Thus we conclude that the presence of hydrogen in some active form raises the measured potential of the system and that the direction of the approach to the steady state is determined by the presence or absence of oxygen gas in the system.

The increase of potential to a steady state in cells 1, 2, 3, 4, 5, 6 and 10 is explained by the slow removal of the initial layer of iron oxide from the iron electrode. Our method of deoxygenating the solution does not remove the oxide film from the iron; this takes place slowly by means of electrochemical changes within the cell. The decrease of potential in cells 7, 8 and 9 is caused by the disappearance of the small amount of oxygen, which is acting as an electron sink and at a lower potential than the Hg_2SO_4–Hg electrode. The amount of oxygen involved was too small to effectively change the activity of the ferrous salt, or the final equilibrium potential. Large quantities of oxygen would greatly change the activity of the electrolyte by the introduction of OH ions

$$2e^- + {}^1/_2O_2 + H_2O \longrightarrow 2OH^-$$

These two opposing effects are strikingly illustrated in Fig. 2.

BALTIMORE 18, MD.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FACULTY OF SCIENCE, ALEXANDRIA UNIVERSITY]

The Oxidation–Reduction Potential of the Sexa- and Quinquevalent Molybdenum System

BY H. K. EL-SHAMY AND A. M. EL-AGGAN

RECEIVED APRIL 16, 1952

Spectrophotometric measurements have shown that in hydrochloric acid solutions of normality less than 3, molybdenum-(V) produces a brown color, while at acid normalities above 5.75, the color is emerald green. These colors correspond to two different series of ionic species which show strong absorption at wave lengths of 395 and 450 mμ, respectively. Other ionic species exist at intermediate acidities. The oxidation–reduction potentials of the Mo(VI)–Mo(V) system have been determined against a hydrogen electrode over a range of hydrochloric acid concentrations from 8 *N* to less than 0.01 *N*. The E_0 value obtained by graphical extrapolation was 0.4826 v. at 30 ± 0.02°. Measurements against a calomel electrode at the same temperature gave 0.4825 v.

The work so far done on molybdenum solutions does not completely solve the problem of the constitution of sexa- and quinquevalent molybdenum ions, especially in acid solutions. Foerster, Fricke and Hausswald[1] in their determinations of the oxidation–reduction potentials of the sexa- and quinquevalent molybdenum ions in 2, 4 and 8 *N* hydrochloric acid, suggested a single formula for the molybdenum ion in each state of oxidation, irrespective of the acidity. The observed potentials were found, however, to differ considerably from those calculated, especially in 2 and 4 *N* acid. This was attributed to a profound effect of the acid on quinquevalent molybdenum ions in solution, which manifested itself in the color change from green to brown as the solutions passed from 8 to 2 *N* acid.

Tourky and El-Shamy[2] tried to elucidate the change in constitution of the molybdenum ions accompanying the color change. They established the most probable formulas for the sexa- and quinquevalent molybdenum ions in 8–6 and 4–2 *N* hydrochloric acid, and postulated the existence of two different forms within these two acid ranges.

In the present article measurements are reported of the oxidation–reduction potentials of the sexa- and quinquevalent molybdenum system against both hydrogen and calomel electrodes over a wide range of acid concentration. This study necessitated the carrying out of spectrophotometric measurements for the purpose of obtaining information on the effect of hydrochloric acid on molybdenum ions in solution, especially in connection with changes in the chemical nature of quinquevalent molybdenum ions corresponding to the change in color on passing through the range of acidity from 8 *N* to less than 0.01 *N* hydrochloric acid.

Experimental

The preparations and analyses of the solutions used were carried out as described in an earlier publication.[2] A Unicam quartz spectrophotometer (model 3p500), covering a range from 200–1000 mμ, was used in the light transmission measurements, which were accurate to about 0.2% under the conditions used. Glass cells of 1.00 cm. optical length were used. The results are expressed in terms of optical density, *D*, defined by the relationship $D = \log_{10}(I_0/I)$, where I_0 and I are the incident and transmitted light intensities, respectively.

In making measurements, three glass cells were used; one containing a blank solution of hydrochloric acid and the other two containing test solutions. The cells, which were not thermostated, were allowed to stand in the instrument to attain the temperature of the cell compartment prior to measurement. Since small temperature variations may occur within the instrument, check measurements were made with a fresh series of solutions. The effect of ordinary fluctuations in room temperature (25 ± 1°) was not usually serious. Measurements were made at wave lengths between 350–600 mμ, in which region there was selective absorption for the systems investigated. A hydrogen lamp was used as a light source. The cells were always cleaned, washed and dried with specially prepared and spectroscopically pure reagents. The filled cells were carefully wiped with lint-less cloth.

The measurements were made on hydrochloric acid solutions containing equimolecular amounts of sexa- and quinquevalent molybdenum. The acidity varied from 8–0.01 *N*, while the molybdenum content was kept in the range 0.01–0.004 *M*. Similar investigations were done on solutions containing only sexavalent molybdenum. These were found to have no absorption bands in the spectral region investigated. The shape of the curves obtained and the position of the maximum could, therefore, be considered to

---

[1] F. Foerster, E. Fricke and R. Hausswald, *Z. physik. Chem.*, **146**, 177 (1930).

[2] A. R. Tourky and H. K. El-Shamy, *J. Chem. Soc.*, No. 1, 140 (1949).

be more or less characteristic of the absorbing system, depending mainly on the chemical nature of the quinquevalent molybdenum ions in solution. Moreover, for the same acid concentration, the position of the maximum was found to be constant. In agreement with Beer's law, the value of the extinction coefficient was independent of the molybdenum content.

Solutions containing both sexa- and quinquevalent molybdenum ions were not made by mixing together the appropriate amounts of Mo(V) and Mo(VI) solutions. This usually resulted in the formation of molybdenum blue, especially on mixing solutions less than 2 *N* in hydrochloric acid content. A stock solution containing equimolecular amounts of sexa- and quinquevalent molybdenum and 8 *N* with respect to free hydrochloric acid was prepared and kept in a storage bottle, provided with a Zintl buret, under an atmosphere of carbon dioxide. The various solutions were then prepared by careful dilution with oxygen-free conductivity water. In this way no signs of molybdenum blue were observed. The composition of the stock as well as of the other solutions was checked by analysis whenever possible.

Absorption Measurements.—The assumption that two different series of ionic species of quinquevalent molybdenum ions probably predominate in solution was verified. Moreover, the results allowed a better understanding of the parallelism between the extent of chemical transformation and color change, and also of the true equilibria among the colored components predominating in solution at different ranges of acidity.

It is obvious from the absorption curves shown in Fig. 1 that in the emerald green solutions (8–5.75 *N* hydrochloric acid) a series of ionic species, probably chloro complexes, predominate which show strong absorption at a wave length of 450 mμ. Another series of ionic species, which are probably hydrolytic products, predominate in the brown solutions (3–0.01 *N* hydrochloric acid), showing strong absorption at a wave length of 395 mμ. Other ionic species probably exist at intermediate acidities (and colors) as shown by the gradual shift in the position of the maximum from 450 to 395 mμ. on changing the acidity from about 6 to 3 *N* hydrochloric acid.

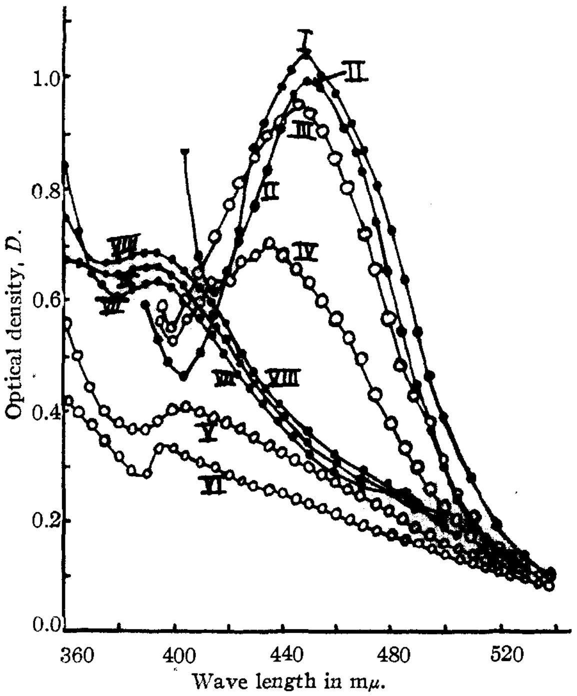

Fig. 1.—I, 7 *M* HCl, Mo(VI) = Mo(V) = 0.0342 *M;* II, 5.75 *M* HCl, Mo(VI) = Mo(V) = 0.00855 *M;* III, 4.5 *M* HCl, Mo(VI) = Mo(V) = 0.00428 *M;* IV, 4.0 *M* HCl, Mo(VI) = Mo(V) = 0.00428 *M;* V, 3.5 *M* HCl, Mo(VI) = Mo(V) = 0.00428 *M;* VI, 3.0 *M* HCl, Mo(VI) = Mo(V) = 0.00428 *M;* VII, 2.0 *M* HCl, Mo(VI) = Mo(V) = 0.00856 *M;* VIII, 0.1 *M* HCl, Mo(VI) = Mo(V) = 0.01 *M;* IX, 0.001 *M* HCl, Mo(VI) = Mo(V) = 0.01 *M.*

The Oxidation–Reduction Potentials of the Mo(VI)/(Mo(V) System.—The results obtained against the hydrogen electrode support the view of the presence of two different series of ionic species of quinquevalent molybdenum, one predominating in solutions of acidity higher than 5.75 *N* and the other in hydrochloric acid solutions less than 3 *N*. In the latter case the oxidation–reduction potentials when plotted against the square root of the ionic strength lay on a line which could be extrapolated to $\mu = 0$, and thus permitted evaluation of E_0. The value obtained was in good agreement with that obtained against the calomel electrode.

Measurements against the Hydrogen Electrode.—A series of cells were made in which the concentration ratios of sexa- and quinquevalent molybdenum ions and of free hydrochloric acid were maintained constant, but in which their absolute concentrations were varied, by dilution, from cell to cell. The sexa- and quinquevalent molybdenum ionic concentrations were equal to each other in each cell, but were made much lower than those of the free acid. The cell used was of the type

$$\text{Pt} \mid \text{Mo(VI), Mo(V), HCl}\ (m) \mid \text{HCl}\ (m) \mid \text{H}_2$$

with equal acid concentrations in both half-cells.

Solutions containing sexa- and quinquevalent molybdenum ions were prepared and analyzed as mentioned before. The oxidation–reduction half-cell was a modified form of that used by Hart and Partington.[3]

The measurements were performed in an air thermostat adjusted at 30 ± 0.02°, a very sensitive mirror galvanometer and a platinum–iridium meter bridge being used. The standard cadmium cells were always kept inside the thermostat and checked against each other. The readings for each cell were taken over a period of 24 hours. Equilibrium, however, was usually attained after a few hours and the final results did not diverge on the average by more than 0.5 mv. At high dilutions, a true equilibrium leading to reliable results was usually obtained only after 6–8 or sometimes 15 days.

A special electrolytic cell was devised to produce pure hydrogen the pressure of which could be easily adjusted. The gas was passed first through a purification system to remove any trace of oxygen and then washed before being admitted to the cell by passing through a bubbler containing hydrochloric acid solution of the same temperature and concentration as that of the hydrogen half-cell. Sufficient hydrogen was fed to the electrode to ensure saturation with the gas. The hydrogen electrode was found to assume its equilibrium within 4 hours after the passage of hydrogen commenced. Reproducibility and constancy were secured when the electrode was completely immersed in solution. The bubbling of hydrogen through the solution should be reasonably continuous (a few bubbles every few seconds) and the coating of platinum black should be sufficiently thick. The electrode vessel, together with the side tube, was then filled with hydrochloric acid solution of the same concentration as that in the molybdenum half-cell.

---

(3) A. B. Hart and J. R. Partington, *J. Chem. Soc.*, 1532 (1940).

In Fig. 2 the observed e.m.f. values were plotted against $\sqrt{\mu}$. The results show the presence of two systems; one above 5.75 N and another below 3 N hydrochloric acid. This view is borne out by the fact that the two sets of potentials do not lie on a single line but intersect at the point (a) corresponding to 5.75 N hydrochloric acid. The point (b) indicates, empirically, the limit of the lower system or acidity. In between (a) and (b), other ionic species probably exist.

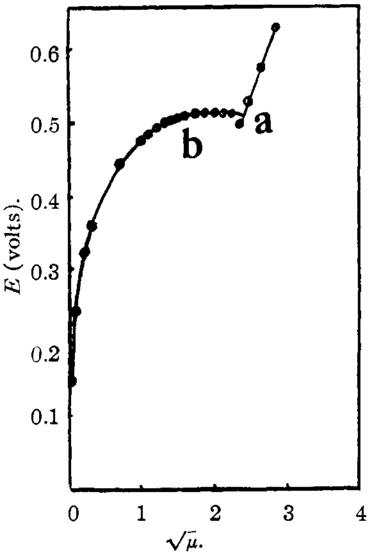

Fig. 2.

The cell reaction giving rise to the e.m.f. may be represented schematically as

$$MoO_2^{\cdot\cdot} + {}^1/_2H_2 + H^{\cdot} = MoO^{\cdot\cdot\cdot} + H_2O$$

corresponding to the half-cell reaction of the equation

$$MoO_2^{\cdot\cdot} + 2H^{\cdot} + e = MoO^{\cdot\cdot\cdot} + H_2O$$

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

$$E = E_0 + \frac{(RT)}{nF} \ln \frac{(MoO_2^{\cdot\cdot})(H^{\cdot})^2}{(MoO^{\cdot\cdot\cdot})}$$

in which E_0 is the apparent standard oxidation–reduction potential and the brackets refer to activities. This equation can be written in the form

$$E - \frac{RT}{nF} \ln (H^{\cdot})^2 - \frac{RT}{nF} \ln [MoO_2^{\cdot\cdot}]/[MoO^{\cdot\cdot\cdot}] = E_0 + \frac{RT}{nF} \ln f_2/f_1$$

In this equation $[MoO_2^{\cdot\cdot}]$ and $[MoO^{\cdot\cdot\cdot}]$ refer to concentrations in moles per liter and f_2 and f_1 are the respective activity coefficients.

Since $[MoO_2^{\cdot\cdot}]$ is made equal to $[MoO^{\cdot\cdot}]$ and $(H^{\cdot})^2$ approximately equals $[HCl]^2 f^2_{HCl}$, the above equation may be transformed into

$$E - \frac{2RT}{nF} \ln [HCl] = E_0 + \frac{RT}{nF} \ln f^2_{HCl} f_2/f_1$$

The values for the left hand side of this equation are plotted against $\sqrt{\mu}$ on a curve shown in Fig. 3. Extrapolation to zero ionic strength should yield the value of E_0, since at infinite dilution all activity coefficients become equal to unity and the potential of the hydrogen electrode at one atmosphere is taken to be zero. This value was found to be 0.4826 v.

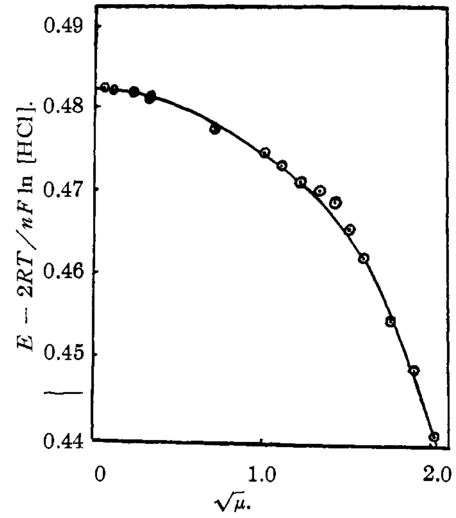

Fig. 3.

Measurements against the Calomel Electrode.—To test the reproducibility of the above measurements, the potential of the molybdenum half-cell against the calomel electrode was measured. Calomel electrodes with the same hydrochloric acid concentrations as were used in the molybdenum half-cells could be applied as reference electrodes, and in this way the liquid junction potentials were completely eliminated. The cell used was of the type

Pt | Mo(VI), Mo(V), HCl (m) ¦ HCl (m), Hg_2Cl_2 | Hg

with equal acid concentration in both half-cells.

Both the preparation and analyses of solutions and the procedure for making measurements were the same as described above. The method of preparing the calomel half-cell was essentially that described by Ellis.[4] Clean and dry calomel vessels were used, with stopcocks smeared with a small quantity of fresh silicone grease. Purified mercury was introduced in each calomel vessel so as to fill part of the vessel together with the capillary tube at the bottom of the cell. The calomel, which is a mixture of chemically and electrolytically prepared mercurous chloride, was mechanically shaken for at least two days with hydrochloric acid solution of the concentration to be used so as to bring it into equilibrium with the acid. The cell was then charged with the proper amount of this calomel and with the acid with which it had been shaken. For each acid concentration three calomel electrodes were similarly prepared for the purpose of comparison with each other. Calomel electrodes prepared in this manner, except when the acid was very highly diluted, attained their true potentials within 30 minutes after coming to the temperature of the thermostat in which they were placed and then remained constant.

The cell reaction giving rise to the e.m.f. can be written as

$$MoO_2^{\cdot\cdot} + 2H^{\cdot} + Cl^- + Hg = MoO^{\cdot\cdot\cdot} + H_2O + {}^1/_2Hg_2Cl_2$$

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

$$E = E_0' + \frac{RT}{nF} \ln \frac{(MoO_2^{\cdot\cdot\cdot})(H^{\cdot})^2(Cl^-)}{(MoO^{\cdot\cdot\cdot})}$$

where $E_0' = E_0 - E_{0Hg}$, and E_{0Hg} was taken as the standard potential of the calomel electrode Hg |

---

(4) J. H. Ellis, THIS JOURNAL, **38**, 737 (1916).

Hg_2Cl_2, $(Cl^-) = 1$. This value at 30° was evaluated by graphical extrapolation of the e.m.f. values for the cell $Hg|Hg_2Cl_2, HCl|H_2$ at 30° derived from the data of Ellis[4] and E_0 was the required potential of the molybdenum system referred to the standard hydrogen electrode.

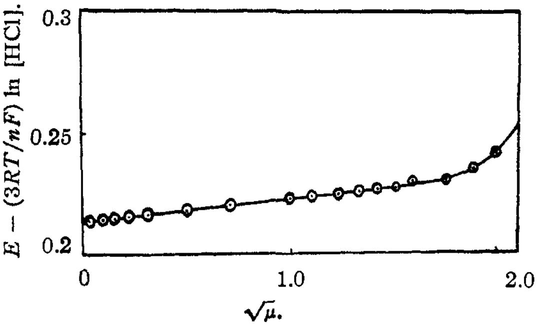

Fig. 4.

The equation for the relationship between E and E_0 can be rearranged as

$$E - \frac{3RT}{nF}\ln[\mathrm{HCl}] = E_0' + \frac{RT}{nF}\,\mathrm{n}\, f_2 f^3{}_{\mathrm{HCl}}/f_1$$

The values for the left-hand side of this equation are plotted against $\sqrt{\mu}$ on the curve shown in Fig. 4. From the plot it becomes clear that graphical extrapolation can lead to a reliable limiting value for E_0' which was found to be 0.2145 v. This gave $E_0 = 0.2145 + 0.2680 = 0.4825$ v. which agrees very well with the value 0.4826 v. obtained against the hydrogen electrode. The fact that the set of oxidation–reduction potentials below 3 N acid, when plotted against $\sqrt{\mu}$, lie on a straight line which can be extrapolated to zero ionic strength, permits the evaluation of E_0 if it is assumed that the profound effect of hydrochloric acid on the molybdenum ions would vanish at infinite dilution. However, in the absence of any other evidence as to the species of molybdenum ions present in solution at zero acid concentration, it is necessary to be very cautious with regard to designation of the extrapolated value as a true standard potential of the Mo(VI)–Mo(V) system.

ALEXANDRIA, EGYPT

[CONTRIBUTION FROM THE COATES CHEMICAL LABORATORY, LOUISIANA STATE UNIVERSITY]

Theory of Irreversible Waves in Oscillographic Polarography

BY PAUL DELAHAY

RECEIVED AUGUST 14, 1952

A theoretical treatment of irreversible oscillographic waves is developed for the case of a linear variation of the electrode potential. This treatment is based on the following hypotheses: 1. The rate of electron transfer is proportional to the concentration of the substance reacting at the electrode surface. 2. The rate of electron transfer is an exponential function of the electrode potential. The boundary value problem is solved by expressing the concentration of reacting species at the electrode surface in terms of the flux of this substance at the electrode surface, and by solving the resulting integral equation. The current–potential curve exhibits a peak whose height is proportional to various factors among which the most important are: the concentration of reducible substance, the square root of the rate of potential change, the number of electrons involved in the over-all electrochemical process, the square root of the transfer coefficient, and the square root of the number of electrons involved in the rate-determining step. The potential corresponding to the peak of the wave is calculated, and it is shown that this potential is a function of the rate of potential change. The theoretical conclusions are in good agreement with experimental data for the reduction of zinc tetrammine ion. Some features of the oscillographic method in which the anodic wave is recorded immediately after the cathodic wave, are also discussed.

Introduction

In a series of papers,[1–4] it was recently shown that the polarographic method is a powerful tool in the quantitative study of the kinetics of irreversible electrode processes. In conventional polarography it is not possible to study in the same experiment both the cathodic and anodic reactions corresponding to an oxidation-reduction system, but this result can be achieved by applying the oscillographic method originated by Heyrovsky[5] and improved by Sevcik.[6] In this oscillographic method, a substance Ox is reduced at the dropping mercury electrode by varying rapidly the potential of this electrode toward increasingly cathodic values. The substance Red resulting from the reduction of substance Ox is then reoxidized by bringing the potential back to its original value. By comparing the cathodic and anodic patterns thus obtained, one can decide whether the electrode process is virtually reversible or irreversible. These studies of the Czechoslovak school, although interesting, were of a purely qualitative nature, and the value of this very ingenious method would be enhanced if a quantitative treatment of irreversible oscillographic waves were available. Such a treatment is reported here.

The present work constitutes the solution of one of the three fundamental problems of the theory of oscillographic polarography. The other two problems deal with electrode processes for which it can be assumed that equilibrium is achieved either between two soluble species or between a soluble and an insoluble species. The theory of the former type of oscillographic waves was reported independently by Randles[7] and Sevcik,[6] whereas the treatment of the latter type of waves was developed in this Laboratory.[8]

---

(1) P. Delahay, THIS JOURNAL, **73**, 4944 (1951).

(2) P. Delahay and J. E. Strassner, *ibid.*, **73**, 5219 (1951).

(3) J. E. Strassner and P. Delahay, *ibid.*, **74**, 6232 (1952).

(4) P. Delahay, *ibid.*, in course of publication.

(5) J. Heyrovsky, *Faraday Soc. Disc.*, **1**, 212 (1947); several references to previous papers dealing with the same topic are quoted in this review.

(6) A. Sevcik, *Collection Czechoslov. Chem. Commun.*, **13**, 349 (1948).

(7) J. E. B. Randles, *Trans. Faraday Soc.*, **44**, 327 (1948).

(8) T. Berzins and P. Delahay, THIS JOURNAL, **75**, 555 (1953).