spheric moisture may well have interfered with these measurements. The precision of the vinylidene chloride value is considerably lower than that of the other measurements. It is known that liquid vinylidene chloride dissolves oxygen and rapidly reacts with it to form a peroxide (10, 11). Thus, it seems likely that this reaction is taking place in the gas phase in the diffusion cell causing loss of precision in the measurements.

Of the systems studied, only carbon dioxide and n-pentane have been investigated previously. Andrew (1) obtained 0.165 ± 0.003 cm^2 sec^{-1} for the diffusion coefficient of carbon dioxide in air at 293°K while Holsen and Strunk (6) found 0.142 ± 0.0007 and 0.177 ± 0.0017 cm^2 sec^{-1} at 276.2 and 317.2°K, respectively. Agreement with the present result is within experimental error when allowance is made for the small temperature difference. Lugg (9) obtained 0.0842 ± 0.00182 cm^2 sec^{-1} for n-pentane in air at 298°K, in excellent agreement with the present result.

Values of the diffusion coefficients for several systems were calculated as described previously (2, 15) using a kinetic theory equation (5), together with values of the collision integral for a Lennard-Jones 6–12 potential function tabulated by Hirschfelder et al. (5). Molecular interaction parameters for like-like interactions calculated from viscosity measurements and tabulated (5) were combined using the Hudson-McCoubrey combining rules (8). The ionization potentials used in this calculation were Stevenson and Hipple's value for isobutane (12), Honig's value for propane and n-pentane (7), Tate and Baker's value for dichlorodifluoromethane (13) and values for other compounds given by Herzberg (4).

For carbon dioxide and nitrous oxide two sets of values of the intermolecular interaction parameters were used. Diffusion coefficients calculated with the two sets are, for all practical purposes, the same. The discrepancy between experimental and theoretical values is about 8%. For the three hydrocarbons, agreement between experimental and theoretical results is excellent.

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Electromotive Force Studies of Cell, Cd$_x$Hg$_y$|CdSO$_4$(m)|Hg$_2$SO$_4$, Hg, in Dioxane–Water Media

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From the emf measurements of cell, Cd$_x$Hg$_y$|CdSO$_4$(m)|Hg$_2$SO$_4$, Hg, at 25°, 30°, and 35°C, the −ΔG°, −ΔH°, and −ΔS° for the reaction, Cd + H$_2$SO$_4$ → CdSO$_4$ + 2Hg, have been calculated. The dissociation constants of CdSO$_4$ in dioxane–water media are 8.5 × 10^{-4}, 4.0 × 10^{-5}, and 2.5 × 10^{-8}, respectively, in 20, 40, and 60% by wt of dioxane in dioxane–water media at 25°C. The effect of temperature appears to be small.

In this communication the electromotive force studies of cadmium sulfate in dioxane–water media have been reported. For the purpose the cell,

$$Cd_xHg_y|CdSO_4(m), \text{dioxane}(X)\ H_2O(Y)|Hg_2SO_4, Hg \quad (1)$$
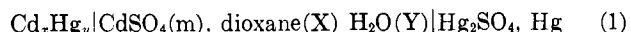
has been set up and the emf measured at different temperatures. From these the thermodynamic properties of the system have been evaluated.

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EXPERIMENTAL

BDH, AR-grade cadmium sulfate was used in preparing the solution. The concentration of the stock solution was checked by estimating sulfate gravimetrically and cadmium by EDTA titration.

The purification of the solvents has been described earlier (1). Hg, Hg$_2$SO$_4$ electrode was set up in the manner reported in our earlier communication. The cadmium amalgam (11% Cd) was prepared and the cell filled following the method of Harned and Fitzgerald (3) in an atmosphere of nitrogen instead of under vacuum. Pure and presaturated nitrogen was bubbled through

Table I. Electromotive Force Measurements of Cell I

$m \times 10^2$	25°C	30°C	35°C
	20% Dioxane		
1.448	1.0710	1.07095	1.07045
2.695	1.06485	1.06305	1.06245
2.887	1.06315	1.06265	1.06160
3.632	1.06095	1.06035	1.05970
3.867	1.06245	1.06170	1.06020
4.808	1.05990	1.05900	1.05900
	40% Dioxane		
1.938	1.03855	1.033835	1.03825
3.625	1.03295	1.03255	1.03230
4.335	1.03185	1.03110	1.03070
5.085	1.03045	1.03010	1.02980
5.816	1.02985	1.02925	1.02880
7.328	1.02815	1.02770	1.02755
	60% Dioxane		
0.851	1.0215	1.0218	1.0224
0.972	1.0195	1.0201	1.0214
1.012	1.0190	1.0198	1.0205
1.193	1.0178	1.0182	1.0189
1.270	1.0168	1.0174	1.0176
1.353	1.0164	1.0168	1.0175

solution to remove dissolved air. A deaerated solution was used in the work. H-shaped vessels were used in setting up the cells. The emf of the cells, set up in pairs, were measured with a Leeds & Northrup K2 potentiometer. Duplicate measurements agreed within ±0.2 mV.

RESULTS

The observed emf values at temperatures 25°, 30°, and 35°C and in solvents containing 20, 30, and 60% by weight of dioxane are reported in Table I.

Harned and Fitzgerald determined the equilibrium constant for the ion-pair formation in cadmium chloride in aqueous solution from the emf studies of the cell

$$Cd_xHg_y|CdCl_2(m)|AgCl, Ag$$
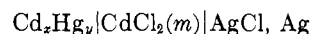
The same line of treatment of data with some modifications was adopted by Hefley and Amis (4) in their emf studies of cadmium chloride in ethanol–water media. The experimental data in the present work have been analyzed in the same way.

In a solution of cadmium sulfate the electrolyte may be assumed to ionize as follows:

$$CdSO_4 \rightleftharpoons [Cd^{2+}SO_4^{2-}] \rightleftharpoons Cd^{2+} + SO_4^{2-}$$
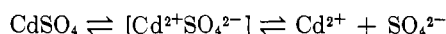
If α is the degree of dissociation of cadmium sulfate and m is the molal stoichiometric concentration of cadmium sulfate, then application of the law of mass action to the above equilibrium gives for the ion-pair dissociation constant,

$$K = \frac{\alpha^2 m}{1 - \alpha} \times \gamma_{Cd^{2+}} \times \gamma_{SO_4^{2-}} \qquad (2)$$

$\gamma_{Cd^{2+}}$ and $\gamma_{SO_4^{2-}}$ refer to the molal activity coefficients of the ionic species indicated by subscripts; the activity coefficient of the neutral species has been taken here as unity. Equation 2 is a quadratic equation in α which, on solution, gives for the real root,

$$\alpha = \frac{-K + \sqrt{K^2 + 4\,mK\gamma_i^2}}{2\,m\,\gamma_i^2} \qquad (3)$$

where

$$\gamma_i = \gamma_{Cd^{2+}} = \gamma_{SO_4^{2-}}$$

and which is given according to the Debye-Huckel extended theory by the expression,

$$-\log \gamma_i = \frac{4\,AI^{1/2}}{1 + \rho I^{1/2}}$$

where

$$A = \text{D.-H. constant}$$

$$= \frac{1.823 \times 10^6}{(DT)^{3/2}}$$

and

$$\rho = \frac{35.57 \times a°}{(DT)^{1/2}}$$

$a°$ = ionic diameter given in Angstrom unit
D = dielectric constant of the medium
T = absolute temperature

and

I = ionic strength of the medium
$= 4\,\alpha m$

Also the emf equation for the cell, A, is given by

$$E + 2.3026\,\frac{RT}{F}\log \alpha m - 2.3026\,\frac{RT}{F} \times \frac{4\,AI^{1/2}}{1 + \rho I^{1/2}} =$$

$$E°' = E° - BI \qquad (4)$$

where the terms have their usual significance.

By process of successive approximation, the values of K and $E°'$ were obtained. The value of standard potential for the cell, $E°$, was determined by extrapolating $E°'$ against ionic strength to zero. In our calculations we have taken a simple picture, although a more complex type of ion-pair formation as for example $2CdSO_4 \rightleftharpoons Cd^{2+} + Cd(SO_4)_2^{2-}$ have been reported. It may be mentioned that the value of ionic diameter of Cd^{2+} or SO_4^{2-} needed for the calculation of the activity coefficient has been taken to be 4.5 Å and for the sake of simplicity, the temperature variation of ρ has not been taken into account. The values of the dissociation constant, K, as calculated for the different media are given in Table II. Table III contains the values of $E°'$ at different temperatures and Table IV the values of $E°$ at 25, 30, and 35°C in 20, 40, and 60% wt/wt of dioxane. The variation of K-values at 25° with dielectric constant is represented in Figure 1.

Thermodynamic Properties of System. The enthalpy change $\Delta H°$, entropy change $\Delta S°$ and the free energy change $\Delta G°$ for the reaction occurring in the cell, namely,

$$Cd + Hg_2SO_4 \rightarrow CdSO_4 + 2Hg$$
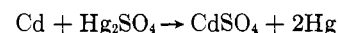
have been calculated from the emf's at the three different temperatures. These are given in Table V.

As seen from Table V, the standard free energy change of the cell process increases (becomes continually less negative) as the percentage of dioxane in the solvent increases. This is in

Table II. Dissociation Constant of CdSO₄ in Dioxane–Water Media

Temp, °C	K		
	Dioxane, wt %		
	20	40	60
25	8.5 × 10⁻⁴	4.0 × 10⁻⁵	2.5 × 10⁻⁸
30	8.5 × 10⁻⁴	4.0 × 10⁻⁵	2.0 × 10⁻⁸
35	8.5 × 10⁻⁴	4.0 × 10⁻⁵	2.0 × 10⁻⁸

Table III. Molal Potential of Cell I at Different Ionic Strengths

m × 10²	I × 10³			E°', V		
	25°C	30°C	35°C	25°C	30°C	35°C
		20% Dioxane				
1.448	2.64	2.69	2.82	0.9181	0.9150	0.9115
2.695	4.88	5.05	5.27	0.9198	0.9153	0.9116
2.887	5.21	5.39	5.66	0.9191	0.9157	0.9117
3.632	6.63	6.97	7.32	0.9197	0.9161	0.9126
3.867	7.18	7.53	7.82	0.9219	0.9176	0.9138
4.808	9.16	9.69	10.00	0.9218	0.9184	0.9151
		40% Dioxane				
1.938	8.36	8.91	9.18	0.8563	0.8530	0.8498
3.625	14.76	16.31	16.89	0.8589	0.8554	0.8522
4.335	17.92	20.17	20.90	0.8601	0.8563	0.8529
5.085	21.28	23.93	25.14	0.8607	0.8573	0.8540
5.816	24.70	28.28	29.95	0.8618	0.8582	0.8548
7.328	32.79	39.07	42.01	0.8631	0.8595	0.8564
		60% Dioxane				
8.51	71.96	63.72	64.27	0.7355	0.7281	0.7238
9.72	77.48	68.66	69.20	0.7352	0.7281	0.7246
10.12	79.26	70.15	70.76	0.7353	0.7283	0.7242
11.93	86.94	76.92	77.64	0.7362	0.7289	0.7248
12.70	90.07	79.70	80.42	0.7360	0.7289	0.7242
13.53	93.36	82.59	83.34	0.7364	0.7292	0.7250

Table IV. Standard Molal Potential of Cell I

Dioxane, wt %	E°, V ± 0.00025		
	25°C	30°C	35°C
20	0.9163	0.9134	0.9098
40	0.8540	0.8510	0.8476
60	0.7358	0.7278	0.7240

Table V. Thermodynamic Properties of Cell I

Percentage of dioxane, wt/wt	Temp, °C	−ΔG° ± 0.02, kcal mol⁻¹	−ΔH° ± 0.15, kcal mol⁻¹	−ΔS° ± 0.5, cal mol⁻¹ deg⁻¹
20	25	42.28	51.2	30.0
	30	42.14		
	35	41.98		
40	25	39.40	48.2	29.5
	30	39.26		
	35	39.11		
60	25	33.95	50.0	54.0
	30	33.58		
	35	33.40		

Table VI. Standard Free Energies of Ion-Pair Dissociation of CdSO₄

% of dioxane, wt/wt	Calcd with Denison-Ramsay eq, kcal mol⁻¹	Calcd from exptl values, kcal mol⁻¹
0	2.9	0.390
20	4.19	0.500
40	6.0	0.715
60	10.4	1.190

agreement with the observations of Hefley and Amis. This possibly means that the process becomes less spontaneous at unit activity of reactants as the nonaqueous component of the solvent increases. This increase of standard free energy with decrease of dielectric constant of the solvent might be due, among other things, to the difference in the nature and extent
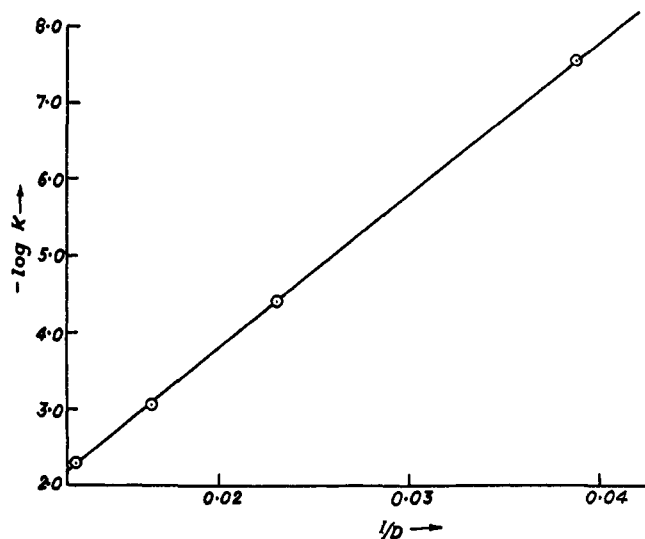

Figure 1. Variation of K-values at 25°C with dielectric constant

of solvation, change in structure of the solvent and increased energy necessary to prevent association of the ions. Perhaps the greatest cause of the decrease in spontaneity, in fact, the cause which probably predominates, is the greater energy requirement to prevent association of the ions in lower dielectric constant media.

As seen from Table V, the values of $\Delta S°$ are always negative and the general tendency is to become more negative as the dielectric constant decreases. The negative values of entropy in media with higher percentages of organic component indicate a greater ordering effect in this solvent perhaps arising from the fact that for the same number of molecules ordered in this media as contrasted with water, greater weight and volume fraction of the solvent are ordered as remarked by Amis and co-workers (4).

The free energy changes corresponding to the dissociation process of the CdSO₄ in different solvents at 25°, 30°, and 35°C have been evaluated from the experimentally determined dissociation constants, K. These are given in Table VI. The values for $\Delta G°$ for the ion pair may also be computed by using Denison and Ramsay's (2) expression represented by equation $\Delta G° = N\ \epsilon²/aD$. These calculated values are also given in Table VI. In computing the $\Delta G°$'s by this equation, for a, the average value of the ion size parameter of Cd^{2+} and SO_4^{2-} has been used. The large difference between the calculated and the experimental values of $\Delta G°$ is possibly due to the uncertainty in the ionic radius parameter used in the calculation and/or to the use of macroscopic value of the dielectric constant.

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