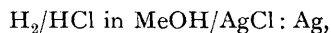


## THE USE OF AMALGAM ELECTRODES FOR DETERMINING ACTIVITIES IN METHYL ALCOHOL.

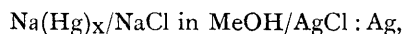
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Owing to the impracticability of making precise freezing-point determinations in methyl alcohol solutions, measurements of *E.M.F.* assume a peculiar importance as the principal source of information as to the activities of electrolytes in this solvent. The restrictions imposed by the limited number of truly reversible electrodes and by the presence of complex ions even in dilute solutions virtually confine us to measurements of the halides of hydrogen, the alkali metals and the alkaline earth metals. Nonhebel and Hartley<sup>1</sup> have carried out measurements of the *E.M.F.* of the cell,



over a range of molality from  $M/2$  to  $M/2000$  and have used the results to calculate the activity of hydrogen chloride in methyl alcohol. The present note is concerned with an attempt to carry out similar measurements with the cell,



It was hoped that, as in the case of hydrogen chloride, it would be possible to carry out accurate measurements in sufficiently dilute solution to permit of the evaluation of absolute activity coefficients by graphical extrapolation to infinite dilution. Such a method avoids the element of uncertainty introduced by the alternative method of assuming a value of the activity coefficient for a given concentration, based on conductivity data or other considerations. For the purposes of such graphical extra-

polaration, measurements may be made with either the single cell indicated or with a combination of two such cells forming a concentration cell without transport, provided, in the latter case, that the concentration pairs are chosen so as to provide a continuous "ladder" from the strong to the dilute solutions.<sup>2</sup> It was thought preferable to avoid the double cells used by previous workers on methyl alcohol,<sup>3</sup> as these might conceal any secondary effects at the pair of intermediate amalgam electrodes.

Measurements were therefore carried out with the cell,  
 $\text{Na(Hg)}^x/\text{NaCl}$  in

$\text{MeOH/AgCl:Ag}$ ,

over a range of molality from  $M/10$  to  $M/2000$ . The methyl alcohol was prepared in the manner described by Hartley and Raikes<sup>4</sup> except that the final distillation into the block tin condenser was carried out in a stream of dry nitrogen. The product showed a specific conductivity averaging 0.003 gemmhos and a viscosity test indicated a maximum water content of 0.015 per cent. Merck's sodium chloride, dried on a quinoline bath, was dissolved

in the methyl alcohol in flasks filled with nitrogen. The silver-silver chloride electrodes were chloridised in an approximately decinormal solution of sodium chloride in methyl alcohol; the two electrodes employed in each measurement agreed with one another to 0.1 millivolt. The sodium amalgam was prepared by the electrolysis of saturated aqueous sodium carbonate and was filtered through a very fine capillary into the amalgam reservoir where it was kept under an atmosphere of nitrogen. Its concentration was estimated by treatment with a known excess of standard acid in the manner described by Richards and Conant.<sup>5</sup>

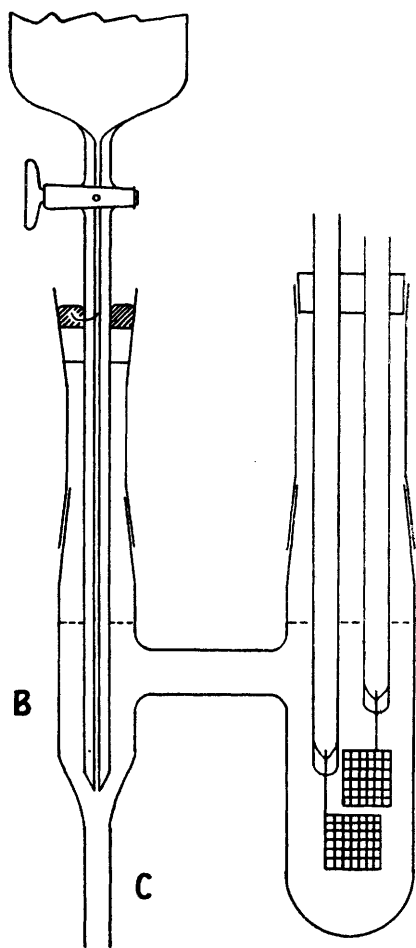


FIG. 1.

After a few preliminary measurements, a cell of the type illustrated in Fig. 1 was employed. The right limb A contains the pair of silver-silver chloride electrodes. The left limb B contains the streaming amalgam electrode. The volume of A was about 40 cubic centimetres while B had a capacity of three or four cubic centimetres to ensure the most rapid rate of renewal of solution round the amalgam tip for a given expenditure of solution. Preliminary experiments had shown that if the left limb had as large a capacity as that on the right, decomposition was so fast as to cause the *E.M.F.* to drop steadily from the first measurement onwards, at a rate dependent on the dilution of the solution. For similar reasons the amalgam tip was ground to a conical form and placed at the point where the solution stream would be approaching its maximum velocity. With the modified form of cell illustrated there was no falling off of *E.M.F.* with time nor did the *E.M.F.* vary appreciably with the rate of solution flow. The cell was filled with nitrogen before the solution was admitted. The solution entered B from behind at a point just above the amalgam tip, after passing through a long zig-zag of thin-walled tubing to ensure temperature equilibrium. Both solution and amalgam left the cell at C. The rate of solution flow was about 8 to 10 cubic centimetres per minute; the rate of amalgam flow was varied from 1 to 30 drops per second corresponding to expenditures of  $\frac{1}{8}$  to 10 cubic centimetres of amalgam per minute. A wide range of amalgam concentrations (from 0.4 per cent. to 0.001 per cent.) was tried; the most satisfactory concentration from the point of view of steadiness of *E.M.F.* was in the neighbourhood of 0.04 per cent. There was some indication of the advantages of "matching" the amalgam concentration to the concentration of the solution being measured, as recorded by Knobel.<sup>6</sup> On the other hand amalgams as dilute as 0.00135 per cent. and 0.00294 per cent., similar to those used by recent workers, invariably failed to give a steady *E.M.F.*

The most interesting point on the experimental side which emerged from the measurements was the dependence of the *E.M.F.* of the cell upon the rate of flow of the amalgam. From the outset of the experiments it became clear that the potentiometer null-point could be shifted by comparatively small changes in the rate of flow. The point was investigated in some detail by carrying out runs in which the rate of flow was changed many times and the corresponding *E.M.F.* was measured at frequent intervals. In these runs two amalgams of concentrations 0.041 per cent. and 0.00294 per cent. were used and three solutions, M/20, M/200 and M/2000 respectively. Three standard rates of flow were employed, namely 2 drops per second, 8 drops per second and a rate described as "semi-continuous" in which individual drops could scarcely be discerned. With the more dilute amalgam, *E.M.F.* readings were most irregular and it seemed almost impossible to predict even the sense in which a change in the rate of flow would affect the *E.M.F.* At different times in the same run a change from 8 drops per second to "semi-continuous" might cause the *E.M.F.* to rise 3 millivolts or to drop 6 millivolts. A lowering of *E.M.F.* with increase in the rate of amalgam flow seemed to be more frequent than the opposite effect. With the stronger amalgam the results were much more consistent and of an interesting nature. As an example the experiment with 0.041 per cent. amalgam in a solution 0.0568 molar is represented in Fig. 2. The abscissae give the time in minutes from the beginning of the run, the ordinates represent potentiometer readings in ohms, one ohm corresponding to 0.3 mv.

The results suggest that the cell has a characteristic *E.M.F.* for every

rate of amalgam flow, and no evidence is afforded that there is any limiting rate above which further increases in the rate of flow have no effect on the *E.M.F.* It was further observed that, on changing the rate of flow, equilibrium was not established instantaneously but that the *E.M.F.* drifted during a period of one-half to two minutes towards the value characteristic of the new rate of flow.

The cause of these phenomena is obscure. Other workers have recorded no observations of a similar nature. This may perhaps be connected with the fact that the majority of measurements have been made with double cells in which effects of the nature described would tend to neutralise each other. It is difficult to believe that decomposition at the amalgam surface is entirely responsible for the effect and that the increase of *E.M.F.* with rate of flow is simply due to diminished decomposition. If this were so, one would expect the effect of changing the speed from 2 to 8 drops per

second to be as great as, or even greater than, that of a further increase to the "semi-continuous" rate of about 30 drops per second. One would also expect the effect to be most marked in the most dilute solutions and almost absent from a solution as concentrated as  $M/20$ , whereas it is roughly the same at all concentrations from  $M/20$  to  $M/2000$ . It seems more likely that electrocapillary and electrokinetic effects are partially or wholly responsible for this

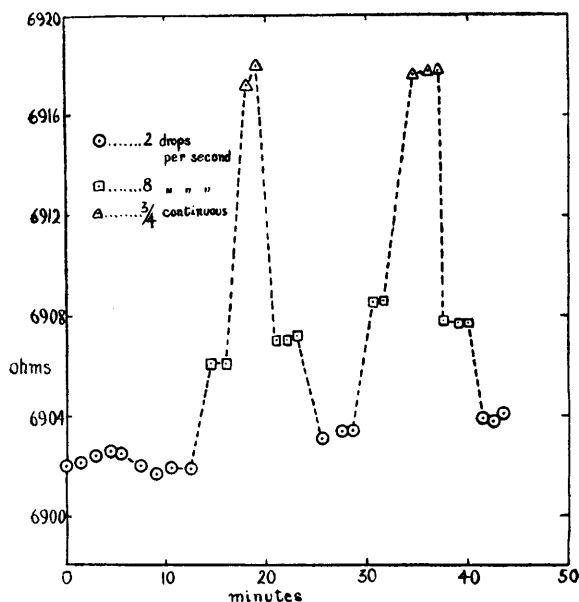


FIG. 2.

phenomenon which, whatever its causes, destroys all assurance that we are measuring the true equilibrium which we are seeking.

Another equally unexpected effect was brought to light when a series of *E.M.F.*'s, measured at a fairly uniform rate of amalgam flow in a range of solution concentration from  $M/6$  to  $M/2000$ , were plotted so as to arrive at a value for  $E_0$ , the *E.M.F.* of the cell with a solution of unit activity. From the values of Richards and Conant<sup>5</sup> all *E.M.F.*'s were reduced so as to refer to the sodium metal electrode. From these reduced *E.M.F.*'s the four functions  $E_0'$ ,  $E_{0A}$ ,  $E_0$  (Debye), and  $E_0$  (Milner) were calculated, as described by Hartley and Nonhebel<sup>1</sup> from the equations:

$$(1) E_0' = E + 0.11831 \log c.$$

$$(2) E_{0A} = E + 0.11831 \log c + 0.11831 \log \frac{\Delta c}{\Lambda_0}.$$

$$(3) E_0 \text{ (Debye)} = E + 0.11831 \log c + 0.11831 \log f \text{ (Debye).}$$

$$(4) E_0 \text{ (Milner)} = E + 0.11831 \log c + 0.11831 \log f \text{ (Milner).}$$

The volume concentrations  $c$  were obtained by multiplying the concentrations per thousand grammes of solution by 0.7864, the density of pure methyl alcohol. The results are given in the following table :

M.	$\sqrt{c}$	E.	$E_0'$	$E_{0A}$	$E_0$ (Debye).	$E_0$ (Milner).
0.00067	0.0229	3.0476	2.6591	2.6565	2.6534	2.6551
0.00085	0.0258	3.0324	2.6568	2.6513	2.6504	2.6523
0.00166	0.0362	3.0280	2.6870	2.6825	2.6780	2.6807
0.00395	0.0558	3.0032	2.7066	2.6993	2.6927	2.6970
0.00726	0.0759	2.9816	2.7167	2.7063	2.6978	2.7039
0.00817	0.0801	2.9772	2.7178	2.7075	2.6978	2.7042
0.01654	0.1140	2.9483	2.7252	2.7110	2.6967	2.7062
0.01654	0.1140	2.9497	2.7266	2.7124	2.6981	2.7076
0.0361	0.1683	2.9129	2.7298	2.7106	2.6877	2.7025
0.0568	0.2109	2.9023	2.7424	2.7194	2.6897	2.7088
0.0748	0.2420	2.8886	2.7428	2.7175	2.6833	2.7046
0.1581	0.3510	2.8586	2.7510	2.7184	2.6633	—

The four functions should converge to a common limiting value at infinite dilution, equal to  $E_0$  the *E.M.F.* of the cell with a sodium chloride solution of unit activity. When plotted against the square root of the concentration we should expect that, as in the case of hydrogen chloride in methyl alcohol, the curves of the four functions should approach linearity below  $\sqrt{c} = 0.10$  and should approach the axis of zero concentration at a finite angle.

In Fig. 3,  $E_0'$  and  $E_0$  (Debye) are plotted against the square root of the concentration; these two functions only are plotted for the sake of clear-

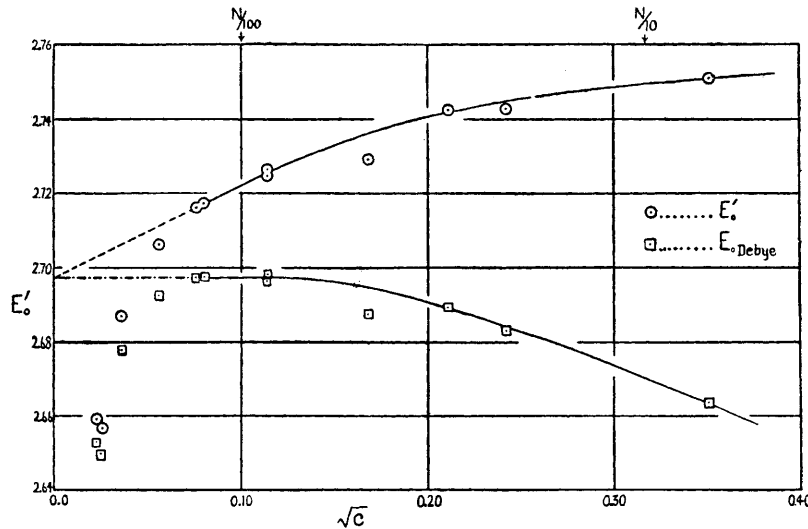


FIG. 3.

ness. Contrary to expectation both functions are seen to fall rapidly below  $\sqrt{c} = 0.07$  and to approach the vertical axis asymptotically instead of merging into straight lines which, in the case of the Debye function, would be horizontal if the hypothesis is an accurate representation of the facts. The difference between the anticipated and the observed results corresponds

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to differences of 20 to 45 millivolts in the *E.M.F.*'s measured. It is difficult to connect this with the variation of *E.M.F.* with rate of flow, because the extent of that effect seemed to be roughly independent of the concentration; it is unlikely that it is due to decomposition of the amalgam because three of the points plotted (which are in agreement with the rest of the values) are the result of measurements made with the highest rate of amalgam flow. The cause of the phenomenon is at present obscure but, in view of the general agreement between experimental activity values and the Debye theory, the rapid fall of values of  $E_0'$  in very dilute solutions must be assumed not to correspond to true equilibria. There is distinct evidence that the effect has been encountered by other workers using amalgam electrodes.

In the presence of a disturbing influence of such magnitude it is difficult to arrive at any value for  $E_0$  from which activities might be calculated. The best that we can do is to assume that the limiting slope of  $E_0'$  and similar curves is represented by the points between  $\sqrt{c} = 0.12$  (above which concentration all *E.M.F.* measurements indicate appreciable curvature in  $E_0'$ ) and  $\sqrt{c} = 0.07$  (below which it is clear from Fig. 3 that the secondary effect at high dilutions is becoming pronounced). This throws the whole responsibility on four *E.M.F.* determinations; drawing a straight line through the corresponding values for  $E_0'$  and  $E_0$  (Debye), we get lines cutting the axis of zero concentration at  $E_0 = 2.697$  volts. Such an extrapolation assumes that all the *E.M.F.*'s below  $\sqrt{c} = 0.07$  are subject to an unknown experimental error and that the true *E.M.F.*'s over this concentration range are such as would give  $E_0'$  values lying on the rectilinear extrapolation.

A table of activities at round concentrations calculated on this basis is given below. The third column gives the activity coefficient calculated from the smoothed  $E_0'$  curve of Fig. 3; the fourth column gives the corresponding activity coefficient for hydrogen chloride in methyl alcohol; the fifth column gives the value corresponding to the limiting Debye equation,

$$-\log_{10} f = A\sqrt{c},$$

while the sixth column was obtained by adjusting a suitable value of  $\alpha$  in the equation,

$$-\log_{10} f = \frac{Ac}{1 + \alpha\sqrt{c}}$$

For methyl alcohol  $A = 2.112$  and  $\alpha$  was made equal to 1.00.

$c$ .	$\sqrt{c}$ .	$f$ .	$f(\text{HCl})$ .	$f(\text{Debye} - 1)$ .	$f(\text{Debye} - 2)$ .
0.0001	0.0100	0.943	0.966	0.953	0.953
0.0005	0.0223	0.890	0.927	0.897	0.899
0.001	0.0316	0.856	0.900	0.858	0.862
0.005	0.0707	0.705	0.785	0.709	0.725
0.01	0.1000	0.615	0.707	0.615	0.643
0.05	0.2236	0.408	0.516	0.337	0.411
0.10	0.3162	0.367	0.442	0.215	0.311

As in the case of hydrogen chloride, the  $\log f/\sqrt{c}$  curve turns off too sharply in the more concentrated solutions to be represented by the above equations. Up to a concentration of  $c = 0.01$ , however, the activity coefficients correspond closely to the limiting equation of Debye. Too much importance

must not be attached to this result owing to the uncertainty attaching to the extrapolation to  $E_0$  and to the sensitiveness of the  $\log f$  slope to small changes in  $E_0$ . The latter is such that the difference between the limiting slopes of Milner and of Debye corresponds to a difference of no more than eight millivolts in  $E_0$ . The agreement with the Debye slope does however tend to confirm the view that some secondary effect intervenes at about  $\sqrt{c} = 0.07$  and to support the rather arbitrary method of extrapolation which ignores the experimental values below this latter concentration.

Reviewing the results of these preliminary measurements with an amalgam cell in methyl alcohol, it may be said that two unexpected phenomena were disclosed, both of which placed unsuspected obstacles in the way of accurate activity determinations by the *E.M.F.* method. It was found that the *E.M.F.* depended on the rate of flow apparently without limit and irrespective of the concentration of the solution. It was further found that, at concentrations of about  $M/200$  and below, an unknown factor intervened to make the *E.M.F.* twenty to forty millivolts lower than those corresponding to ionic activities of the solutions calculated from Debye and Hückel's equation.

The first of these phenomena needs further detailed investigation before we can feel any certainty as to the significance of an *E.M.F.* measured under these conditions. The influence of the bore of the capillary dropper must be examined as well as that of the concentration of the amalgam and the solution. Comparisons with an electrode of the overflowing cup type would probably be illuminating. The second phenomenon, corresponding to even greater aberrations in the *E.M.F.*'s measured, is particularly important in view of the limitations it places upon the determination of activities by extrapolation to infinite dilution.

### Note on the Transport Number of the Sodium Ion.

Measurements were made for three pairs of solutions with the liquid-junction concentration cell,

Ag : AgCl/NaCl, conc.  $c_1$ /NaCl conc.  $c_2$ /AgCl : Ag.

The absence of the amalgam electrode made it possible to obtain values concordant to 0.03 mv. The fourth column in the following table gives the value of the *E.M.F.* measured in this way; the fifth column gives the *E.M.F.* of the corresponding concentration cells without liquid junction. The latter were calculated from the *E.M.F.*'s of the single amalgam cell by interpolation on a smoothed curve of  $(E + 0.11831 \log M)$ . The last column gives the values of  $\eta_{Na}$ , the transport number of the sodium ion.

$M_1$ .	$M_2$ .	$\sqrt{M_1 M_2}$ .	E (Liquid Junction).	E (no Liquid Junction).	$\eta_{Na}$ .
0.1790	0.0180	0.0568	0.04415	0.0937	0.471
0.0991	0.00999	0.03146	0.04414	0.0902	0.489
0.0180	0.00204	0.00606	0.04514	0.0901	0.501

The drift of the transport number with concentration may be wholly or partially due to the secondary effect which depresses the *E.M.F.* of the amalgam cell at high dilutions.

Although the values of  $(E + 0.11831 \log M)$  were smoothed like the curve of  $E_0'$  in Fig. 3 to neutralise this disturbing effect, it is probable that the depression of *E.M.F.* is not entirely effaced by the smoothed values

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used for the more dilute solutions. However that may be, the values for the transport number give additional confirmation that the *E.M.F.*'s of the amalgam cell below  $\sqrt{c} = 0.07$  cannot represent true equilibrium, for if the experimental *E.M.F.*'s are used over this concentration range, the transport number varies rapidly in dilute solution yielding values which are incompatible with the known mobilities of the two ions.

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