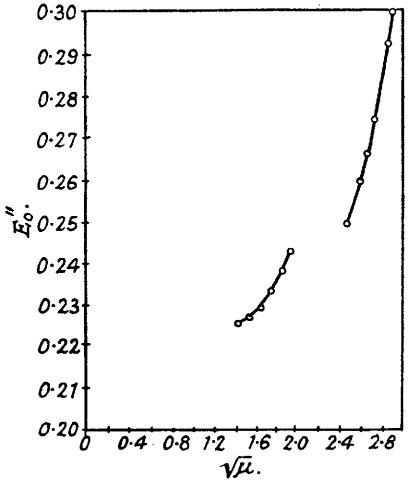
in which $E_0' = E_0(\mathrm{Mo^{VI}/Mo^{V}}) - E_0$ (calomel) and the brackets refer to activities. This equation can be written in the form

$$E - (RT/nF)\ln[\mathrm{H}^{\cdot}]^2[\mathrm{Cl}'] - (RT/nF)\ln[\mathrm{MoO_2}^{\cdot\cdot}]/[\mathrm{MoO}^{\cdot\cdot\cdot}] = E_0' + (RT/nF)\ln f_2/f_1 \quad . \; . \quad (2)$$

In this equation $[\mathrm{MoO_2}^{\cdot\cdot}]$ and $[\mathrm{MoO}^{\cdot\cdot\cdot}]$ refer to concentrations in mols. per litre and f_1 and f_2 are the respective activity coefficients. Since $[\mathrm{MoO_2}^{\cdot\cdot}]$ is made equal to $[\mathrm{MoO}^{\cdot\cdot\cdot}]$ and $[\mathrm{H}^{\cdot}]^2[\mathrm{Cl}'] = [\mathrm{HCl}]^3 f^3_{\mathrm{HCl}}$, the above equation may be transformed into

$$E - 3(RT/nF)\ln[\mathrm{HCl}] = E_0' + (RT/nF)\ln f_2 f^3_{\mathrm{HCl}}/f_1 \quad . \; . \; . \; . \; . \; . \quad (3)$$

Extrapolation of the left-hand side in equation (3) against the square root of the ionic strength u to $u = 0$ should yield the value of E_0', since at infinite dilution all activity coefficients become unity. The values of the left-hand side of the equation designated by the term E_0'' as plotted against $\sqrt{u}$ are shown in the figure, but neither graphical nor theoretical extrapolation (using the least-square method) of either of the two curves leads to reliable results. However, the curves are of interest as they provide further evidence for the existence of two different forms within the two acid ranges.



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