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THERMODYNAMIC PROPERTIES OF MOLYBDENUM (III) CHLORIDE IN MOLTEN ALKALI METAL CHLORIDES

Sidney M. Selis
Electrochemistry Department

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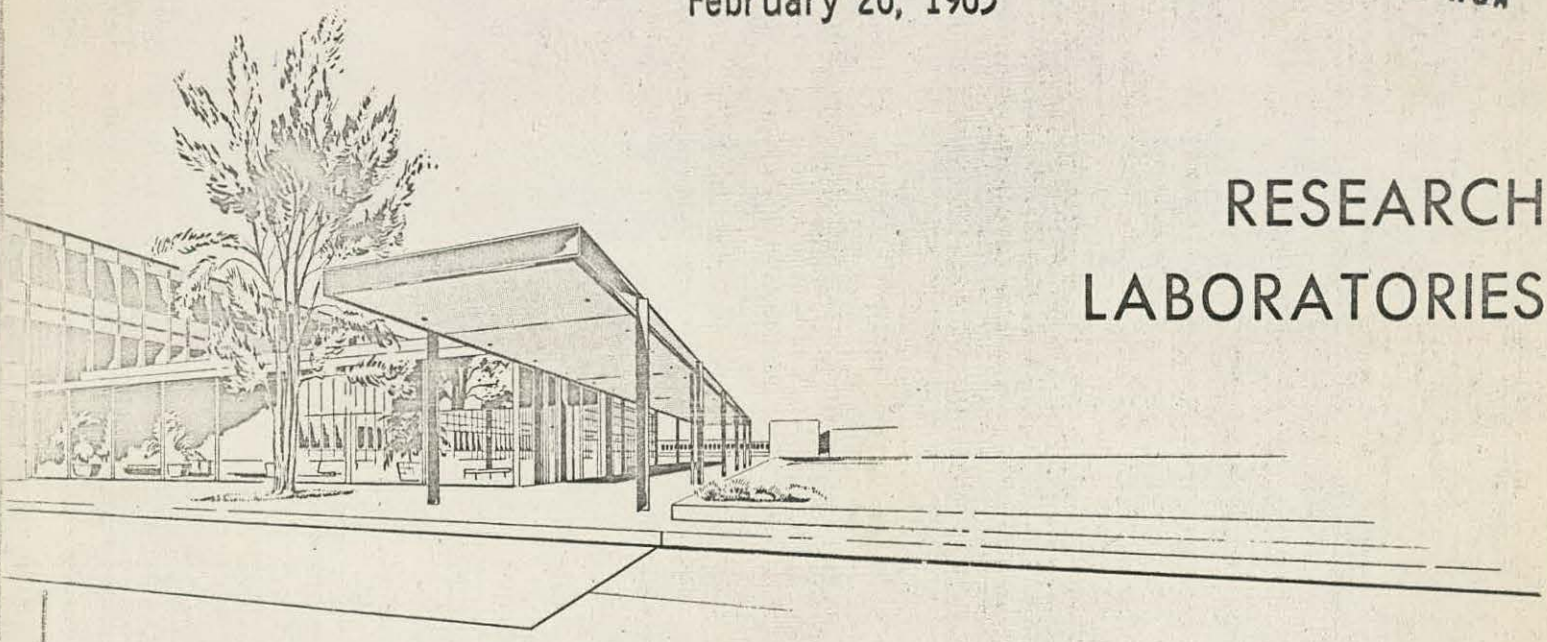

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By

Sidney M. Selis
Electrochemistry Department
Research Laboratories, General Motors Corporation
Warren, Michigan

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Research Laboratories, General Motors Corporation
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ABSTRACT

Using e.m.f. methods, partial thermodynamic values in molten LiCl-KCl have been precisely determined from 460° to 540° C in the Mo concentration range of 0.01 to 1 mole per liter. At 460° C the free energy of formation of the molybdenum (III) chloride in a decimolar solution is -67,000 ± 100 calories per mole, and the corresponding entropy change is -23 ± 1 calories per degree per mole. Extrapolated to 450° C, the potential of Mo/Mo(III) (1 molar in LiCl-KCl) *vs.* Pt/Pt(II) (1 molar) is -0.603 ± 0.002v.

There is a strong solvent cation effect due to coulombic, steric, and other contributions, and the excess free energy of $MoCl_3$ in KCl is much more negative than in LiCl-KCl.

BACKGROUND

In 1954 Senderoff and Brenner reported some preliminary experiments with molybdenum electrodes in molten mixtures of LiCl-KCl-K_3MoCl_6 (1). Although no rigorous proof was provided, they suggested that molybdenum metal is in equilibrium with Mo(III). It was shown that anodization of the metal occurs with unit efficiency assuming a three-electron change, and reduction of molybdenum (III) chloride to the metal also takes place with unit efficiency. Moreover, large anodic and cathodic current densities are accompanied by relatively small overpotentials.

Recently Ryzhik and Smirnov measured the equilibrium potentials of Mo/Mo(III) electrodes in molten KCl at 780°-940° C (2). They used the reference electrode Cl^-/Cl_2 (in pure liquid KCl), and their data were satisfactory for the calculation of partial thermodynamic quantities for molybdenum (III) chloride in the liquid potassium chloride solvent. Later in this paper there will be a comparison of these results with the present ones obtained at lower temperatures using the molten lithium chloride-potassium chloride solvent.

The present study was made with cells of the type $Mo/MoCl_3$ in LiCl-KCl//LiCl-KCl//$PtCl_2$ in LiCl-KCl/Pt. The solutions of molybdenum and platinum chlorides were dilute. Molybdenum (III) and platinum (II) ions were therefore unimportant carriers of current, and liquid junction potentials were consequently negligible. The temperature region was 460°-540° C, limited at the lower end by the solubility of the

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8 cm in length. The larger one had an outside diameter of 26 mm, and the diameter of the other was 13 mm. At the bottoms were fritted disks of medium porosity. Holes of 2-3 mm diameter were blown out at a distance of 5-10 mm from the tops so that these compartments could be lowered and raised with a stainless steel hook.

After these compartment cups were lowered, the cell was again capped and evacuated. The electrolyte seeped through the fritted disks to fill the compartments. Meanwhile the temperature was increased as needed for the experiment. A rapid flow of purified argon was started, and the cap was replaced with one through which were inserted four parallel Vycor tubes having outside diameters of 8-10 mm. Before they were lowered, the air inside them was removed and argon was introduced.

One of these tubes was a sheath for the thermocouple, and another was a guard for the carbon rod counterelectrode. They were immersed in the electrolyte outside the compartment cups. The other two tubes contained the platinum leads to the platinum and to the molybdenum electrodes; the connection of platinum to molybdenum was done by spot-welding, using a short intervening piece of nickel ribbon. The platinum electrode was contained in the smaller cup, and the larger one was for the molybdenum.

Temperatures were measured with a chromel-alumel thermocouple calibrated at the melting points of zinc and aluminum. Temperatures could be maintained constant to within $\pm$ 0.5° C. While final adjustments of temperature were being made, the platinum electrode was

generated by anodizing the platinum metal using the carbon countercathode. Current density was 10-20 ma/cm^2, and the coulometric delivery was measured. The amount of electrolyte in the compartment was later determined using the Volhard procedure. Concentration of $PtCl_2$ in the compartment was about 0.05 mole/l (known precisely).

The molybdenum electrodes were similarly formed and later analyzed for quantity of electrolyte. After the potential was measured for one concentration, current passage was resumed to obtain the next composition. The concentration ranges are shown in Fig. 1. As much as an hour was required for a potential to become steady after a composition was changed, but once stable, the reading would generally not vary more than one or two millivolts in a half hour. These readings were made with a null-balancing potentiometer, the button switches being closed only momentarily.

As shown in Fig. 1, values were verified by using cells in which the molybdenum (III) was added at the beginning as K_3MoCl_6. This was weighed out with the lithium and potassium chlorides. Purification of the electrolyte was the same except that magnesium metal was not used.

RESULTS

When the measurements with a cell were completed and the molybdenum and platinum compartments were analyzed, the molybdenum electrode composition could be defined and the potentials could be expressed with respect to $Pt/PtCl_2$ (1 molar in LiCl-KCl) through the use of the

Nernst relationship. In Fig. 1 are plotted molybdenum electrode potentials vs. log concentration of molybdenum (III) for five temperatures; replicate experiments were run in order to obtain these data. The behavior is linear, and the slopes, determined by the method of least squares, are compared in Table I with the slopes calculated with the Nernst equation, assuming n = 3.

Relationship [1] gives the potentials of $Pt/PtCl_2$ (1 molar in LiCl-KCl) with respect to Cl^- (in LiCl-KCl)/Cl_2 at different

$$E_{Pt/PtCl_2//Cl^-/Cl_2} = -0.3223 + 0.000334\ (t - 450) \qquad [1]$$

temperatures as determined by Laitinen and Pankey (3); in their work and in the present study, platinum leads were used from all electrodes and so there are no corrections for thermoelectric e.m.f. By using relationship [1], molybdenum electrode potentials are normalized to the chlorine electrode.

The partial quantities for the formation of $MoCl_3$ can now be calculated using relationships [2] through [4].

$$\overline{F} = n\mathcal{F}E \qquad [2]$$

$$\overline{S} = -n\mathcal{F}(\partial E/\partial T)_P \qquad [3]$$

$$\overline{H} = \overline{F} + T\overline{S} \qquad [4]$$

E is the potential of the molybdenum electrode and has the negative sign when it is more anodic than the reference; n and $\mathcal{F}$ have the usual significance, and n is 3. Using these equations, thermodynamic quantities have been calculated; the values are listed in Table II. $\overline{F}$, $\overline{S}$, and $\overline{H}$ are, respectively, the partial molar free energy, entropy, and enthalpy of formation, and a negative value for $\overline{F}$ means that the

formation occurs spontaneously. Concentrations are given on both molarity and mole fraction scales, the transformation being made with the density data of Van Artsdalen and Yaffe (5). Free energies and enthalpies in Table II are for a temperature of 460° C.

E was plotted against temperature for fixed concentrations; the curves are linear for the temperature region 460°-540° C and for the concentration ranges shown in Fig. 1. Using the method of least squares, a value of $(\partial E/\partial T)_p$ was found for each concentration and then plotted against log concentration. Again the behavior could be described as linear, and the method of least squares was again used to find the straight line. Referring to relationship [3], partial molar entropy was calculated for the concentrations as shown in Table II. The average deviation from the mean is also given.

Partial enthalpies, shown in Table II, were determined according to relationship [4]. The average deviation is based on the deviations in the free energy and entropy determinations.

DISCUSSION

One of the contributions of the present work is the determination of the Mo/Mo(III) potential which can be put in the e.m.f. series developed by Laitinen and co-workers (3, 6). For this series, the metal chlorides are dissolved in LiCl-KCl to the extent of 1 mole/l at 450° C. By extrapolation the molybdenum value is -0.603 ± 0.002v with respect to $Pt/PtCl_2$ (1 molar). It is more noble than Sb/Sb(III) by 32 mv and less noble than Bi/Bi(III) by 50 mv.

As already seen, only partial quantities for $MoCl_3$ in solution are available, and they cannot be related to pure liquid $MoCl_3$. For this reason, activity coefficients and activities are not calculated, nor are any relative partial quantities listed. This limitation goes further, because it means that one cannot calculate the stability constant for a complex such as $[MoCl_6]^{\equiv}$.

There is another standard state which might be employed where it is useful and that is the infinitely dilute solution of the solute in the LiCl-KCl electrolyte. But precise Nernst behavior is displayed over the entire concentration range at all temperatures in this system, and with the present data, reference to the infinitely dilute solution is a trivial calculation.

It is clear that $MoCl_3$ or Mo^{+++} are only formal representations of molybdenum (III) species in solution. In the present study the solutions are very dilute, and it is reasonable that the clusters of anions around the molybdenum ions constitute discrete and finite complexes. Because of this solvation the excess chemical potential of molybdenum (III) is lowered (becomes more negative), and the degree of lowering depends on the alkali metal cation, for instance, Li^+ or K^+. The radius of lithium ion is smaller than that of potassium ion, and both coulombic and steric effects operate so as to keep chloride ions bonded more strongly to the smaller of the two alkali metal cations. This causes the anions in the LiCl-KCl to be less readily available for solvation and stabilization of Mo^{+++}. The excess free energy of Mo^{+++} will therefore be less negative. A general discussion of these and other effects on ion stability in melts is given by Blander (7).

The potential temperature data of Ryzhik and Smirnov (2) are precisely linear, and the present author has extrapolated them to 500° C. For their cell containing 2.58 wt % Mo in molten KCl (2.12 mole % of $MoCl_3$), the potential vs. Cl^-/Cl_2 is -1.403v. The molybdenum electrode with the same mole fraction composition in the LiCl-KCl solvent exhibits a potential of -0.910v vs. Cl^-/Cl_2 at 500° C. The effect is in the predicted direction but the magnitude is much larger than expected on the presumption that the difference in values is due essentially to variations of the molybdenum electrodes and not the chlorine electrodes.

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TABLE I

NERNST BEHAVIOR OF THE MOLYBDENUM ELECTRODES

Temperature (° C)	$(\partial E/\partial \log [Mo^{+++}]_T$ (v)	
	Calculated	Observed
460	0.0485	0.0471
480	0.0498	0.0550
500	0.0512	0.0508
520	0.0525	0.0578
540	0.0538	0.0569

TABLE II

PARTIAL THERMODYNAMIC QUANTITIES FOR THE FORMATION OF $MoCl_3$ (l) IN MOLTEN LiCl-KCl*

Concentration (moles/liter)	Concentration (mole fraction)	$\overline{F}$ (cal/mole) (460° C)	$\overline{S}$ (cal/deg/mole)	$\overline{H}$ (cal/mole) (460° C)
0.010		-70,100 ± 100	-16 ± 1	-81,900 ± 800
	0.0005	-69,700	-17	-82,500
	0.001	-68,700	-20	-83,000
0.060		-67,700	-22	-83,600
	0.003	-67,300	-23	-83,900
0.100		-67,000	-23	-84,100
	0.006	(-66,200)	-25	(-84,500)
0.200		(-66,000)	-26	(-85,100)
	0.010	(-65,500)	-27	(-85,100)
0.300		(-65,500)	-27	(-85,100)
0.400		(-65,100)	-28	(-85,300)

*Values in parentheses are based on extrapolated curves.

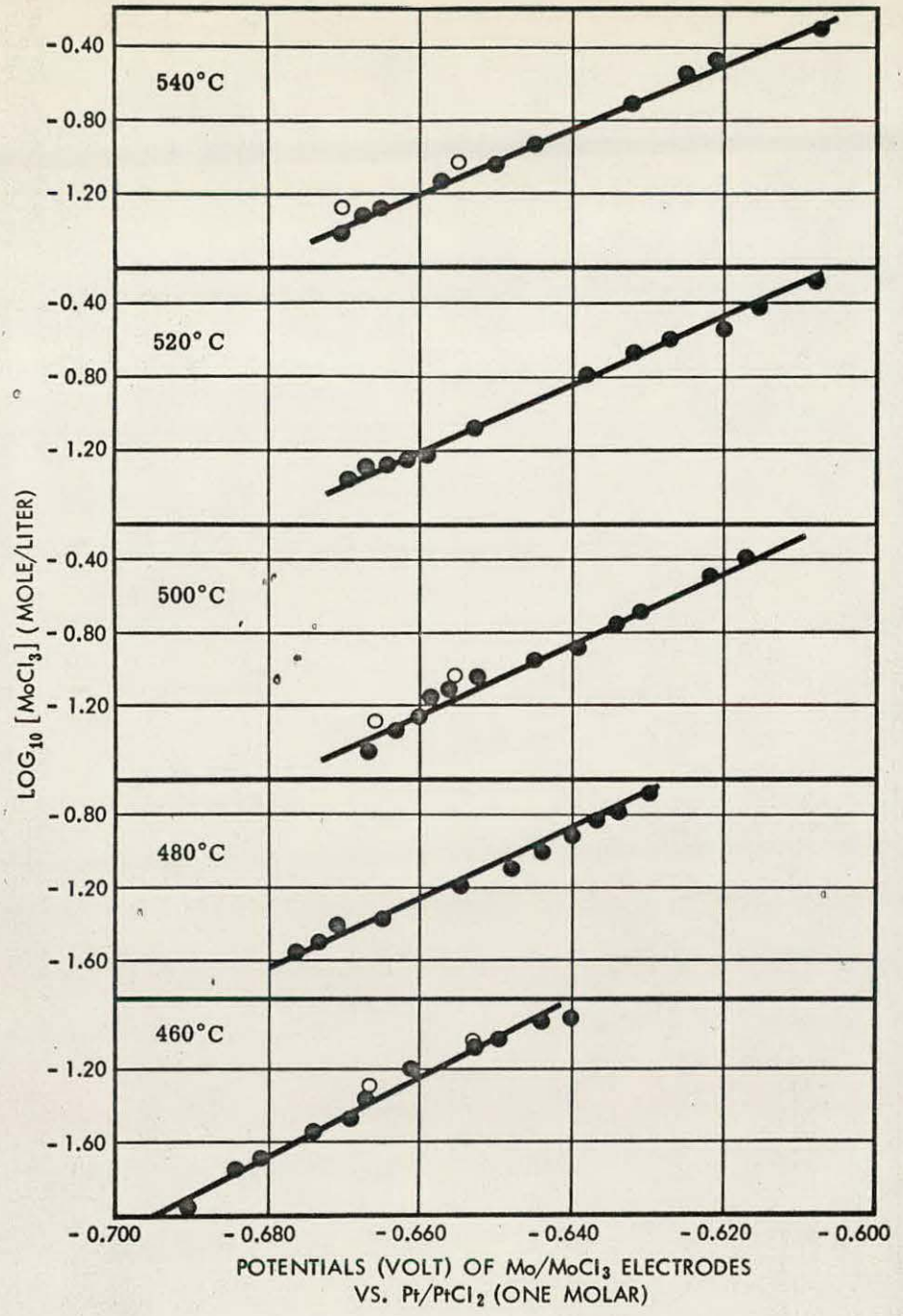

Fig. 1. Potentials of molybdenum electrodes with respect to the platinum reference. ●, additions by current passage; O, additions with K_3MoCl_6.