

**1049.** *Washburn Numbers in the Methanol–Water–Hydrochloric Acid System at 25°.*

By D. FEAKINS.

A novel e.m.f. method for determining Washburn numbers in the methanol–water–hydrochloric acid system has been investigated. Values of the Washburn number for dilute solutions of hydrochloric acid in 10%, 20.22%, and 43.12% mixtures of methanol by weight with water have been obtained together with values of  $\Delta E_m^\circ$  which are differences between the standard e.m.f.s of the cells  $H_2|HCl|AgCl-Ag$  and  $H_2|HCl|Hg_2Cl_2-Hg$  in water and the mixed solvents.

If electrodes exist which are reversible to both types of ion yielded by the dissociation of a binary electrolyte, then its thermodynamics may be investigated in any solvent medium by means of the appropriate chemical cell. Thus cells of types (I) and (II)



have been used to investigate the thermodynamics of hydrochloric acid in a large number of organic solvents and their mixtures with water.

<sup>1</sup> Ives and Janz, "Reference Electrodes," Academic Press, New York, 1961, p. 191.

<sup>2</sup> Ref. 1, p. 143.

In particular, if  ${}^aE$  = e.m.f. of such a cell in solvent medium a, and  ${}^bE$  = e.m.f. of the same cell in solvent medium b at any arbitrary concentrations, then

$$F({}^aE - {}^bE) = \Delta G_t^* \tag{1}$$

where  $\Delta G_t$  is the free energy of transfer of one mole of the electrolyte from one solvent medium to the other. If the corresponding standard e.m.f.s are  ${}^aE^\circ$  and  ${}^bE^\circ$ , then

$$F({}^aE^\circ - {}^bE^\circ) = \Delta G_t^\circ, \tag{2}$$

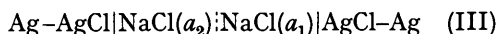
the difference in the solvation energy of the electrolyte in the two solvent media.

This quantity may not easily be obtained for many electrolytes because of the lack of suitable reversible electrodes, and this work has not been much extended beyond hydrochloric acid. The important results of Åkerlöf,<sup>3,4</sup> the significance of which has escaped general attention, for alkali chlorides in methanol-water mixtures, were obtained by using amalgam electrodes. It would be desirable, if possible, for these to be confirmed by an independent method.

Grunwald and Bacarella<sup>5</sup> have developed a vapour-pressure method which may be used to determine the rate of free-energy change with respect to solvent composition for any electrolyte in a binary solvent mixture. This valuable method does not appear to have the precision of an e.m.f. method.

This situation prompted the present study of cells with transport. While it has not yet been possible to determine the desired thermodynamic information from cells of this sort, some other results are available which may be thought to justify this preliminary account.

A cell of the type (III), where the solvent medium was an equimolar mixture of

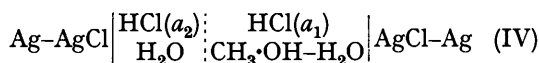


methanol and water was used by Butler and Gordon<sup>6</sup> to obtain activity coefficients for the electrolyte *relative to a standard state in that medium*. The equation

$$E = \frac{2RT}{F} \int_{a_1}^{a_2} t_+ d \ln a, \tag{3}^\dagger$$

where  $a$  is the mean ion activity of the electrolyte and  $t_+$  the cation transport number, will be precise if the concentration of the electrolyte is not greatly different in the two half-cells (see below). The required activity coefficients may be found from the e.m.f. measurements if  $t_+$  is known as a function of the concentration of the electrolyte over the measured range of concentrations. This type of cell will not give  $\Delta G_t$ .

Accordingly cells of the type (IV) have been examined in this work. The e.m.f. of



such a cell is given by Scatchard<sup>8</sup> as

$$E_- = \frac{2RT}{F} \int_{a_1}^{a_2} t_+^M d \ln a + \frac{RT}{F} \int_{a_{w,1}}^{a_{w,2}} w_w d \ln a_w; \tag{4}$$

$a_1$  and  $a_2$  are the mean ion activities of the acid in the mixed solvent and in water, respectively, referred to the same standard state, conveniently the hypothetical standard

\* The appropriate algebraic signs of the quantities in equations (1) and (2) and the direction of transfer can be determined by inspection in particular cases.

† The Stockholm convention<sup>7</sup> is used, so that  $E$  is the potential of the right-hand electrode with respect to the left-hand electrode.

<sup>3</sup> Åkerlöf, *J. Amer. Chem. Soc.*, 1930, **52**, 2353.

<sup>4</sup> Gurney, "Ionic Processes in Solution," McGraw-Hill Co., New York, 1953, p. 222.

<sup>5</sup> Grunwald and Bacarella, *J. Amer. Chem. Soc.*, 1958, **80**, 3840.

<sup>6</sup> Butler and Gordon, *J. Amer. Chem. Soc.*, 1948, **70**, 2276.

<sup>7</sup> See ref. 1, p. 26.

<sup>8</sup> Scatchard, *J. Amer. Chem. Soc.*, 1953, **75**, 2883.

state of unit activity *in water* on the molal scale;  $a_{W,1}$  and  $a_{W,2}$  are the activities of water in the two solvent media. In such a system all transport numbers are measured with respect to one component regarded as stationary. In this case we have chosen to regard the methanol as stationary, so that  $t_+^M$  is the cation transport number, and  $w_W$  the transport number of water, both with respect to methanol. We adopt Agar's<sup>9</sup> terminology and call  $w_W$  the Washburn number of water. We regard  $w_W$  as positive if the net transport of water would be towards the negative electrode in an electrolysis. Equation (4) is strictly applicable to cell (III), but only differs significantly from expression (3) when the water activities in each half-cell differ appreciably. For cell (III) this will only arise when the electrolyte concentrations in the two half-cells differ appreciably.

If the water in cell (IV) is regarded as stationary, then

$$E_- = \frac{2RT}{F} \int_{a_1}^{a_2} t_+^W d \ln a + \frac{RT}{F} \int_{a_{M,1}}^{a_{M,2}} w_M d \ln a_M. \quad (5)$$

In equation (5),  $t_+^W$  is the cation transport number and  $w_M$  the Washburn number of methanol, both with respect to water;  $a_{M,2}$  and  $a_{M,1}$  are the activities of methanol in the two solutions.

By considering hypothetical transport number experiments we deduce that

$$t_+^W = t_+^M + \frac{x}{X_W} \cdot w_W, \quad (6)$$

where  $x$  and  $X_W$  are respectively the mole fractions of the acid and of water in the solution. In most of the experiments reported  $x \ll X_W$ , and  $w_W$  is small. The two transport numbers then differ inappreciably from each other and from the transport number which would be found from a Hittorf experiment if the relative movement of solvent were neglected. If, for example, the analysis were based on the molality of the solute then, if  $t_+^H$  is the transport number so calculated:

$$t_+^H = t_+^M + \frac{xw_W}{X_W} \left[ 1 + \frac{X_M M_M}{X_W M_W} \right]^{-1}, \quad (7)$$

where  $X_M$  is the mole fraction of methanol, and  $M_M$  and  $M_W$  are the molecular weights of methanol and water, respectively. In subsequent discussion we put

$$t^M = t^W = t^H = t. \quad (8)$$

We may also deduce that

$$w_W/w_M = -X_W/X_M. \quad (9)$$

Consider equation (4). Following Åkerlöf,<sup>3</sup> we may express the mean ion activity of a (1:1) electrolyte in a mixed solvent with respect to the molal standard state in pure water as

$$\ln a_1 = \ln m_1 + \ln \gamma_{S,1} + \ln \gamma_\infty; \quad (10)$$

$m_1$  is the molality,  $\gamma_{S,1}$  the mean ion activity coefficient with respect to a standard state in the mixed solvent, and

$$2RT \ln \gamma_\infty = \Delta G_t^\circ, \quad (11)$$

the free energy of transfer of the electrolyte between the molal standard states in the two media, water and the mixed solvent.  $\gamma_\infty$  is thus unity in pure water.

Combining equations (4) and (11), we have

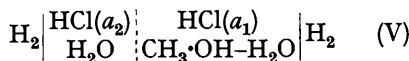
$$E_- = \frac{2RT}{F} \int_{m_1}^{m_2} t_+ d \ln m + \frac{2RT}{F} \int_{\gamma_{S,1}}^{\gamma_{S,2}} t_+ d \ln \gamma + \frac{2RT}{F} \int_{\gamma_\infty}^1 t_+ d \ln \gamma_\infty + \frac{RT}{F} \int_{a_{W,1}}^{a_{W,2}} w_W d \ln a_W \quad (12)$$

<sup>9</sup> Agar, in "The Structure of Electrolytic Solutions," ed. Hamer, John Wiley and Sons, New York, 1959, p. 218.

All the quantities in the first, second, and fourth terms on the right-hand side of (12) are, in principle, measurable, making possible the determination of the third term and hence of  $\Delta G_t^\circ$ . This method could thus be used for any electrolyte yielding one ion for which a reversible electrode exists.

In practice, there is as yet no independent method of determining Washburn numbers accurately in dilute electrolyte solutions. In the present work, therefore, the procedure has been reversed to determine Washburn numbers in hydrochloric acid solutions, since here the  $\Delta G_t^\circ$  term can be independently determined.

The published standard e.m.f.s of the cells (I) and (II) in methanol–water mixtures show poor inter-agreement, so that  $\Delta G_t^\circ$  values could not be calculated therefrom with any certainty. This difficulty was overcome by using cell (V) in addition to cell (IV).



For cell (V) we have

$$E_+ = \frac{-2RT}{F} \int_{a_1}^{a_2} t_- d \ln a + \frac{RT}{F} \int_{a_{w,1}}^{a_{w,2}} w_w d \ln a_w. \quad (13)$$

Put

$$\frac{RT}{F} \int_{a_{w,1}}^{a_{w,2}} w_w d \ln a_w = \chi.$$

Examining  $\chi$ , we find that  $a_w$  is a function, not only of the water concentration, but also of the electrolyte concentration, although the effect of the latter may be discounted in sufficiently dilute solutions.  $w_w$  may be expected also to be a function of these two variables. In studying the system, the solvent composition was held constant in the mixed solvent half-cell and  $\chi$  determined at various electrolyte concentrations. These results were used to obtain  $\chi^\circ$ , the value of  $\chi$  at infinite dilution.

Subtracting equation (13) from equation (4) we obtain:

$$E_- - E_+ = \frac{2RT}{F} \int_{a_1}^{a_2} d \ln a = E \text{ (say)}. \quad (15)$$

Examining equation (4), we note that since  $t_+$  and  $a$  are functions of two variables, the solvent-composition and the electrolyte-concentration, the first term on the left-hand side may not in general be integrated unless the path of the integration is known, that is, unless the composition of the junction between the two half-cells is known at all points. The problem may be greatly simplified if  $a_1 = a_2$ , or nearly so. For let  $x$  be a variable specifying the position of a point in the junction. Let  $t_+^{(1)}$  and  $t_+^{(2)}$  be the cation transport numbers in the mixed and aqueous media respectively. We may then put

$$t_+ = \frac{1}{2} (t_+^{(1)} + t_+^{(2)}) + f(x) = \bar{t}_+ + f(x). \quad (16)$$

Then

$$\frac{2RT}{F} \int_{a_1}^{a_2} t_+ d \ln a = \frac{2RT}{F} \bar{t}_+ \int_{a_1}^{a_2} d \ln a + \frac{2RT}{F} \int_{a_1}^{a_2} f(x) d \ln a. \quad (17)$$

The first term on the right-hand side is a perfect differential and may be evaluated directly. Regarding the second term, we know that the variation of the transport number across the junction is small and, if the outer solutions are of equal activity, the variation of activity within the junction should also be small. The probable order of magnitude of this term was calculated by assuming a continuous-mixture junction. When mixtures containing 10% or 20.22% of methanol by weight are employed in the mixed solvent half-cell, this term is negligibly small (<0.01 mv) for solutions of equal activity, because of the very small variation in  $t_+$ . If a solution containing 43.12% of methanol by weight is employed, this assumption leads to a value of 0.05 mv for the term. No attempt was

made to allow for this term in the final calculations: it was simply added into the experimental error. That this term is very small is borne out in practice by the excellent time-stability of the e.m.f. and its independence of accidental disturbance of the liquid junction.

These quantities were estimated graphically, and the additional uncertainty introduced when  $a_1$  is not quite equal to  $a_2$  was estimated in the same way. For the present experimental results, this is negligible for all the systems in which 10% and 20.22% methanol solutions are used in the mixed half-cell, and is less than 0.01 mv for all except one of the systems in which 43.12% methanol is used, in which it is less than 0.02 mv.

Combining equations (4), (14), (15), and (17) gives

$$E_- = \bar{t}_+ E + \frac{2RT}{F} \int_{a_1}^{a_2} f(x) d \ln a + \chi. \quad (18)$$

and neglecting the second term on the right-hand side gives

$$E_- = \bar{t}_+ E + \chi. \quad (19)$$

In measurements,  $a_1$  was adjusted to be approximately equal to  $a_2$ , either by using Schwab and Ziegenbalg's<sup>10</sup> data, or Harned and Thomas's,<sup>11</sup> or by a short series of experimental trials. (In a few measurements recorded here, the adjustment was not made quite as closely as is practically possible, but it is sufficiently close for the theoretical treatment developed here to be correct.) It will be seen that, if  $a_1$  is not very different from  $a_2$ , then  $E$  is small, and it is not necessary to know  $\bar{t}_+$  with high precision. With the values of  $E$  obtained in the present work, a precision of a few per cent in  $\bar{t}_+$  is all that is required. The range of acid concentrations employed in all the solvent media for the determination of  $\chi^\circ$  was small, and it has thus been possible to neglect the variation of  $t_+$  with acid concentration. The rather larger variation of  $t_+$  with methanol concentration has been allowed for by employing for all acid concentrations values interpolated from the measurements of Erdey-Grúz and Majthényi,<sup>12</sup> made by a moving-boundary method at a concentration of 0.025 mole/litre.

A by-product of the measurements is the determination, from equation (15), of the quantity  $\Delta G_t^\circ$ . This may be used to find the differences in standard e.m.f. of the cells (I) or (II) in water on the one hand and methanol-water mixtures on the other.

#### EXPERIMENTAL

E.m.f.s were measured with a Pye Precision Vernier potentiometer in conjunction with a sensitive galvanometer and a standard cell.

The experimental cell differed only in a few features from the one described by Covington and Prue.<sup>13</sup> Two electrode compartments supplied with gas-saturators were connected with a central compartment by side-arms drawn out into jets, and carrying greased taps which enabled the three compartments to be isolated from each other. The three compartments could be detached from each other at greased cone-and-socket joints: this facilitated the cleaning and setting-up of the cell. The aqueous solution filled one electrode compartment and the central compartment, and the solution in the mixed solvent filled the other compartment, the junction being formed therefore at the tip of the side-arm from the latter compartment, with the less dense solution above the denser.

After the electrode compartments had been filled, the cell was clamped firmly in the bath of a thermostat at  $25^\circ \pm 0.01^\circ$ , with the isolating taps closed. The aqueous solution was then poured into the central compartment, so forming the liquid junction, and a silver-silver chloride electrode was inserted through a greased ground joint in this compartment, thus sealing it off from the atmosphere. This electrode was only used in the hydrogen electrode measurements.

In dilute solutions of acid, two totally electrolytic electrodes, freshly prepared by Claussen

<sup>10</sup> Schwab and Ziegenbalg, *Z. Elektrochem.*, 1958, **62**, 172.

<sup>11</sup> Harned and Thomas, *J. Amer. Chem. Soc.*, 1935, **57**, 1666; 1936, **58**, 761.

<sup>12</sup> Erdey-Grúz and Majthényi, *Acta Chim. Acad. Sci. Hung.*, 1958, **16**, 417.

<sup>13</sup> Covington and Prue, *J.*, 1955, 3701.

and French's method,<sup>14</sup> were first inserted through ground joints in the electrode compartments. A slow stream of nitrogen was passed through the solutions: this was found to be essential to ensure readings which did not drift with time. A slight further improvement in stability was effected by shielding the electrodes from the light. (The author thanks Dr. R. W. Pittman for this suggestion.) Immediately before a reading was taken, the nitrogen supply was cut off, the electrode compartments were closed to the atmosphere, and the isolating taps were opened. When an e.m.f. constant to  $\pm 0.01$  mv had been recorded for 1 hr., the electrodes were reversed and the procedure was repeated. The true e.m.f. of the cell,  $E_-$ , was the mean of the two readings so obtained, and was thus free from the bias potential between the electrodes, which was normally small. The whole procedure needed 4–6 hr. Checks were made in the early stages of the work on the stability of the cell by repeating the whole procedure after 24 hr.; it was rarely found that a drift of more than 0.01 mv had occurred.

The silver-silver chloride electrodes were then removed, a flow of hydrogen was substituted for nitrogen, and two hydrogen electrodes made by the method of Hills and Ives<sup>15</sup> were inserted in each compartment. When fully equilibrated, the two electrodes in a particular compartment normally differed from each other in potential by less than 0.01 mv. To take a measurement, the e.m.f. between each pair of hydrogen electrodes and the central silver-silver chloride electrode was read off in turn, the difference between these readings giving the overall e.m.f. between the hydrogen electrodes,  $E_+$ . Only one connecting tap was thus open at any time, and the disturbance of the liquid junction which might have occurred if both had been simultaneously open with the hydrogen passing was avoided. Equilibrium (overall e.m.f. constant to  $\pm 0.01$  mv for 1 hr.) was normally reached in 4–12 hr., and remained constant often for another 24 hr.

In the solutions dilute in acid ( $< 0.1m$ ) there was no reason to believe that the minute amounts of silver chloride dissolved during the silver-silver chloride measurements would adversely affect the hydrogen electrode measurements. The order of measurement described above was thus used for these concentrations, as it was slightly more convenient practically than the reverse order. In the 1m- and 4m-solutions, the hydrogen electrodes behaved irreversibly in solutions saturated with silver chloride, and there was the further problem that the solubility of silver chloride is such in these solutions that it is rapidly stripped from the electrodes unless the solutions are previously saturated with it.

For these measurements, the hydrogen electrode measurements were made first, the middle compartment containing solution previously saturated with silver chloride. Before the silver-silver chloride measurements were made, the solutions in the electrode compartments were replaced by solutions which had previously been saturated with silver chloride.

Conductivity water was obtained from a still of the type described by Stuart and Wormwell.<sup>16</sup> Burrough's "AnalaR"-quality methanol was refluxed for 3 hr. with silver oxide (see ref. 17), dried for one week ( $\text{CaSO}_4$ ), and distilled through a 4 ft. vacuum-jacketed column packed with Fenske helices, with rejection of substantial head and tail fractions; it had  $n_D^{25}$  1.3265.

Hopkin and Williams's "AnalaR" hydrochloric acid (the samples used gave a negative test for bromide<sup>18</sup>) was used to prepare a solution of the constant-boiling composition. This was used for all except the 1m- and 4m-solutions, for which the original "AnalaR" acid was employed.

## DISCUSSION

Most of the measurements were made with a 43.12% solution by weight of methanol in water in the "mixed" half-cell, since the effect under examination is larger here than in the 10% and 20.22% mixtures.

Table 1 gives values of  $E_-$ ,  $E_+$ ,  $E$ , and  $\chi$  at various molalities of acid for these three mixtures, together with the cation transport numbers appropriate to each solvent mixture and to water.

<sup>14</sup> Claussen and French, *Trans. Faraday Soc.*, 1955, **51**, 708.

<sup>15</sup> Hills and Ives, *J.*, 1951, 305.

<sup>16</sup> Stuart and Wormwell, *J.*, 1930, 85.

<sup>17</sup> Leighton, Crary, and Schipp, *J. Amer. Chem. Soc.*, 1931, **53**, 3017.

<sup>18</sup> Pinching and Bates, *J. Res. Nat. Bur. Stand.*, 1946, **37**, 311.

TABLE 1.

Molality of HCl in mixed solution ( $m_1$ )	Molality of HCl in aq. solution ( $m_2$ )	$E_-$ (mv)	$E_+$ (mv) (corr. to 760 mm.)	$E$ (mv)	$\chi$ (mv)
Water: $t_+ = 0.827$					
10% Methanol: $t_+ = 0.831$					
0.005143	0.005865	0.02	0.23	-0.21	0.19
0.01053	0.01200	0.33	0.20	+0.13	0.22
0.03834	0.04401	0.43	0.19	+0.24	0.23
20.22% Methanol: $t_+ = 0.833$					
0.005872	0.007609	0.23	0.54	-0.31	0.49
0.01005	0.01297	0.13	0.45	-0.32	0.40
0.01548	0.02017	0.59	0.39	+0.20	0.42
0.01677	0.02184	0.57	0.38	+0.19	0.41
0.02039	0.02634	0.31	0.38	-0.07	0.37
43.12% Methanol: $t_+ = 0.797$					
0.004898	0.007977	0.05	1.05	-1.00	0.87
0.006965	0.01132	0.13	1.10	-0.97	0.91
0.01169	0.01909	0.50	0.98	-0.48	0.89
0.01992	0.03217	0.34	1.09	-0.75	0.95
0.03787	0.06111	0.89	0.66	+0.23	0.70
0.05488	0.08606	0.11	0.94	-0.83	0.78
0.06718	0.1065	0.78	0.85	-0.07	0.84
0.1014	0.1559	0.19	0.86	-0.67	0.73
0.1083	0.1607	-1.08	1.02	-2.10	0.63
0.9136	1.2044	-0.03	0.63	-0.66	0.50
3.936	4.506	-0.35	0.51	-0.86	0.34

The values of  $\chi$  obtained when the "mixed" half-cell contained 43.12% methanol were extrapolated to infinite dilution against the molality of the acid in the mixed solvent, all but the results in the two most concentrated solutions being used. Over the range studied, the variation in  $\chi$  is small. A linear dependence of  $\chi$  on  $m$  was assumed for the extrapolation range: much more accurate results would be required to find the true dependence. While  $\chi^\circ$  is 0.95 mv the "smoothed" value of  $\chi$  at 0.1m is 0.75 mv, showing a downward trend in  $\chi$  with increasing concentration. This is continued, though not in a linear fashion, up to the two highest concentrations used. The variation of  $a_w$  with acid concentration in the dilute solutions should be negligible, so that the trend in  $\chi$  may reasonably be taken as a trend in  $w_w$ , but in higher acid concentrations, the expected variations of  $a_w$  from its value in dilute solution may be large. Further analysis of these results is at present impossible in the absence of the requisite activity data.

The variation of  $\chi$  with  $m$  being small for the system involving the 43.12% mixture, the  $\chi^\circ$  values for the systems involving 10% and 20.22% mixtures could reasonably be

TABLE 2.

System .....	H <sub>2</sub> O-10% CH <sub>3</sub> ·OH	H <sub>2</sub> O-20.22% CH <sub>3</sub> ·OH	H <sub>2</sub> O-43.12% CH <sub>3</sub> ·OH
$w_w$ .....	0.14	0.13	0.13

identified with the mean of the results at low concentrations and have been so calculated. The errors on each value of  $\chi^\circ$  are about  $\pm 10\%$  in each case, including  $\pm 0.05$  mv in the case of the system involving the 43.12% mixture for the uncertainty in computing the liquid junction potential.

Values of  $w_w$  were calculated for each system (the values of  $a_w$  found by Butler, Thomson, and MacLennan<sup>19</sup> were used). The values so obtained are of course mean values between those applicable in the particular solvent mixture and in water, and are shown in Table 2. No directly comparable literature values are available, since other determinations refer to concentrated acid solutions, to non-electrolytes other than

<sup>19</sup> Butler, Thomson, and MacLennan, *J.*, 1933, 674.

methanol, and these present in high dilution. Nevertheless the results are of the same order as those found for example by Büchbock<sup>20</sup> ( $w_w = 0.29$  for 1.1N-HCl in 2.2% resorcinol) by a Hittorf determination, and by Longworth<sup>21</sup> ( $w_w = 0.35, 0.20,$  and  $0.32$  for, respectively, 1.5% raffinose in 0.2N- and 1.0N-HCl and 1.5% resorcinol in 1.0N-HCl) by a moving boundary method.

The interpretation of  $w_w$  is necessarily speculative. A reasonable first assumption is that the chloride ion does not move large quantities of one non-electrolyte with respect to the other. It is a large ion, the electrostatic field at its surface is weak, and its electrostatic interactions with the solvent molecules are therefore weak also. No significant additional interactions of a quantum-mechanical nature are possible. Any contribution it may make to  $w_w$  is further reduced by its small transport number ( $t_- \approx 0.2$ ) in the solutions concerned. If we assume then that the contribution made to  $w_w$  by the chloride ion is very small, it follows that the hydrogen ion itself also moves only very small amounts of water with respect to methanol or *vice versa*. This is to be expected as the ion is moving largely by its "proton-jump" mechanism, as the high values of  $t_+$  in all the solvent media used indicate. Preliminary measurements on alkali chlorides, employing results from cells of type (IV) together with Åkerlöf's results, indicate that for lithium, sodium, and potassium chlorides in 10% methanol the  $w_w$  values are of an order of magnitude higher (1.4–1.9).

Rearranging equation (15) with  $k = 2.3026RT/F$ , we obtain

$$E = 2k(\log_{10} a_2 - \log_{10} a_1). \quad (20)$$

From equation (10) we have

$$(E - 2k \log_{10} a_2) = -2k(\log m_1 + \log \gamma_{s,1} + \log \gamma_\infty). \quad (21)$$

Put

$$2k \log \gamma_\infty = \Delta E_m^\circ, \quad (22)$$

which is the difference in the standard molal e.m.f.s of cells (I) or (II) in water and the corresponding cell in the mixed solvent.

Values of  $a_2$  can be computed from the molalities and the activity coefficients of hydrochloric acid in aqueous solution. For the latter the unpublished results of Gupta, Hills, and Ives have been used.

$$\text{Now,} \quad \log \gamma_{s,1} = \frac{-A\sqrt{c_1}}{1 + aB\sqrt{c_1}} + bm_1 - \log(1 + 0.002M_{xy}m_1), \quad (23)$$

where  $A$  and  $B$  are the appropriate Debye-Hückel constants,  $M_{xy}$  is the mean molecular weight of the solvent, and  $a$  has been taken as 4.3. Substituting (23) and (22) in (21) and rearranging gives

$$2k \log_{10} a_2 - E - 2k \log m_1 + \frac{2kA\sqrt{c}}{1 + aB\sqrt{c}} + 2k \log(1 + 0.002M_{xy}m_1) = \Delta E_m^\circ + bm_1. \quad (24)$$

Putting all the terms on the left-hand side of equation (24) equal to  $\Delta E_m^{\circ'}$ , we then have

$$\Delta E_m^{\circ'} = \Delta E_m^\circ + bm_1. \quad (25)$$

For the 43.12% and 20.22% mixtures,  $\Delta E_m^{\circ'}$  was plotted against  $m_1$  to give straight-line plots which were extrapolated to zero  $m_1$  to give  $\Delta E_m^\circ$  (see Table 3). The density and dielectric constant data of Schwab and Ziegenbalg<sup>10</sup> were used in these calculations. In the case of the 10% mixture,  $\Delta E_m^\circ$  values were determined directly for each concentration by using Harned and Thomas's<sup>11</sup> data for  $\gamma_s$  in this mixture, and the value in Table 4 is

<sup>20</sup> Büchbock, *Z. phys. Chem.*, 1906, **55**, 563.

<sup>21</sup> Longworth, *J. Amer. Chem. Soc.*, 1947, **69**, 1288.



an average of the three values so obtained. All the present  $\Delta E_m^\circ$  values are accurate to  $\pm 0.1$  mv.

TABLE 3.

10% Methanol									
$m_1$ .....	0.005143				0.01053		0.03834		
$\Delta E_m^\circ$ (v) .....	0.00700				0.00668		0.00696		
20-22% Methanol									
$m_1$ .....	0.005872	0.01005	0.01548	0.01677	0.02039				
$\Delta E_m^\circ$ (v) .....	0.01390	0.01388	0.01397	0.01400	0.01400				
43-12% Methanol									
$m_1$ .....	0.004898	0.006965	0.01169	0.01992	0.03787	0.05488	0.06718	0.1014	0.1083
$\Delta E_m^\circ$ (v) .....	0.02694	0.02700	0.02712	0.02742	0.02740	0.02790	0.02820	0.02871	0.02870

TABLE 4.

$\Delta E_m^\circ$  values, in volts.

MeOH concn.	10%	20%	20-22%	43-12%	43-3%
Harned and Thomas <sup>11</sup> .....	0.0070	0.0136	—	—	—
Austin, Hunt, Johnson, and Parton <sup>22</sup> .....	—	—	—	—	0.0285
Oiwa <sup>23</sup> .....	0.0069	0.0130	—	0.0277	—
Schwab and Ziegenbalg <sup>10</sup> .....	—	—	0.0135	0.0265	—
This work .....	0.0069	—	0.0138	0.0269	—

TABLE 5.

Mean molal activity coefficients of hydrochloric acid at rounded concentrations for 43-12% mixtures.

Molality	0.005	0.01	0.02	0.05	0.1
A.H.J.P. <sup>22</sup> (43-3%) .....	0.891	0.857	0.817	0.752	0.702
Oiwa .....	0.893	0.859	0.815	0.745	0.700
S.Z. ....	0.896	0.866	0.826	0.763	—
This work * .....	0.895	0.864	0.825	0.759	0.716

\* For the calculation of  $\gamma_s$ ,  $A = 0.774$ ,  $aB = 1.625$ ,  $M_{xy} = 22.19$ ,  $b = 0.147$ .

In Table 4, the results are compared with those of Austin, Hunt, Johnson, and Parton,<sup>22</sup> Oiwa,<sup>23</sup> and Harned and Thomas,<sup>11</sup> who have measured standard e.m.f.s of cell (I) in the various solvent media. A value of 0.2224 v, the mean to the nearest 0.1 mv of three independent closely concordant determinations,<sup>24</sup> is used for  $E_m^\circ$  in aqueous solution, where a value has not been given by the authors. Also shown are Schwab and Ziegenbalg's<sup>10</sup> results from cell (II); these authors measured  $E_m^\circ$  values both in water and in the mixed solvents. All values are quoted to the nearest 0.1 mv; thus differences between 20% and 20-22% solutions, and 43-3% and 43-12% solutions, are negligible. Oiwa's results have been interpolated to give a value for the 43-12% solution. This should be accurate to  $\pm 0.2$  mv.

The agreement between these results is most unsatisfactory, especially for the 43-12% solution, where the largest difference found, 2 mv, is some ten times the sum of the experimental errors on each determination. The present results agree well with the others for the 10% solution, with all except Oiwa's for the 20-22% mixtures, and are closest to Schwab and Ziegenbalg's for the 43-12% mixtures. This situation would repay further investigation.

Activity coefficients have been calculated in the case of the 43-12% mixture only, and are compared with those of other workers at rounded acid concentrations in Table 5. Oiwa's results are interpolated, and those of Austin, Hunt, Johnson, and Parton relate

<sup>22</sup> Austin, Hunt, Johnson, and Parton, unpublished work; see Parsons, "Handbook of Electrochemical Constants," Butterworths, London, 1959, pp. 32, 74.

<sup>23</sup> Oiwa, *J. Phys. Chem.*, 1956, **60**, 754.

<sup>24</sup> Harned and Ehlers, *J. Amer. Chem. Soc.*, 1932, **54**, 1350; 1933, **55**, 2179; Bates and Bower, *J. Res. Nat. Bur. Stand.*, 1954, **53**, 283; Harned and Paxton, *J. Phys. Chem.*, 1953, **57**, 531.

to a 43.3% mixture. Again, while there is fair agreement between the present results and those of Schwab and Ziegenbalg, the same unsatisfactory spread of results is observed otherwise.

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THE GEORGE SENTER LABORATORY,  
BIRKBECK COLLEGE,  
LONDON, W.C.1.

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