from the other two mentioned before, provided it is assumed that no chemical reaction takes place between the resins and active degraded products. Thus, three different kinds of anion activities are formed as a result of the (n,γ) reaction on $[Pt(en)_2]Cl_2$.

Of all the compounds investigated in the present research, *trans*-$[Pt(en)_2Cl_2]Cl_2$ appears to be most suitable for preparing high specific activity radioplatinum by the (n,γ) process, assuming that radiation decomposition due to γ's from the pile is about the same in all the compounds.

The present investigation indicates that in the (n, γ) reaction with complex compounds of platinum a considerable fraction of the total activity exists as degraded products. The formation of active degraded products which have different stabilities toward caustic soda can explain the difference in retention values observed by Sue and Kayas[5] with cobalt complexes containing mono, bi and tridentate groups.

The author wishes to express to Professor R. R. Williams, Jr., his appreciation for many helpful suggestions and discussions and for encouragement during the progress of the work.

NOTRE DAME, INDIANA

NOTES

State of Mo(VI) in Acid Solutions

BY MARK M. JONES

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The fact that molybdenum trioxide dissolves in aqueous solutions of strong mineral acids has been known for many years.[1-4] That molybdenum trioxide forms compounds with sulfuric acid has also been demonstrated by the isolation of $MoO_2 \cdot SO_4$ and several related substances.[2,3,5] These compounds have led to the postulation of the ion MoO_2^{+2} in these compounds and in acidic solutions of molybdic anhydride[6] and it was to test this that the present work was undertaken.

If molybdenum trioxide dissolves in acids to form the ion MoO_2^{+2} and water, this reaction may be represented by the equilibrium

$$MoO_3(s) + 2H^+ \rightleftarrows MoO_2^{+2} + H_2O \qquad (1)$$

which has an equilibrium constant

$$K = \frac{a_{MoO_2^{+2}}\, a_{H_2O}}{a_{MoO_3(s)}\, a_{H^+}^{2}} \qquad (2)$$

This expression may be simplified by making use of the fact that the activity of the molybdenum trioxide will be a constant at any given temperature and that the activity of the water in dilute solutions will also remain constant. If the molybdenum in solution is present as MoO_2^+, then the relationship between the solubility of the trioxide and the concentration of acid will be determined by equation 2. If we take logarithms of equation 2 we obtain after simplification

$$2 \log a_{H^+} + \log K^1 = \log a_{MoO_2^{+2}} \qquad (3)$$

Here $K^1 = K(a_{MoO_3(s)}/a_{H_2O})$. If we make the further assumption that $a_{MoO_2^{+2}}$ is equal to the solubility of the trioxide in the acid solutions we obtain

$$2 \log a_{H^+} + \log K^1 = \log S \qquad (4)$$

where S is the concentration of molybdenum in moles per liter. Thus if the molybdenum trioxide dissolving in an acid solution is present as MoO_2^{+2}, a plot of the logarithm of the solubility as ordinate against logarithm of the hydrogen ion activity as abscissa should be a straight line with slope of 2.[7]

Experimental.—The solubility of molybdenum trioxide was determined in aqueous perchloric acid solutions of various concentrations. The molybdenum trioxide used was the Merck & Co., Inc., A.C.S. Reagent. The perchloric acid solutions were prepared by dilution of 72% perchloric acid from the G. F. Smith Chemical Co. and were analyzed by titration against a standard sodium hydroxide solution. To prepare a solubility sample, 10 g. of molybdenum trioxide and 100 ml. of the perchloric acid solution were put into a 250-ml. flask. The flask was then tightly stoppered and put into a constant temperature bath at 25 ± 0.5° and shaken frequently. The solutions were allowed to equilibrate a minimum of two weeks before analysis. For analysis a sample was removed through a filter paper into a 25-ml. pipet. The sample was then put into a tared container, evaporated to dryness and the residue weighed. The solid obtained upon evaporation of these solutions was the yellow hydrated oxide, $MoO_3 \cdot 2H_2O$,[8-12] and was weighed as such. Samples taken from the same solution, a week or more apart, showed no significant differences or trends.

Results and Discussion.—The results are presented in Table I. The hydrogen ion activity in these solutions was obtained from data in Conway.[13] In Fig. 1 a plot of log S *versus* log a_{H^+} (equation 4) is given. Although a fair straight line may be drawn through these points its slope is not 2 but rather 0.68. It is possible to make a correction for the activity coefficient of the MoO_2^{+2} ion in this solution, basing it upon data for the UO_2^{+2} ion in

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(1) J. J. Berzelius, *Pogg. Ann.*, **6**, 380 (1826).

(2) C. Schultz-Sellack, *Ber.*, **4**, 14 (1871).

(3) W. Muthmann, *Ann.*, **238**, 126 (1887).

(4) J. M. Ruegenberg and E. F. Smith, THIS JOURNAL, **22**, 772 (1900).

(5) J. Meyer and V. Stateczny, *Z. anorg. Chem.*, **122**, 19 (1922).

(6) F. H. Nicholls, H. Saenger and W. Wardlaw, *J. Chem. Soc.*, 1443 (1931).

(7) See Fig. 1.

(8) A. Vivier, *Compt. rend.*, **106**, 602 (1888).

(9) A. Rosenheim and I. Davidson, *Z. anorg. Chem.*, **37**, 315 (1903).

(10) A. A. Blair and J. E. Whitefield, THIS JOURNAL, **17**, 759 (1895).

(11) A. Travers and L. Malaprade, *Bull. soc. chim.*, [4] **39**, 1409 (1926).

(12) A. Rosenheim and A. Bertheim, *Z. anorg. Chem.*, **34**, 430 (1903).

(13) B. E. Conway, "Electrochemical Data," Elsevier Publishing Co., Amsterdam, 1952, p. 75.

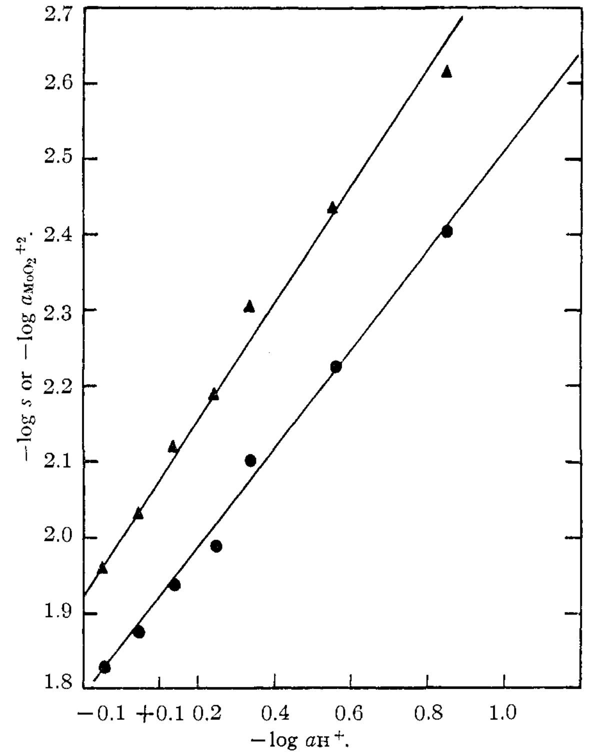

Fig. 1.—Test of the equilibrium (1): ●, log *s*; ▲, log $a_{MoO_2^{+2}}$.

perchlorate solutions.[14] If we assume that the activity coefficients of MoO_2^{+2} and UO_2^{+2} are equal at equal ionic strength, we can estimate the activity of MoO_2^{+2} in these solutions. These values are given in Table I (column five). A plot of log $a_{MoO_2^{+2}}$ *versus* log a_{H^+} is also shown in Fig. 1 and again the data do not support the equilibrium 2.

TABLE I

SOLUBILITY OF MOLYBDENUM TRIOXIDE IN PERCHLORIC ACID

$HClO_4$, *M*	Mo, *M* × 10^3	−log a_{H^+}	−log *S*	−log $a_{MoO_2^{+2}}$
0.182	3.96	0.852	2.404	2.612
.364	5.98	.559	2.225	2.432
.546	7.99	.337	2.100	2.304
.728	10.3	.246	1.989	2.188
.910	11.7	.138	1.934	2.116
1.092	13.5	.042	1.872	2.029
1.274	15.0	−.046	1.826	1.959

There are two possible explanations for the results obtained. The first and most obvious is that the activity coefficient of the ion MoO_2^{+2} changes with ionic strength in a manner radically different from that of UO_2^{+2}. There are two reasons for objecting to this interpretation. Firstly the change in activity coefficient observed with UO_2^{+2} is fairly typical for electrolytes of this charge type in the region of ionic strength considered. Secondly, the change of activity coefficient required to make the data conform to the MoO_2^{+2} equilibrium is much greater than has yet been observed for electrolytes in this region of ionic strength and would, in itself, indicate that the molybdenum in solution was not present as a simple ion.

The alternate explanation, favored by the author, is that the molybdenum in solution is not present as simple MoO_2^{+2} ions. The fact that solutions of molybdic acid in water are complex is well established.[15,16] Molybdenum trioxide in solution has a marked tendency to form polymeric aggregates of high molecular weight (though not colloidal[17,18]). There is other evidence which supports the existence of polymers in these solutions and this is that molybdenum trioxide in 100% sulfuric acid is dimeric.[16,19] In view of the high dielectric constant of sulfuric acid it would be expected that ionization, if possible, would occur in this solvent. Although experimental evidence is quite scarce, the formation of complexes of various sorts involving MoO_3 and SO_3 has often been assumed to explain the constitution of the "molybdenyl sulfates."[5,20,21] An interpretation capable of explaining the known facts is one in which MoO_3 reacts with hydrogen ions to give complexes in solution. Equilibria of the type

$$x\mathrm{MoO_3} + 2\mathrm{H^+} \rightleftarrows [(\mathrm{MoO_2})(\mathrm{MoO_3})_{x-1}]^{+2} + \mathrm{H_2O} \quad (5)$$

are capable of explaining the known experimental facts. The formation of MoO_2SO_4 in the presence of SO_3 would be the result of a competition between MoO_3 and SO_3, the solubility would not be proportional to the square of the hydrogen ion activity,[22] and the high molecular weight of the species in solution is readily understood.

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[14] Reference 10, p. 83.

[15] Reference 12, p. 435.

[16] A. Mazzucchelli and G. Zangrilli, *Gazz. chim. ital.*, **40**, II, 66, 72 (1910).

[17] L. Wohler and W. Engels, *Kolloidchem. Beihefte*, **1**, 454 (1909–1910).

[18] Reference 12, p. 431.

[19] E. Beckmann, *Z. physik. Chem.*, **53**, 133 (1905).

[20] R. F. Weinland and H. Kühl, *Z. anorg. Chem.*, **54**, 259 (1907).

[21] L. Forsen, *Compt. rend.*, **172**, 681 (1921).

[22] Although a combination of equilibria of the type (5) leads to the relationship $S = (\mathrm{H^+})^2 \sum_{x=1}^{x=\infty} (x+1) K_x$ among the solubility, the hydrogen ion concentration, and the equilibrium constants, this is obtained only by ignoring activity coefficients. When the activity coefficients are taken into account, and they would be very important for species of the type postulated, no such simple relationship is found.

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On the Analysis of Irreversible Polarographic Waves

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The general system of polarographic processes involving reversible electrode reactions and one chemical reaction in solution has been solved for the plane electrode by Koutecky.[1,2] A special case of this system, that in which the product of a reversible electrode reaction is converted by a chemical reaction to an inactive form, was solved independently by the author in a recent article.[3] The resulting equation for the half-wave potential ($E_{1/2}$) of the instantaneous current as a function

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[1] Proceedings of the International Polarographic Congress, Vol. I, p. 826 (1951).

[2] J. Koutecky, *Collection Czech. Chem. Communs.*, **18**, 183 (1953).

[3] D. Kern, THIS JOURNAL, **76**, 1011 (1954).