

THE POLAROGRAPHIC DIFFUSION COEFFICIENT OF CADMIUM ION IN
0.1 M POTASSIUM CHLORIDE

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In connection with the determination of polarographic diffusion coefficients by a modified Cottrell technique³ it was considered necessary to re-determine independently the diffusion coefficient of cadmium ion in 0.1 M KCl. The method chosen was one first employed by GRAHAM¹ since this technique would allow an absolute determination of the diffusion coefficient.

EXPERIMENTAL

The experimental equipment consisted of a cylindrical tube closed at one end and filled with a solution containing the substance in question. This was carefully submerged below the level of a large outer reservoir of liquid initially containing none of the substance. Diffusion then takes place from the inner solution into the outer reservoir. The diffusion was terminated at the end of two or three days and an analysis of the outer solution made, to determine the amount of substance diffused out of the inner tube.

A glass vial 3.59 cm in length and with an internal diameter of 1.43 cm was used as the diffusion cell. The open end was ground with carborundum to give a flat edge. The diffusion cell was attached to a glass rod which could slide smoothly through a length of glass tubing inserted in a rubber stopper cover.

A known volume of temperature-equilibrated 0.1 M KCl solution was pipetted into a clean, dry 100-ml beaker and the diffusion cell filled with a 2.39 mM solution of cadmium chloride dissolved in the same KCl solution. The open end of the diffusion cell was kept above the level of the outer potassium chloride solution while the entire apparatus was allowed to equilibrate with the constant temperature bath. The temperature was kept constant at $25.00 \pm 0.05^\circ$ and the entire system insulated against vibration. After approximately one hour, the diffusion cell was slowly and carefully lowered into the potassium chloride solution. Diffusion was allowed to take place from 1-3 days, after which time the cell was carefully removed, the outer KCl solution stirred and a sample of this removed for analysis. The analytical measurements were made polarographically with a Fisher Eledropode. The galvanometer scale and shunts of the eledropode had been previously calibrated. Three trials were made.

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RESULTS AND DISCUSSION

If the volume of the outer KCl solution is sufficiently large, the concentration of cadmium ion at the open end of the diffusion cell may be considered equal to zero. This system then corresponds to that of linear diffusion out of a cylinder, and can be described by the following relationship²:

$$\Delta m = 2AC_0(Dt/\pi)^{1/2}$$

where Δm is the number of moles of cadmium ion which have diffused into the outer KCl solution in time, t (sec); C_0 (moles/cm³) is the initial concentration of cadmium ion in the diffusion cell; A (cm²), the cross-sectional area of the cell and D (cm²/sec), the diffusion coefficient. The values obtained for the diffusion coefficient are listed in Table I.

TABLE I
DIFFUSION COEFFICIENT OF CADMIUM

Trial	Δm (moles · 10 ⁶)	t (sec · 10 ⁻⁵)	D (cm ² /sec · 10 ⁵)
1	6.28	2.96	0.772
2	4.89	1.76	0.785
3	3.55	0.869	0.837

These D -values are approximately 10% greater than the value at infinite dilution of 0.720×10^{-5} cm²/sec calculated from the Nernst relation and experimental values obtained by other investigators^{4,5,6} for this ion. This large discrepancy suggests that the transport of cadmium from the inner diffusion cell to the outer solution may involve some initial mixing in addition to diffusion. Most of the mixing probably occurs when the inner cell is first submerged below the level of the outer solution.

The equation predicts that, in the absence of any initial mixing, a plot of Δm

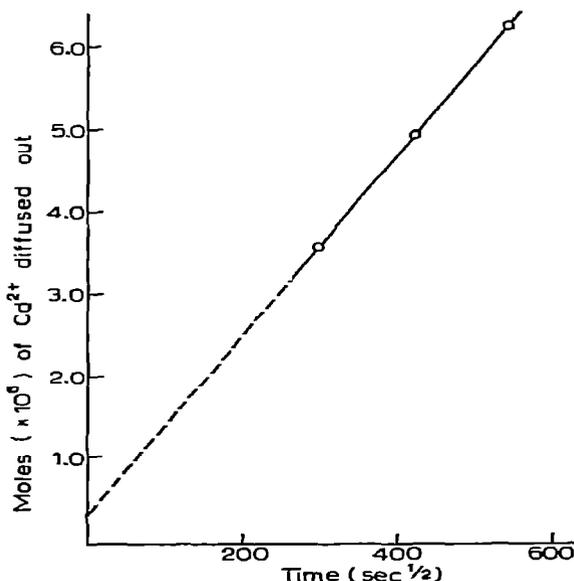


Fig. 1. Linear relation between Δm and $t^{1/2}$.

against $t^{\frac{1}{2}}$ should yield a straight line which passes through the origin at zero time. A slight amount of mixing is unavoidable in such boundary formations; however, this would result in the curve intersecting the Δm axis at zero time. Assuming that the same amount of substance is transported out of the diffusion cell each time it is submerged, then the intercept on the Δm axis should correspond to the amount of cadmium ion transported across the boundary solely by initial mixing. Such a plot is shown in Fig. 1. The observed linearity of Δm with $t^{\frac{1}{2}}$ supports the assumption that substantially the same amount of substance was lost initially in all three trials. This corresponds to 0.31×10^{-6} moles of Cd^{2+} . Using this value, the number of moles of cadmium transported by diffusion alone was determined and a new value for D calculated. These are shown in Table 2.

TABLE 2
DIFFUSION COEFFICIENT VALUES OBTAINED AFTER CORRECTION FOR INITIAL MIXING

<i>Trial</i>	<i>m(uncorr.)</i> (moles · 10 ⁶)	<i>m(corr.)</i> (moles · 10 ⁶)	<i>D(corr.)</i> (cm ² /sec · 10 ⁵)
1	6.28	5.97	0.696
2	4.89	4.58	0.688
3	3.55	3.24	0.694

The agreement between the three individual D -values is considerably improved and the average value of 0.693×10^{-5} cm²/sec is more in accord with values previously reported. Table 3 lists the D -values obtained for cadmium ion by other investigators using a variety of methods.

TABLE 3
DIFFUSION COEFFICIENT VALUES FOR Cd^{2+} IN 0.1 *M* KCl AT 25° OBTAINED BY DIFFERENT INVESTIGATORS

<i>D</i> (cm ² /sec · 10 ⁵)	<i>Method</i>	<i>Investigator</i>
0.693	Graham	D. J. MACERO
0.700	Diaphragm cell	C. L. RULFS ⁵
0.717	Cottrell Method	M. VON STACKELBERG, <i>et al.</i> ⁶
0.720	Chronopotentiometry	C. N. REILLEY, <i>et al.</i> ⁴

The value $0.700 \pm 0.013 \times 10^{-5}$ cm²/sec which represents a weighted average of the diffusion coefficient values listed in Table 3, was selected as the best available value for the diffusion coefficient of cadmium ion in 0.1 *M* KCl at 25°.

SUMMARY

The diffusion coefficient of cadmium ion in 0.1 *M* potassium chloride at 25° was determined by an absolute method. Straight calculations using the equation derived by JOST yielded values which were too high when compared to the infinite dilution value of 0.720×10^{-5} cm²/sec. A correction for initial mixing was made which yielded

more reasonable values for D . The value of 0.706×10^{-5} cm²/sec which represents a weighted average of the diffusion coefficient values obtained in this and other investigations was selected as the best available value for the diffusion coefficient of cadmium ion in 0.1 M KCl at 25°.

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