empirical constants, B, C, D, E, . . . in equation 16 for sodium chloride in 50 wt.% dioxane–water is their small magnitude. This is brought out most clearly by comparison of the actual values in Table II with the following values, obtained by extrapolation of the data of Scatchard and Benedict[14,18] to 50 wt.% dioxane: $B = 6.4$; $C = -6.4$; $D = 3.9$; $E = -1.4$. The effect may be attributed to short-range ionic interactions whose relative importance increases rapidly with decreasing dielectric constant. If to a first approximation attention is paid only to the formation of short-range ion pairs, then $\gamma = \gamma'\alpha$, where α is the free-ion fraction and γ' the molal activity coefficient of the free ions.[19] Upon introducing the ion-pair dissociation constant $K = \alpha^2(\gamma')^2m/(1 - \alpha)$, and writing $\ln \gamma'$ in a form analogous to (16): $\ln \gamma' = -S\cdot(\alpha m)^{1/2} + B'\ \alpha m + C'(\alpha m)^{3/2} + \ldots$, the following power series was obtained for $\ln \gamma$

$$\ln \gamma = -Sm^{1/2} + (B' - K^{-1})m + (C' + 5S/2K)m^{3/2} + (D' - 3S^2/K + 3B'/K + 3/2K^2)m^2 + \ldots \quad (23)$$

Equation 23 shows that the limiting-law term, $Sm^{1/2}$, is unaffected by the short-range interactions, but each of the higher terms is multiplied by a coefficient reflecting the ionic association. Equation 23 allows only for ion-pair formation; to a better approximation ionic interactions of higher order than pairwise also need be included. Such refinement will cause addition of further terms to the coefficients of m^2, $m^{5/2}$, . . . , but the coefficients of m and $m^{3/2}$ will remain unchanged. Thus the empirical value of B equals $B' - K^{-1}$.

Upon using for B' the value 6.4, extrapolated from the data of Scatchard and Benedict,[14] K is estimated as *ca.* 0.3. In spite of the crudeness of this estimate, the value is at least of the right order of magnitude: In 70 wt.% dioxane–water K for sodium chloride was found to be[20] 5.35×10^{-3} at 25°. Using the equation $K = 1000/[32\ \pi N\cdot q^3Q(b)]$ to describe the solvent dependence,[13] K is estimated as 0.10 for 50 wt.% dioxane.

Possibly a better estimate of B' may be made on the basis of the equation $\ln \gamma' = -S(\alpha m)^{1/2}/[1 + S(\alpha m)^{1/2}]^{2/3}$, which was derived and tested in previous papers[19b,20] for systems where $q >> \mathring{a}$. Upon expansion in power series, it turns out that $B' = 2S^2/3$, or 10.0 for 50% dioxane. Correspondingly, $K = (B' - B)^{-1}$ is estimated at 0.145, in better agreement with the value 0.10 obtained above.

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[19] (a) N. Bjerrum, *Kgl. Danske Videnskab Selskab, Math-fys. Medd.*, **7**, No. 9 (1926); (b) H. P. Marshall and E. Grunwald, *J. Chem. Phys.*, **21**, 2143 (1953).

[20] E. L. Purlee and E. Grunwald, THIS JOURNAL, **79**, 1366 (1957).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF FLORIDA STATE UNIVERSITY]

The Effect of Solvent Change on the Standard Chemical Potential of Electrolytes. Comparison of Vapor Pressure and E.M.F. Data for HCl, NaOH and K_W in the System Dioxane–Water[1]

BY GEORGE BAUGHMAN AND ERNEST GRUNWALD

RECEIVED DECEMBER 9, 1957

The rate of change of the standard chemical potential with changing mole fraction of water, dF^0/dZ_1, was obtained in 50.00 wt. % dioxane–water for HCl and NaOH from vapor pressure data. Values at 25.00° were: for HCl, $d(F^0_{H^+} + F^0_{Cl^-})/dZ_1 = -7.9$ kcal.; for NaOH, $d(F^0_{Na^+} + F^0_{OH^-})/dZ_1 = -17.6$ kcal. The value for HCl may be compared with the value, -8.0 kcal., deduced from potentiometric data for the cell H_2/HCl, dioxane–water/AgCl–Ag. The values for HCl and NaOH, when combined with a previous value[2] for NaCl, lead to -19.8 ± 1.0 for $d \ln K_w/dZ_1$, where K_w is the autoprotolysis constant. This differs significantly from the potentiometric value of -22.3. The discrepancy may be due to lack of reversibility of the Ag–AgCl electrode at high *p*H in the dioxane-rich solvent compositions.

Precision measurements of the activities of the solvent components may be used to obtain thermodynamic data for electrolytes in mixed solvents. A suitable method was reported in the preceding paper.[2] Results of this method will now be compared with results based on the e.m.f. of reversible cells in order to have a cross-check on the validity of both methods. Two systems were selected: (i) Hydrogen chloride in dioxane–water, because potentiometric data for the cell (1) were already

$$\text{Pt–H}_2(g,\ 1\ \text{atm})/\text{HCl}(m),\ \text{dioxane}(Z_2),\ \text{water}(Z_1)/\text{AgCl–Ag} \quad (1)$$

available for a number of solvent compositions[3-6]; (ii) Sodium hydroxide in dioxane–water, because these data, taken in conjunction with the data for HCl and NaCl[2], may be compared with potentiometric values[7] of the autoprotolysis constant K_W.

The mathematical symbols that will be used have been defined in the preceding paper.[2]

Experimental Part

Reagents and Solutions.—Constant boiling aqueous hydrochloric acid was prepared from reagent grade acid[8] and

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[1] Work supported by the Office of Naval Research. Reproduction in whole or in part is permitted for any purpose of the United States Government.

[2] E. Grunwald and A. L. Bacarella, THIS JOURNAL, **80**, 3840 (1958).

[3] H. S. Harned and J. O. Morrison, *ibid.*, **58**, 1908 (1936); H. S. Harned, *ibid.*, **60**, 336 (1938); H. S. Harned and C. Calmon, *ibid.*, **60**, 2130 (1938); 20, 45, 70 wt. % dioxane.

[4] E. L. Purlee and E. Grunwald, *ibid.*, **79**, 1366 (1957); 70 wt. % dioxane.

[5] H. P. Marshall and E. Grunwald, *J. Chem. Phys.*, **21**, 2143 (1953), extrapolations.

[6] A. F. Butler, Ph.D. Thesis, Florida State University, Tallahassee, Fla., August, 1956; 50 wt. % dioxane; experimental methods similar to those of ref. 4.

[7] H. S. Harned and L. D. Fallon, THIS JOURNAL, **61**, 2374 (1939); 20, 45, 70 wt. % dioxane.

[8] C. W. Foulk and M. Hollingsworth, *ibid.*, **45**, 1220 (1923).

was compared with potassium acid phthalate obtained from the National Bureau of Standards. A saturated aqueous solution of sodium hydroxide was prepared from reagent grade pellets and pure water. The solution was filtered to remove solid sodium carbonate and stored in a polyethylene bottle. The purification of dioxane and water and the preparation of the solutions from them and the HCl and NaOH solutions followed previous practice.[2] The solvent always was made up to contain 50.00 wt. % dioxane and 50.00 wt. % water, due allowance being made for the water in the constant boiling HCl and saturated NaOH. The HCl molality was computed from gravimetric data and the NaOH molality from acid-base titration. The NaOH molality was checked at the conclusion of each run by titration of the liquid left in the final saturator, and the differences were within acceptable limits.

Procedure.—The vapor pressure apparatus and experimental techniques were the same as reported previously.[2] Each experiment was carried out at least in duplicate. The replicability of individual determinations was ±0.0002 for the mass ratios and ±0.002–0.009 wt. % for the vapor compositions. The corresponding uncertainties in ln α_1/α_2 are ±0.00030 and ±0.00014–0.00063, respectively.

Calculation of ln α_1/α_2.—All calculations were based on the slightly-imperfect-real-gas model, using virial coefficients reported elsewhere.[9] Solute concentrations were sufficiently low so that the quantity

$$Z_1 \ln \alpha_1 + Z_2 \ln \alpha_2 = -2(M_{12}/1000)\left(m - \int_0^m m \,\mathrm{d} \ln \gamma_\pm\right)_{Z_1}$$

did not have to be treated as an unknown. Hence *both* ln α_1 and ln α_2 could be calculated when either the mass ratio or the vapor composition was measured. In actual practice, both of these quantities were measured, and therefore two independent values were obtained for ln α_1/α_2 at each concentration.

It was convenient to precalculate ln α_1/α_2 for 50.00 wt. % dioxane–water as a function of mass ratio and of vapor composition for a number of values of $(Z_1 \ln \alpha_1 + Z_2 \ln \alpha_2)$; experimental data were then evaluated by interpolation on large-scale graphs.

For NaOH, $\int_0^m m \,\mathrm{d} \ln \gamma_\pm$ was computed both from the Debye–Hückel limiting law and by assuming ln $\gamma_\pm$ to be equal to that for sodium chloride in 50 wt. % dioxane–water.[2] For HCl, the most accurate value of the integral was obtained by using ln $\gamma_\pm$ as deduced from potentiometric data.[6] However, the actual values of ln α_1/α_2 were insensitive, within their experimental error, to the somewhat arbitrary assumption made here, as will be shown in a later section. Therefore, even though potentiometric data were used in the evaluation of the vapor pressure data for HCl, the values of ln α_1/α_2 are virtually independent of this fact.

Results

Comparison of Data for HCl.—It follows from the thermodynamic relationships obtained in the preceding paper[2] that the vapor pressure and e.m.f. data are related by the equations

$$1000 \ln \alpha_1/\alpha_2 = mM_{12}\beta_{\mathrm{H^+,Cl^-}} + 2M_{12}\int_0^m (\partial \ln \gamma_\pm/\partial Z_1)_m \,\mathrm{d}m - 2(M_1 - M_2)\int_0^m (\partial \ln \gamma_\pm/\partial m)Z_1 \,\mathrm{d}m \quad (2)$$

$$\beta_{\mathrm{H^+,Cl^-}} = (1/RT)[\mathrm{d}(F^0_{\mathrm{H^+}} + F^0_{\mathrm{Cl^-}})/\mathrm{d}Z_1 = -(\mathfrak{F}/RT)(\mathrm{d}E^0/\mathrm{d}Z_1) \quad (3)$$

In equation 3, $\mathfrak{F}$ is the Faraday charge and E^0 the standard e.m.f. of cell (1) on the mole fraction scale. The right side of equation 2 is obtainable from e.m.f. data and the left side from vapor pressure data.

The relevant potentiometric data are listed in Table I. The evaluation of the integral involving $\partial \ln \gamma_\pm/\partial m$ is simplified by the fact that, for 50% dioxane–water in the concentration range of interest, activity coefficients are described satisfactorily by the equation

$$\ln \gamma_\pm = -3.866m^{1/2}/(1 + 2.474m^{1/2}) \quad (4)$$

as demonstrated in Table II. The integral involving $\partial \ln \gamma_\pm/\partial Z_1$ was evaluated as follows: ln $\gamma_\pm$ was plotted *vs.* Z_1, using the data indicated in Table I, for a number of conveniently spaced concentrations in the range $0 < m < 0.07$. At each concentration, $\partial \ln \gamma/\partial Z_1$ was calculated for $Z_1 = 0.8302$ (50 wt.% dioxane) from the smooth plot by numerical differentiation.[10] The results were then plotted *vs.* m and integrated numerically.[10]

TABLE I

POTENTIOMETRIC RESULTS FOR THE SYSTEM DIOXANE–WATER, 25.00°

Dioxane, wt. %	E^0(v.)[a] Cell (1)	Source of ln $\gamma_\pm$, HCl[b]	log Kw[b,c]
20	0.00554	Ref. 3	−14.620
45	− .0196	Ref. 3	−15.735
50	− .0284[d]	Table II	−16.046[d]
70	− .0993	Ref. 3, 4	−17.835

[a] Based on refs. 3–5. [b] For 45 and 70% dioxane, reported values[3,7] were corrected to the new value of $E°$. [c] Molal scale, based on ref. 7. [d] Interpolated.

TABLE II

TEST OF EQUATION 4 FOR ACTIVITY COEFFICIENTS OF HCl IN 50.00 WT. % DIOXANE–WATER, 25.00°

	$\gamma_\pm$	
m	Obsd., ref. 6	Calcd., eq. 4
0.003623	0.816	0.817
.005420	.786	.786
.01805	.678	.677
.02788	.633	.633
.04393	.588	.587
.05946	.558	.555
.07404	.538	.533

Of the three terms on the right in equation 2, the first is by far the most important, and the calculation of $\mathrm{d}E^0/\mathrm{d}Z_1$ for 50% dioxane was done with special care. To minimize subjective error, large-scale plots of E^0 *vs.* Z_1 were constructed by four different people and differentiated numerically.[10] The final average is thought to be accurate to 2%.

The results of the calculation are summarized in Table III, where potentiometric and vapor pressure results are compared. The agreement of comparable values of ln α_1/α_2 is adequate; at 0.05060 m, one of the values, from the vapor composition data, is a little out of line, but this value is less precise than the others and is still within the limit of error. Another way of testing the data is in terms of $\mathrm{d}(F^0_{\mathrm{H^+}} + F^0_{\mathrm{Cl^-}})/\mathrm{d}Z_1$. The potentiometric value, $-\mathfrak{F}\mathrm{d}E^0/\mathrm{d}Z_1$, is −8000 ± 180 cal. The average value computed from the vapor pressure and other relevant data *via* equation 2 is −7900 cal. In this second calculation, the vapor pressure data contribute the term $1000RT(\ln \alpha_1/\alpha_2)/mM_{12}$ which amounts to about three quarters of the total.

Results for NaOH.—Values of ln α_1/α_2 for solutions of NaOH in 50.00 wt. % dioxane–water were computed from independent measurements of

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(9) A. L. Bacarella, A. Finch and E. Grunwald, *J. Phys. Chem.*, **60**, 573 (1956).

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TABLE III

COMPARISON OF POTENTIOMETRIC AND VAPOR PRESSURE RESULTS FOR HCl IN 50.00 WT. % DIOXANE-WATER, 25.00°

m	$\frac{\mathfrak{F}}{RT}\frac{dE^0}{dZ_1}$	$\int_0^m \frac{\partial \ln \gamma_\pm}{\partial Z_1} dm$	$\int_0^m m \, d \ln \gamma_\pm$
0.02467	$13.5_0 \pm 0.3$	0.0470	-0.0030_3
0.05060	$13.5_0 \pm .3$	0.1230	-0.0074_5

	1000 ln α_1/α_2		
m	Potentiom.	Mass ratio	Vapor comp.
0.02467	7.58 ± 0.3	$7.4_3 \pm 0.3$	$7.5_2 \pm 0.14$
0.05060	$14.1_1 \pm .3$	$14.3_6 \pm .3$	$15.5_6 \pm .5$

the mass ratio and of the vapor composition. The mean deviation of the two sets of values was less than 0.0004, and average values are listed in Table IV. The calculation requires prior knowledge of $\gamma_\pm$ as a function of m, but the results are very insensitive to the exact function chosen, as illustrated for two plausible functions in Table IV.

TABLE IV

DATA FOR NaOH in 50.00 WT. % DIOXANE-WATER AT 25.00°

	$\gamma_\pm$ from limiting law		$\gamma_\pm$ same as for NaCl		
m	ln α_1/α_2	β^*	ln α_1/α_2	β^*	$\sigma\beta^{*d}$
0.00000	....	$-29.63^{a,b}$	....	$-29.69^{a,c}$	..
.01189	-0.0098_5	-30.7_0	-0.0098_7	-30.7_6	0.9
.02415	$-.0184_0$	-29.7_6	$-.0184_6$	-29.8_4	.5
.03916	$-.0292_2$	-30.4_0	$-.0293_5$	-30.5_1	.3
.0523	$-.0381_5$	-30.7_0	$-.0383_5$	-30.8_2	.2
	Av.	-30.4	Av.	-30.5	

[a] Computed by weighted least squares *via* equation 5. [b] $b = -20.46$. [c] $b = -21.65$. [d] Standard deviation.

The calculation of β_{Na^+, OH^-} was based on the power series expansion, equation 20 of the preceding paper,[2] which was used in the form

$$\beta^* \equiv (1000 \ln \alpha_1/\alpha_2)/M_{12}m - 27.59m^{1/2} = \beta + bm + \ldots \quad (5)$$

At low molalities, β^* should vary linearly with m. For the data in Table IV, there is a slight but statistically insignificant drift in β^* with increasing m. The most probable value for β is -29.7, obtained by least-squares fitting of the data to equation 5. The most probable value for b, -21, is nearly equal to the corresponding quantity for NaCl.[2] On the other hand the data do not preclude the possibility that $b = 0$, in which case the limiting law is valid and $\beta = -30.4$. In any case, it is unlikely that the correct value of β_{Na^+, OH^-} differs from -29.7 by more than ± 1.0.

d ln K_W/dZ_1.—It follows from the definitions of the autoprotolysis constant K_W and of β that

$$d \ln K_w/dZ_1 = \beta_{H^+, OH^-} = \beta_{H^+, Cl^-} + \beta_{Na^+, OH^-} - \beta_{Na^+, Cl^-} \quad (9)$$

Upon substitution of numerical values for HCl, NaOH and NaCl,[2] d ln K_W/dZ_1 is predicted from vapor pressure data to be -19.8 ± 1. On the other hand, from potentiometric data for ln K_W (converted to the mole fraction scale),[7] the corresponding value is -22.3 ± 0.3. The discrepancy between the two values is significant and points to determinate error in at least one of the two sets of measurements. In view of experimental difficulties described by Harned and Fallon,[7] we believe that the determinate error may have occurred in the potentiometric measurements. The experimental difficulty was that the Ag–AgCl electrode did not function reversibly in the alkaline solutions which one has to employ in the measurement of K_W at the higher dioxane concentrations except in the presence of a large excess of sodium chloride.[7] Although Harned and Fallon took pains to minimize this error, the fact that the vapor pressure data are not subject to difficulties of this sort would tend to make them seem more reliable.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE PENNSYLVANIA STATE UNIVERSITY]

Hydrodynamic Voltammetry at Solid Indicator Electrodes[1]

BY JOSEPH JORDAN, R. A. JAVICK AND W. E. RANZ[2]

RECEIVED NOVEMBER 20, 1957

A circulatory electrolysis cell assembly has been devised with controlled hydrodynamic characteristics, for the study at stationary solid indicator electrodes of current–voltage curves in flowing solutions. A new microconical platinum electrode is described and the relevant theoretical limiting current equation is derived. In a range of flow velocities between 25 and 500 cm./sec., oxygen, ferricyanide and aquo-ferric ion at the conical platinum microelectrode yielded sigmoid current–voltage waves with well-defined limiting currents. Implications are discussed to quantitative voltammetric analysis in flowing media. Oscilloscopic evidence is presented that the random fluctuations of the limiting currents, normally observed at the rotated platinum wire electrode, are due to turbulence. A constant limiting current, free of transient fluctuations, was obtained in a purely laminar gravitational flow using a "wall-less" electrolysis cell. The conical platinum microelectrode under suitable experimental conditions approximates the behavior of an electroanalytical flowmeter. Selected applications are considered as examples of an unorthodox approach to the measurement by electrochemical kinetics of rates of physical phenomena.

A time period of more than one and a half decades has now elapsed since the invention of voltammetry at the rotated platinum wire electrode (RPWE).[3] The behavior of the RPWE is intermediate between that of a "convection electrode" and a "diffusion electrode."[4,5] Mass transfer by diffusion and forced convection both are controlling factors of the limiting currents which depend on diffusion coefficients as well as on the prevailing hydrody-

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[1] Abstracted from a doctoral thesis by Richard A. Javick. Presented at the Eighth Pittsburgh Conference of Analytical Chemistry and Applied Spectroscopy, March, 1957.

[2] Department of Engineering Research of The Pennsylvania State University.

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