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VOLTAMMETRY AT HIGH PRESSURE

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Polarography using a dropping mercury electrode provides a useful tool both for the analysis of electrolyte solutions and for the investigation of electron transfer reactions. Laitinen and Kolthoff² have shown that a platinum microelectrode can similarly be used to determine characteristic current-voltage curves. In the present note some experiments are reported in which such a Pt-microelectrode was used to measure current-voltage curves at pressures up to 3000 atm.

Experimental

The apparatus in this work was similar to that used

(1) Now Department of Chemical Engineering, University of Sydney.

(2) H. A. Laitinen and I. M. Kolthoff, *THIS JOURNAL*, **45**, 1061 (1941).

(3) W. R. Hainsworth, H. J. Rowley and D. A. McInnes, *J. Am. Chem. Soc.*, **46**, 1437 (1924).

by Hainsworth, Rowley and McInnes³ to measure the effect of pressure on the e.m.f. of a cell containing a hydrogen electrode. The electrolysis cell consisted of two parts, of which the lower contained a normal calomel electrode, while the upper contained the test solution and the Pt-microelectrode. The calomel electrode was completely enclosed and electrical contact with it was made by a Pt-wire sealed through the cell wall; pressure was transmitted to it *via* the upper cell compartment. The Pt-microelectrode consisted of a short length of 30 gage platinum wire sealed into the end of a glass tube so that $\frac{3}{32}$ in. of the wire was left protruding vertically into the solution. The two cell compartments were connected by a B10 standard taper joint; the male part of the joint was filled with a 3% agar jelly containing the supporting electrolyte. This acted as a salt bridge and prevented the contents of the two cell compartments from mixing. When pressure was applied to the cell the jelly was extruded slightly from the joint and thus transmitted the pressure to the calomel cell.

The test solution was sealed from the air and from the pressure transmitting oil by a layer of purified paraffin oil. It was deoxygenated before the measurements by bubbling purified nitrogen through it.

The whole cell was immersed in oil in a steel bomb which had two insulated electrodes and had previously been used for conductivity measurements.⁴ A Leeds and Northrup potentiometer type K2 was used as the source of the variable voltage and the current flowing through the cell was measured with a calibrated mirror galvanometer.

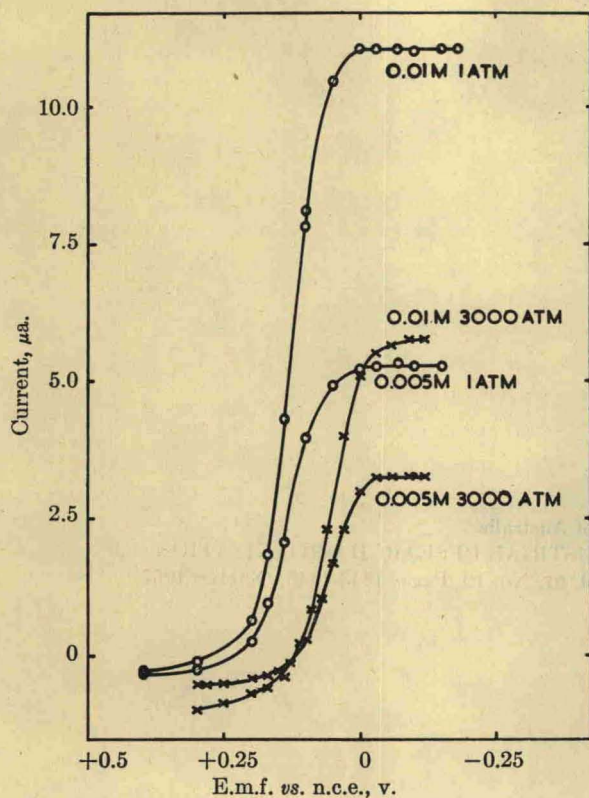


Fig. 1.

Results and Discussion

The reduction of Cu^{++} to Cu^+ in the presence of 0.5 N KCl was investigated. The solutions were made up in conductivity water using A.R. quality $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ which had been recrystallized, and A.R. KCl . Measurements of diffusion currents could be reproduced within $\pm 10\%$ while the error in the half-wave potential was only ± 0.002 volt.

Some current-voltage curves are shown in Fig. 1, and Table I gives the diffusion currents i_d and half-wave potentials $E_{1/2}$ found at various concentrations and pressures. The measured current was corrected for the residual current, which flowed before the reduction wave started, and was plotted as $\log_{10}(i/(i_d - i))$ against the applied e.m.f. The half-wave potential was found from these curves at $\log_{10}(i/(i_d - i)) = 0$. The curves for the measurements at 1 atm. were straight lines with slopes of 16.2 volt^{-1} , indicating that the reaction was reversible and involved the transfer of one electron.⁵ The plots for the measurements at higher pressures were curved at the ends, but all had a linear section of approximately the same slope at the center.

The results show that pressure affects both the diffusion current and the half-wave potential of the reaction. The diffusion current of a Pt-microelectrode is given by²

$$i_d = nFACD/l \quad (1)$$

where n is the number of electrons transferred in the reaction, F the Faraday, A the area of the electrode, C the concentration (mole liter⁻¹) and D the diffu-

(4) J. Buchanan and S. D. Hamann, *Trans. Faraday Soc.*, **49**, 1425 (1953).

(5) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1952, p. 213.

TABLE I

DIFFUSION CURRENT AND HALF-WAVE POTENTIAL OF Cu^{++} - Cu^+ REDUCTION IN APP. 0.5 N KCl MEASURED RELATIVE TO NORMAL CALOMEL ELECTRODE

Pressure, atm.	CuSO_4 , m	i_d , $\mu\text{a.}$	$E_{1/2}$, v.
1	0.01	11.1	0.129
1	.005	5.5	.131
1000	.01	9.0	.105
2000	.01	7.5	.077
2000	.005	4.5	.079
3000	.01	6.7	.059
3000	.0075	5.3	.059
3000	.005	3.8	.059

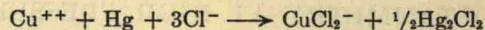
sion coefficient of the reacting ion, and l is the thickness of the diffusion layer. A refinement of this equation has recently been discussed by Pavlopoulos and Strickland.⁸

The decrease of i_d with pressure could be due to changes in D , C and l . In an aqueous solution the volume concentration C will be increased by about 10% at 3000 atm., while the effect of pressure on D is the reciprocal of the effect on the viscosity of the solution and corresponds to a decrease of approximately 23% at 3000 atm. The balance of the decrease in i_d must then be due to an increase in the thickness of the diffusion layer.

The change of diffusion current with concentration at constant pressure was found to be linear within the experimental error, as predicted by eq. 1.

The results also show that the half-wave potential is independent of concentration, but is moved 0.071 volt to a more negative value by an increase in pressure of 3000 atm. This indicates that the reactants are stabilized relative to the products and that the reduction requires a greater driving force at the higher pressure.

Considering the various complexes formed by copper in the presence of excess chloride ions, and the standard potentials involved in their reductions, it is thought that the observed wave corresponds to the reaction



In this reaction ionic charges are neutralized and the effect of pressure is thus similar to that observed in many ionic systems,^{4,7} where it is generally found that an increase in pressure stabilizes the state with the greater number of ionic charges.

One can obtain a quantitative measure of this stabilizing effect from the approximate relation

$$\partial\Delta G/\partial P = -nF\partial E_{1/2}/\partial P$$

where ΔG is the free energy change of the reaction. Using the experimental values of $E_{1/2}$, we find $\partial\Delta G/\partial P = 0.53\text{ cal. mole}^{-1}\text{ atm.}^{-1}$.

Although the work described has been only of an exploratory nature, sufficient results have been obtained to show that voltammetry using a stationary Pt-microelectrode is feasible at high pressures and can yield useful information under these conditions.

(6) S. D. Hamann and W. Strauss, *Trans. Faraday Soc.*, **51**, 1684 (1955).

(7) A. H. Ewald and S. D. Hamann, *Aust. J. Chem.*, **9**, 54 (1956).

(8) T. Pavlopoulos and J. D. Strickland, *J. Electrochem. Soc.*, **104**, 116 (1957).