Electrochemical Measurements with Amalgam Electrodes

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The chemistry of electrolytic solutions can now be investigated with a variety of modern techniques, but there is still plenty of scope for some of the older-established methods. In the study of both ion–ion and ion–solvent interactions, electrochemistry has provided some of the most precise quantitative data, notably from measurements of the e.m.f.s of reversible cells.[1,2] Many metal ions are readily studied in such cells with electrodes in the form of a solution of metal in mercury, which frees the metal from the strains of the solid state and thereby renders it more reproducible thermodynamically. The popularity of these amalgam electrodes has been somewhat limited by the experimental problems attending their operation, but many of these have now been overcome. This Review illustrates the various measurements that can be made, in the hope that these electrodes will attract a more widespread attention and discriminate use in the future. Detailed reviews of other important electrodes are already available.[3,4]

There are many related applications of amalgam electrodes, *e.g.* in electrode kinetics, polarography, and surface chemistry, but these are beyond the scope of this survey and are not specifically covered.

1 The Development of Amalgam Electrodes

A. Historical.—The first outstanding demonstrations of the usefulness and reliability of cells incorporating amalgam electrodes came from Lewis and his associates.[5] They observed that dilute solutions of the alkali metals in mercury were relatively unreactive to water, a finding which led them to determine the standard electrode potentials of sodium, potassium, and lithium from cells with liquid junctions. Later, values in good agreement with these were obtained in the following way from cells without liquid junctions.[6] The electrode potential of a

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[1] R. A. Robinson and R. H. Stokes, 'Electrolyte Solutions', Butterworths, London, 1969.

[2] H. S. Harned and B. B. Owen, 'Physical Chemistry of Electrolyte Solutions', Reinhold, New York, 1958, 3rd Edn.

[3] D. J. G. Ives and J. G. Janz, eds., 'Reference Electrodes', Academic Press, London, 1961.

[4] G. J. Janz and H. Taniguchi, *Chem. Rev.*, 1953, **53**, 397.

[5] (*a*) G. N. Lewis and C. A. Kraus, *J. Amer. Chem. Soc.*, 1910, **32**, 1459; (*b*) G. N. Lewis and F. G. Keyes, *J. Amer. Chem. Soc.*, 1912, **34**, 119; (*c*) G. N. Lewis and W. L. Argo, *J. Amer. Chem. Soc.*, 1915, **37**, 1983.

[6] D. A. MacInnes, 'Principles of Electrochemistry', Dover, New York, 1961, Chaps. 8, 10, and 14.

metal amalgam, relative to that of a silver–silver-halide electrode, is measured by the e.m.f. of a 'single' cell of the type (I). Cell (II), in which the non-aqueous

$$\begin{array}{l|l|l} \text{M(Hg)} & \text{MX} & \text{AgX--Ag} \\ \text{(amalgam)} & \text{(aq.)} & \end{array} \qquad \text{(I)}$$

$$\text{M} = \text{metal, X} = \text{Cl, Br, or I.}$$

solvent gives a conducting solution but does not react with the alkali metal, gives the potential of the pure metal with respect to the amalgam. Its e.m.f. depends

$$\begin{array}{l|c|l} \text{M(Hg)} & \text{MX} & \text{M} \\ \text{(dilute amalgam)} & \text{(in ethylamine} & \\ & \text{or propylamine)} & \end{array} \qquad \text{(II)}$$

only on the relative activities of M in the amalgam and in the pure metal. The electrode potential of the metal M is then the difference between the e.m.f.s of cells (I) and (II). A blue colour, generated at the interface between metal and solution, was noted by Lewis. The suggestion that this colour was due to the solvated electron had been made several years earlier.[7]

The next twenty years saw a steady development in the research. MacInnes and Parker[8] introduced flowing amalgams with a convenient 'double' cell, (III),

$$\begin{array}{l|c|c|c|l} \text{Ag--AgCl} & \text{MCl},m_1 & \text{M(Hg)} & \text{MCl},m_2 & \text{AgCl--Ag} \\ & \text{(aq.)} & \text{(dilute} & \text{(aq.)} & \\ & & \text{amalgam)} & & \end{array} \qquad \text{(III)}$$

a combination which was to be much used for later measurements with the alkali and alkaline-earth metal amalgams.[2] Electrical contact between the two sides of the cell was established through the central electrode itself.

The theory of Debye and Hückel, published[9] in 1923, opened up the study of interionic effects in terms of the activities of electrolytes. Harned's industrious group determined activity coefficients over a range of temperatures for many of the alkali-metal chlorides and hydroxides in water, attaining a remarkable precision.[2] It is unfortunate that their high standards were seldom achieved by other workers, some of whom concentrated on non-aqueous solutions, chiefly of the alcohols.[10] At this time, and even in more recent work, the facility afforded by the Debye–Hückel theory for the extrapolation of results to standard state values appears frequently to have been overlooked. On the interpretative side, however, Hamilton and Butler[11] were early to recognise the importance of a change in the free energy of solvation of an ion in solution with a change in solvent, as opposed to the free energy of solvation itself.

Critical tests of the e.m.f. method for determining activity coefficients of alkali-

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[7] C. A. Kraus, *J. Amer. Chem. Soc.*, 1908, **30**, 1323.

[8] D. A. MacInnes and K. Parker, *J. Amer. Chem. Soc.*, 1915, **16**, 1445.

[9] P. Debye and E. Hückel, *Z. Physik.*, 1923, **24**, 185.

[10] (*a*) A. Macfarlane and H. Hartley, *Phil. Mag.*, 1935, **20**, 611; (*b*) J. H. Wolfenden, C. P. Wright, N. L. Ross-Kane, and R. S. Buckley, *Trans. Faraday Soc.*, 1927, **23**, 491.

[11] R. T. Hamilton and J. A. V. Butler, *Proc. Roy. Soc.*, 1932, **A138**, 450.

metal chlorides in aqueous solution showed that the values from the 'double' cell agreed closely with the corresponding values from freezing point studies[12] and with those from isopiestic measurements.[13] The agreement was poorer for the chlorides of the alkaline-earth metals.[2] Some interest was also directed towards aqueous solutions containing halides of the less reactive metals zinc, cadmium, and lead, which were studied in 'single' cells.[2] The work was no less accurate than previous studies of the alkali-metal salts, but difficulties were encountered in the interpretation of the results because of the tendency of the ions to associate in solution.

Despite the early successes there has been a lack of continuity in the development of amalgam electrodes, together with a shortage of critical experimental accounts. Their reputation has suffered to the extent of their exclusion from a major text[3] on electrodes. In recent years, however, a growing interest in solvation in aqueous,[14,15] non-aqueous,[15,16] and mixed solvents[15–17] has stimulated electrochemists to re-examine the experimental techniques. These have now been brought into line with the advances in instrumentation.

B. The Working Electrodes.—The factors which determine the stability of an electrode potential are not yet clearly understood. The structure of the amalgam–solution interface is undoubtedly important, but of this we have little detailed knowledge. It is pertinent, however, that zinc and alkali metals lower the interfacial tension between mercury and an aqueous solution, lithium enormously so.[18] There is likely to be a parallel effect for the alkaline-earth metals. The performance of an electrode will depend on such factors, for it is essential that equilibrium should be established across the interface before the amalgam has reacted with the solvent to any noticeable extent. Numerous investigations have been directed towards finding the conditions that give the most precise and reproducible electrode potential for each particular amalgam. The concentration of the electrolyte solution and that of the metal in the amalgam, the mode of delivery, and the shape and size of the electrode surface are all factors which have been found critical.

Most of the cells so far studied have employed aqueous solutions. For convenience we therefore divide the electrodes into two categories: one in which the metal in the amalgam is reactive to water, and the other for which hydrolysis is insignificant. These are termed class 'A' and class 'B' electrodes respectively. It is

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[12] R. P. Smith, *J. Amer. Chem. Soc.*, 1933, **55**, 3279.

[13] C. J. Downes, *J. Chem. and Eng. Data*, 1970, **15**, 444.

[14] (*a*) R. W. Gurney, 'Ionic Processes in Solution', Dover, New York, 1953; (*b*) M. J. Blandamer, *Quart. Rev.*, 1970, **24**, 169.

[15] (*a*) J. F. Coetzee and C. D. Ritchie, eds., 'Solute–Solvent Interactions', Marcel Dekker, New York, 1969; (*b*) H. Strehlow, in 'Chemistry of Non-Aqueous Solvents', ed. J. J. Lagowski, vol. 1, Academic Press, New York, 1966.

[16] F. Franks, ed., 'Physico-Chemical Processes in Mixed Aqueous Solvents', Heinemann, London, 1967.

[17] A. K. Covington and P. Jones, eds., 'Hydrogen-Bonded Solvent Systems', Taylor and Francis, London, 1968.

[18] G. Meyer, *Z. phys. Chem.*, 1910, **70**, 315.

Table 1 *Measurements with amalgam electrodes*

Metal	*Concentration of metal in amalgam**	*Type of electrode*	*Concentration range of electrolyte solutions*, mol kg^{-1} †	*Solvent*	*Accuracy* ± mV†	*refs.*
Li	dilute	streaming	0·04—0·30	water	0·2	*a*
				methanol		*b*
				aqueous methanol		*c*
				aqueous dioxan		*d*
				D_2O		*e*
				dimethylformamide		*f*
Na, K, Rb, Cs	dilute	streaming	0·02—0·20	water	0·05	*a*
				methanol		*b*
				aqueous methanol		*c*
				aqueous dioxan		*d*
		various	—	various non-aqueous		*g*
Ca	dilute	dropping	—	water, aqueous ethanol	?	*h*
Sr	dilute	spilling pool	0·03—0·20	water, aqueous methanol	0·5	*h*
		dropping	—	methanol		*i*
Ba	dilute	spilling pool	0·03—0·20	water, aqueous methanol	0·2	*h*
		dropping	—	methanol		*i*
Mg	dilute	dropping	—	methanol		*i*
Cd	saturated or dilute	spilling or stationary pool	0·0005—satd.	water, aqueous methanol	0·01	*j*
				formamide		*k*
				dimethylformamide		*l*

Table 1 (*Cont.*)

Metal	*Concentration of metal in amalgam**	*Type of electrode*	*Concentration range of electrolyte solutions*, mol kg^{-1}†	*Solvent*	*Accuracy* ±mV†	*refs.*
Zn	saturated or dilute	stationary pool	0·0005—satd.	water	0·01	*m*
		dropping	—	methanol		
				aqueous methanol		
				aqueous ethanol		
				aqueous dioxan		
Pb	saturated	stationary pool	0·0004—satd.	water		*n*
				aqueous dioxan		
Cu	saturated	stationary pool	0·05—0·40	water	0·5(?)	*o*
Tl	concentrated or dilute	stationary pool	—	water	0·01	*p*, *q*
In	concentrated or dilute	stationary pool	—	water	—	*q*, *r*

* Dilute amalgams are generally ~0.005 mol kg^{-1}
† Values for aqueous solutions only

[a] Refs. 1, 2, 5, 8, 22—26; R. Huston and J. N. Butler, *J. Phys. Chem.*, 1968, **72**, 4263; [b] Refs. 27, 29; N. A. Ismailov and E. F. Ivanova, *Zhur. fiz. Khim.*, 1955, **29**, 1422; [c] Refs. 27, 30; [d] Ref. 30; [e] Ref. 31; [f] J. N. Butler and J. C. Synnott, *J. Amer. Chem. Soc.*, 1969, **92**, 2602; [g] Ref. 15; ref. 29. (ethylene glycol); ref. 51, (dimethyl sulphoxide); H. Ulich and G. Spiegel, *Z. phys. Chem.*, 1936, **177**, 103, (acetone); V. A. Pleskov, *Russ. J. Phys. Chem.*, 1946, **20**, 163 (liquid ammonia); ref. 65 and Y. M. Povarov, A. I. Gorbanev, Y. M. Kessler, and I. V. Safanova, *Doklady Akad. Nauk. S.S.S.R.*, 1964, **155**, 1411, (*N*-methylformamide); A. J. Dill, L. M. Itzkowitz, and O. Popovych, *J. Phys. Chem.*, 1968, **72**, 4580, (ethanol); V. V, Aleksandrov, V. I. Lebed, T. M. Shikhova, and B. G. Zaslovskii, *Soviet Electrochem.*, 1968, **4**, 637, (ethanol); K. Bräuer and H. Strehlow, *Z. phys. Chem.* (*Frankfurt*), 1958, **17**, 336, (methanol); A. M. Shkodin and L. Ya. Shapovalova, *Soviet Electrochem.*, 1968, **4**, 113, (methanol–dioxan). [h] Refs. 33—39; [i] Ref. 40; [j] Refs. 2, 43, 55, 57; E. C. Noonan, *J. Amer. Chem. Soc.*, 1949, **71**, 102; J. D. Hefley and E. S. Amis, *J. Phys. Chem.*, 1965, **69**, 2082; *J. Electrochem. Soc.*, 1965, **112**, 336; [k] T. Pavlopoulos and H. Strehlow, *Z. phys. Chem.* (*Frankfurt*), 1954, **2**, 89; [l] J. N. Butler, *Adv. Electrochem. Electrochem. Eng.*, 1969, **7**, 77; [m] Refs. 1, 2, 43; G. Corsaro and H. L. Stephens, *J. Electrochem. Soc.*, 1957, **104**, 512; [n] Refs. 2, 58; M. V. Noble and A. B. Garrett, *J. Amer. Chem. Soc.*, 1944, **66**, 231; [o] Refs. 45—48; [p] Refs. 49, 50, 51; [q] L. F. Kozin, *Trudy Inst. Khim. Akad. Nauk Kazakh. S.S.R.*, 1962, **9**, 93; [r] T. W. Richards and J. H. Wilson, *Z. phys. Chem.*, 1910, **72**, 129; J. N. Butler, *J. Phys. Chem.*, 1964, **68**, 1828.

generally recognised that oxygen-free conditions are essential for the proper functioning of electrodes in the first group; this requirement is no less important, however, for electrodes in class 'B'. The results are summarised in Table 1.

Class 'A' Electrodes: Alkali Metals. Solutions of the alkali metals in mercury show negative deviations from Raoults law.[19] The manner in which this non-ideality varies with the metal concentration indicates the formation of a series of compounds of composition MHg_x, where $x = 2, 4, 6, 8, 16$. In a dilute amalgam, the log of the activity, referred to a standard state of unity for the pure metal M, varies linearly with the amalgam composition.[19,20] However, it is only for the potassium electrode that a systematic study has been made of the effect of concentration upon e.m.f. For this work Armbruster and Crenshaw[21] used the electrode concentration cell (IV). They found the working range of

$$\mathrm{M(Hg)}, m_1 \;\Big|\; \underset{\text{(aq.)}}{\mathrm{MX}} \;\Big|\; \mathrm{M(Hg)}, m_2 \qquad \text{(IV)}$$

amalgam concentration to be 0·01 to 0·45 wt % potassium, and that, as expected, the e.m.f. was independent of electrolyte concentration. All forms of amalgam delivery gave identical results, though with dilute electrolyte solutions the cells tended to be unstable, and a jet-type electrode was then preferred.

The difficulties in reproducing the composition of an amalgam complicate studies of the 'single' cells. These uncertainties are removed in the 'double' cell, where the e.m.f. proves to be virtually independent of the concentration of the dissolved metal. In studies of the aqueous potassium chloride system, MacInnes and Parker[8] were able to set up cells which had e.m.f.s constant to ±0·05 mV with both 0·02 and 0·002 wt % potassium amalgams, delivered at a rate of 30 drops per minute from the cup-like tips of upturned capillaries. A more dilute amalgam (0·0002 wt %) was not amenable to study. For lithium[22] it was essential to use the so-called 'streaming' electrode in which the amalgam flows down from fine capillaries of 0·1 to 0·3 mm diameter to give twin jets, breaking at a distance of about 1 cm from the capillary exits. This modification proved to be most popular and satisfactory for all the alkali metals, so that elaborate devices for simultaneously removing drops of amalgam from twin dropping electrodes[23] were no longer needed.

Knobel[24] investigated the thermodynamic properties of potassium hydroxide solutions with the aid of amalgam and hydrogen electrodes, and found that the cells were best-behaved when the concentrations of the amalgam and solution were matched. Steady e.m.f.s were registered when dilute amalgams (0·002 wt % K)

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[19] (*a*) R. W. Millar, *J. Amer. Chem. Soc.*, 1927, **49**, 3003; (*b*) H. E. Bent and J. H. Hildebrand, *J. Amer. Chem. Soc.*, 1927, **49**, 3011.

[20] (*a*) H. E. Bent and E. Swift, *J. Amer. Chem. Soc.*, 1936, **58**, 2216; (*b*) V. L. Balashov and B. P. Kiselev, *Zhur. priklad. Khim.*, 1965, **38**, 1616.

[21] M. H. Armbruster and J. L. Crenshaw, *J. Amer. Chem. Soc.*, 1934, **55**, 2525.

[22] D. A. MacInnes and J. A. Beattie, *J. Amer. Chem. Soc.*, 1920, **42**, 1117.

[23] T. W. Richards and J. B. Conant, *J. Amer. Chem. Soc.*, 1922, **44**, 601.

[24] M. Knobel, *J. Amer. Chem. Soc.*, 1923, **45**, 70.

were used in conjunction with dilute solutions (0·001—0·01m-KOH) and the more concentrated amalgams (0·02—0·20 wt % K) with solutions of higher concentration (>0·1m-KOH). For the higher hydroxide concentrations (0·02m) the results are subject to a small correction for the transfer of water from one side of the 'double' cell to the other during the cell reaction.[2,6]

Harned[2,25] found the effects of amalgam hydrolysis on the composition of the solutions to be negligibly small, and greatly simplified the procedure by dispensing with the cumbersome arrangements needed for the continuous renewal of the electrolyte solutions. In most systems 0·01 and 0·10 wt % amalgams gave highly stable, reproducible potentials (±0·05 mV), but for lithum[26] an amalgam concentration in the range 0·003—0·005 wt % was stipulated, and in this case the maximum stability was only ±0·3 mV. The Harned school experienced difficulties, not previously encountered, when working with electrolyte solutions of molality less than 0·05. This may have been a result of their preference for relatively concentrated amalgams, or it is attributable to their rejection of flowing solutions.[8,22] In these experiments, as in other work with class 'A' electrodes, the possibility cannot be ruled out that some errors originated from the incomplete removal of oxygen.

The work of Åkerlöf[27] marks an important extension of Harned's work into the study of mixed solvents. A modification, (V), of the 'double' cell enabled the

$$\underset{}{\text{Ag–AgCl}} \;\Big|\; \underset{\text{(solvent)}}{\text{MCl}, m} \;\Big|\; \underset{\substack{\text{(dilute}\\\text{amalgam)}}}{\text{M(Hg)}} \;\Big|\; \underset{\text{(water)}}{\text{MCl}, m} \;\Big|\; \text{AgCl–Ag} \qquad \text{(V)}$$

activity coefficients of MCl in methanol–water mixtures to be accurately determined. At the time the results were not fully exploited; it was left to Feakins and Watson,[28] some thirty years later, to calculate values of ΔG_t°, the free-energy change produced when an electrolyte in its molar standard state in water undergoes a hypothetical transfer to a corresponding standard state in another solvent. In the past decade cells of this type have been used to determine ΔG_t° for the transfers of alkali-metal chlorides from water to methanol,[29] to ethylene glycol,[29] and to various dioxan–water and methanol–water mixtures.[30] Studies[31,32] of the transfers of alkali-metal chlorides from water to deuterium oxide throw light on the structural properties of the ions in these solvents. In one instance[31] they yielded unstable e.m.f. readings; the values of ΔG_t° are therefore only approxi-

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[25] H. S. Harned, *J. Amer. Chem. Soc.*, 1925, **47**, 676; 1929, **51**, 416.

[26] H. S. Harned and F. E. Swindells, *J. Amer. Chem. Soc.*, 1926, **48**, 126.

[27] G. Åkerlöf, *J. Amer. Chem. Soc.*, 1930, **52**, 2353.

[28] D. Feakins and P. Watson, *J. Chem. Soc.*, 1963, 4734.

[29] (*a*) J. K. Gladden and J. C. Fanning, *J. Amer. Chem. Soc.*, 1961, **65**, 76; (*b*) B. Scrosati, S. Schiavo, and G. Pecci, *Ricerca Sci.*, 1968, **38**, 467.

[30] (*a*) A. L. Andrews, H. P. Bennetto, D. Feakins, K. G. Lawrence, and R. P. T. Tomkins, *J. Chem. Soc.* (*A*), 1968, 1486; (*b*) H. P. Bennetto, D. Feakins, and K. G. Lawrence, *J. Chem. Soc.*, (*A*), 1968, 1493; (*c*) H. P. Bennetto and D. Feakins, in ref. 17, p. 235.

[31] P. Salomaa and V. Aalto, *Acta Chem. Scand.*, 1966, **20**, 2035.

[32] (*a*) J. Greyson, *J. Phys. Chem.*, 1962, **66**, 2218; (*b*) J. Greyson and H. Snell, *J. Phys. Chem.*, 1969, **73**, 3208.

mate, but are preferred to the figures from cells which made use of ion-exchange membranes[32] in lieu of amalgam electrodes.

Class 'A' Electrodes: Alkaline-earth Metals. Amalgam electrodes of these metals have not been extensively developed. They were first studied by Tamele,[33a] who measured the electrode potential of calcium, and by Lucasse,[33b] who determined the activity coefficients of calcium, strontium, and barium chlorides in water. The method of downward delivery of amalgam from fine capillaries was ineffective, and 'U' shaped tubes were used to give a slow delivery. The results of the latter study are of uncertain accuracy, and the fair agreement with data from a vapour pressure method is misleading. Fosbinder[34] found it necessary to continually scrape the surface of a calcium amalgam in order to remove a crust of calcium hydroxide. To inhibit hydrolysis he resorted to filling the upturned tips of the capillaries and the bottom of the cell, where spent amalgam collected, with a layer of paraffin oil; an interfacial layer of solution presumably conducted sufficient electricity for e.m.f.s to be measured. In a later study[35] a saturated barium amalgam, stored under paraffin oil, was pipetted into the cell. It was claimed that rigorous exclusion of oxygen was unnecessary. The e.m.f. reached a constant value after the amalgam had been in contact with aqueous barium chloride solution for five hours, but this surprising stability could well have resulted from a protective layer of oil carried over from the storage vessel. Soon afterwards, Harned and Mason[36] managed to obtain the activity coefficients of barium hydroxide from measurements with hydrogen reference electrodes in cells of type (III). They apparently had less trouble than their predecessors, and attained a reasonable precision of around ±0·2 mV.

Scatchard and Tefft[37] made a careful and definitive study of the behaviour of the calcium amalgam electrode in 'single' cells. They investigated the variation of e.m.f. with the rate of amalgam flow, getting best results with delivery tubes of 7 mm bore. Even then the e.m.f. altered by 2·5 mV when the rate was increased from a steady drop to a dribble, and consistent readings were acquired only with a 'double' cell in which the rates in the two sides of the cell were matched. The experiments must have been extremely laborious, since large supplies of amalgam were surely needed to maintain a flowing stream for any adequate length of time.

Recently[38] the conditions of large diameter delivery tubes have been simulated with capillaries of 0·1 to 0·4 mm bore, dipping into small cups 6 mm deep and 6 mm in diameter. The amalgam spills over from a pool at a rate determined by the diameter of the capillary tubes. For the barium electrode e.m.f. readings which are both stable and reproducible to ±0·2 mV are obtained with relative

[33] (*a*) M. Tamele, *J. Phys. Chem.*, 1924, **28**, 502; (*b*) W. W. Lucasse, *J. Amer. Chem. Soc.*, 1925, **47**, 743.

[34] R. J. Fosbinder, *J. Amer. Chem. Soc.*, 1929, **51**, 1345.

[35] E. A. Tippetts and P. E. Newton, *J. Amer. Chem. Soc.*, 1934, **56**, 1675.

[36] H. S. Harned and C. M. Mason, *J. Amer. Chem. Soc.*, 1932, **54**, 1439.

[37] G. Scatchard and R. F. Tefft, *J. Amer. Chem. Soc.*, 1930, **52**, 2272.

[38] D. Feakins and A. R. Willmott, *J. Chem. Soc.* (*A*), 1970, 3121.

ease. The strontium electrode rarely shows a comparable stability, and is reproducible only to ±0·5 mV. With a calcium amalgam any real measure of stability seems to be completely absent and, in spite of recent optimism,[39] it must be concluded that the conditions for the reversible operation of the calcium electrode are rather elusive.

The possibility that a magnesium electrode will operate reversibly in aqueous solution is remote, though some evidence[40] suggests that it might work in a non-aqueous medium. Magnesium, strontium, and barium amalgam electrodes have been used in cells containing anhydrous methanol;[40] the results appear to be promising but are difficult to assess and must await confirmation.

Class 'B' Electrodes. This group includes the electrodes of zinc, cadmium, lead, copper, thallium, and indium, mostly used in the form of stationary pools of amalgam. The amalgams are relatively stable, so that with care the activity of a metal in an amalgam can be accurately controlled. Dilute amalgams have been little used in 'single' cells of type (I), preference being given to the saturated or two-phase version. This consists of a solution of the metal in mercury, in isothermal equilibrium with a solution of mercury in the metal. (The activity of the metal is constant by definition.) The transfer of a saturated amalgam to a cell is made difficult by the need to exclude oxygen; this can be done, however, by delivering a heated amalgam to the cell, where it forms two phases on cooling. Thermodynamic properties of the amalgams and of the solutions have been studied with cells of types (VI) and (I) respectively.

Following the introduction by von Helmholtz[41] of amalgam concentration cells (type IV), several workers established the excellent reversible behaviour of pool electrodes.[42,43] The cadmium electrode[43] especially seems to be capable of better than microvolt precision. These cells have since found an important application in thermodynamic studies of metallic solutions, a subject which is comprehensively reviewed elsewhere.[44] Other studies with zinc, cadmium, and lead electrodes in a cell of type (I) have focussed attention on the association of the metal halides in solution, and are described in detail by Harned and Owen[2] (see also Section 3A).

There are few definitive studies of the copper amalgam electrode. Neilsen and Brown,[45] working with the cell (VI), claimed a precision of 0·1 mV for the

$$\underset{\substack{\text{(two-phase}\\ \text{amalgam)}}}{\text{Cu(Hg)}} \;\Big|\; \text{CuSO}_4,\, m \;\Big|\; \text{HgSO}_4\text{–Hg} \qquad \text{(VI)}$$

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[39] J. N. Butler, *J. Electroanalyt. Chem. Interfacial Electrochem.*, 1968, **17**, 309; *cf.* the recent careful work of T. Mussini and A. Pagella, *J. Chem. and Eng. Data*, 1971, **16**, 49.

[40] V. V. Aleksandrov and N. Van-Mao, *Soviet Electrochem.*, 1965, **1**, 254.

[41] H. V. Helmholtz, *Sitzungber. Akad. Berlin*, 1882, **22**, 825.

[42] G. Meyer, *Z. phys. Chem.*, 1891, **7**, 477.

[43] G. A. Hulett and R. E. Dehury, *J. Amer. Chem. Soc.*, 1908, **30**, 1805.

[44] (*a*) J. Chipman, *Discuss. Faraday Soc.*, 1948, **4**, 23; (*b*) J. H. Hildebrand and R. L. Scott, 'The Solubility of Nonelectrolytes', Dover, New York, 1964, Chap. 19.

[45] R. F. Nielsen and D. J. Brown, *J. Amer. Chem. Soc.*, 1927, **49**, 2423.

amalgam electrodes. Their value for the standard potential of copper, 0·3502 V, was several millivolts higher than that obtained by Lewis and Lacey[46] from measurements with an electrode of the metal in contact with finely divided copper. Further investigations[47] with the amalgam electrode failed to reproduce the earlier figures, and at present there is poor agreement between the values for the activity coefficients of aqueous copper sulphate.[48] More research is needed in view of the reported formation of a green precipitate on the amalgam surface.

Following the extensive and precise studies of electrode concentration cells by Richards and his co-workers, the thallium amalgam electrode[49] was used to investigate thallous chloride solutions in cells of type (I). The electrolyte appears to be incompletely dissociated in dilute aqueous solution.

The electrodes so far mentioned are electrodes 'of the first kind'.[6] Amalgam electrodes 'of the second kind' have the form

$$\begin{array}{ll} \text{M(Hg)} \;-\; & \text{MX} \\ \text{(saturated)} & \text{(solid)} \end{array} \qquad \text{(where X = halide or other anion)}$$

and have also been widely studied. The cell (VII), for example, has been used

$$\begin{array}{llllll} \text{Pb(Hg)}- & \text{PbSO}_4 & | & \text{ZnSO}_4 & | & \text{Zn(Hg)} \\ \text{(saturated} & \text{(solid)} & & \text{(aq.)} & & \text{(saturated} \\ \text{amalgam)} & & & & & \text{amalgam)} \end{array} \qquad \text{(VII)}$$

in a determination of the electrode potential of zinc.[6] The thallium amalgam–thallous chloride couple[50] seems to work satisfactorily as a chloride-sensitive electrode in non-aqueous media,[51] although it is impracticable in dilute aqueous solutions because of the relatively high solubility of the thallous salt. The most widely used electrode of this kind is still the cadmium amalgam–cadmium sulphate electrode found in the Weston cell (VIII).[52]

$$\begin{array}{llllll} \text{Cd(Hg)}- & \text{CdSO}_4 & | & \text{CdSO}_4 & | & \text{Hg}_2\text{SO}_4\text{–Hg} \\ \text{(saturated} & \text{(solid)} & & \text{(Sat. aq.} & & \text{(solid)} \\ \text{amalgam)} & & & \text{solution)} & & \end{array} \qquad \text{(VIII)}$$

2. Experimental Methods

In this section we indicate how precise e.m.f. measurements can be made with

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[46] G. N. Lewis and W. N. Lacey, *J. Amer. Chem. Soc.*, 1914, **36,** 804.

[47] (*a*) F. H. Getman, *J. Phys. Chem.*, 1930, **34,** 1454; (*b*) E. Newberry, *J. Amer. Chem. Soc.*, 1929, **51,** 1315; (*c*) F. Müller and H. Reuther, *Z. Electrochem.*, 1941, **47,** 640; 1942, **48,** 682.

[48] D. S. Dhillon and R. L. Blokhra, *Indian J. Chem.*, 1967, **5,** 340.

[49] (*a*) T. W. Richards and F. Daniels, *J. Amer. Chem. Soc.*, 1919, **41,** 1732; (*b*) I. A. Cowperthwaite, V. K. La Mer, and J. J. Barksdale, *J. Amer. Chem. Soc.*, 1934, **46,** 544.

[50] (*a*) C. Knüppfer, *Z. phys. Chem.*, 1898, **26,** 255; (*b*) T. Mussini and P. Longhi, *Ricerca Sci.*, 1965, **A8,** 1352.

[51] (*a*) D. R. Cogley and J. N. Butler, *J. Electrochem. Soc.*, 1966, **113,** 1074; (*b*) M. Salomon, *J. Phys. Chem.*, 1969, **73,** 3299; *J. Electrochem. Soc.*, 1969, **116,** 1392; (*c*) W. H. Smyrl and C. W. Tobias, *J. Electrochem. Soc.*, 1968, **115,** 33.

[52] G. W. Vinal, D. N. Craig, and L. H. Brickwedde, *Trans. Electrochem. Soc.*, 1935, **68,** 139.

most of the cells mentioned earlier. The methods are based on recent extensive investigations,[30,38,53] but other procedures[39,54,55] may be just as effective. Certain aspects are dealt with in detail, for it is felt that the lack of practical information in the literature has contributed to the general disrepute of amalgam electrodes.

A. E.m.f. Measurements.—These are conveniently made with a high precision digital voltmeter. A typical instrument of this kind has an input impedance of $>25\,000$ MΩ and a nominal accuracy of $\pm 0{\cdot}01$ mV or better. When coupled to a data-logger and recorder, it is extremely versatile and ideally suited for reading the outputs of electrochemical cells. Such a system is particularly valuable for studying cells with flowing amalgam electrodes. It is interesting to note the advantages which an automatic recording technique holds over conventional potentiometry:[56]

(i) The elements of subjective error, inherent in potentiometry, are removed.
(ii) The operator is free to manipulate the cells during the measurements.
(iii) Readings can be recorded frequently, say once a second, so that (*a*) variations in e.m.f. can be closely followed (the approach to equilibrium, the equilibrium value itself, and any subsequent departure from the equilibrium which might occur, *e.g.* as a result of solvolysis of an amalgam electrode, are easily recognised); (*b*) an equilibrium e.m.f. value can be determined with a minimum expenditure of amalgam.
(iv) Fluctuations in e.m.f. of the order of 0·03 mV, which are integrated by a potentiometer, are resolved with the voltmeter.

We consider the criterion for a successful cell to be that the e.m.f. at equilibrium should not show fluctuations of more than one or two tenths of a millivolt. If the departure from the average value is greater than this, there is no guarantee that the true equilibrium e.m.f. lies even within the limits of the fluctuations. Under favourable conditions an accuracy of $\pm 0{\cdot}01$ mV is attainable.

B. Cell Design.—A suitable apparatus is illustrated in Figure 1. The cell combines many features of various early cells, but the compartments are somewhat smaller, having a solution capacity of less than 30 ml. Facilities are provided for constructing different cells of the types (I), (III), or (V) (see Section 1), for altering the form of the amalgam electrode, *i.e.* streaming, spilling, or pool, and for changing the electrolyte solutions. Successive measurements can be carried out on a series of solutions of different electrolytic concentrations without dismantling the assembly.

The choice of cell is largely determined by the requirements of the system under study. Measurements with amalgams of the alkali and alkaline-earth

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[53] H. P. Bennetto, A. R. Willmott, P. J. Voice, Ph.D. Theses, 1967, 1969, 1970 respectively, Birkbeck College, University of London, and J. P. Lorimer, unpublished results.

[54] P. A. Rock and R. E. Powell, *Inorg. Chem.*, 1964, **3**, 1993.

[55] P. J. Reilly and R. H. Stokes, *Austral. J. Chem.*, 1970, **23**, 1477; see also J. H. Austin, R. A. Matheson, and H. N. Parton in 'Structure of Electrolyte Solutions', ed. W. J. Hamer, J. Wiley, New York, 1959, chap. 24.

[56] D. Feakins, K. G. Lawrence, and R. P. T. Tomkins, *J. Chem. Soc.* (*A*), 1967, 753.

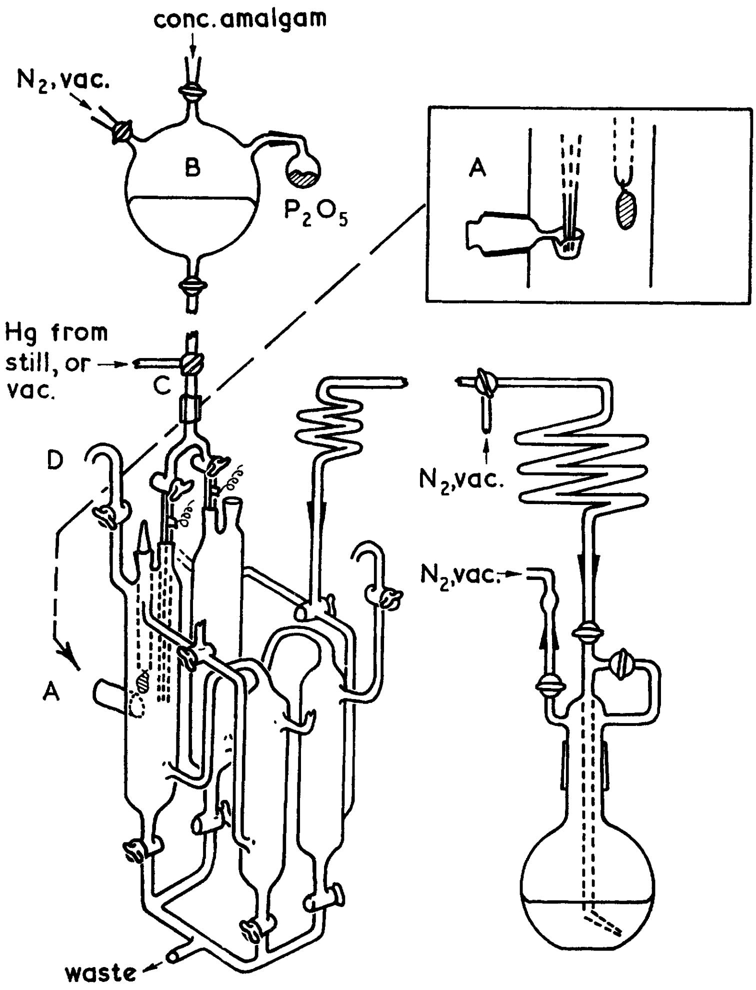

Figure 1 *Cell, with amalgam supply system. Inset: capillary-in-cup assembly.*

metals are best made in 'double' cells (types III and V) in order to avoid the difficulty of maintaining a reproducible metal activity in the amalgam. Cell (I) is suitable for measurements with class 'B' amalgams, but 'double' cells may sometimes be used to advantage with dilute amalgams. A special case arises when the electrolyte exhibits a significant degree of ion-association (see Section 3A) when cells of type (I) are used and the activity of the dilute amalgam must be standardised by reference either to a saturated amalgam electrode or another amalgam of known metal activity. The treatment of similar results from a 'double' cell is inconvenient because of difficulties in the computing of the Debye–Hückel terms.

C. Electrodes.—Streaming electrodes for the 'double' cells are formed with twin capillaries of identical bore. The rate of delivery of the amalgam depends mainly on the capillary radius (rate $\propto r^4$) although the level of amalgam in the supply reservoir and the length of the capillary also have some effect. From 0·2 mm capillaries the rate is sufficiently slow for the accumulation of spent amalgam at the bottom of the cell to present little problem, and for an equilibrium e.m.f. to be determined with a reasonably small volume of amalgam, normally less than 50 ml.

With a barium amalgam, the cells work well when the delivery is modified to give a spilling electrode. Small cups are inserted into the cell compartments (at A in Figure 1). The tips of the capillaries seat well inside the cups, which each have a lip for directing the amalgam spill away from the reference electrode. With a strontium amalgam, measurements are accessible if smaller capillaries replace those of 0·2 mm diameter in a 'capillary-in-cup' assembly. This arrangement also provides for stationary pool electrodes, a variation which is excellent for cadmium; the equilibrium e.m.f.s of two cells, one having a spilling electrode and the other a pool electrode, have been found to agree to within 0·01 mV.[57] Agreement is not as good in the case of a zinc amalgam.[37] The optimum conditions have not yet been established for this electrode, nor for the dilute amalgam electrode of lead.[58] It does seem probable, however, that pool electrodes will perform well for these metals if oxygen is excluded.

The amalgams are generally prepared in high concentration by electrolysis or by direct addition of the metal to mercury. The stock amalgams can then be diluted with pure mercury to the desired concentration ($\sim$0·005 m) and stored under dry nitrogen (B in Figure 1). Dilute amalgam is then delivered to the cell when required.

D. Method.—A typical procedure is described for a single cell of type (I); a 'double' cell demands a similar routine for both sides of the cell. The cell is positioned in a bath at a fixed temperature and, for results of the highest precision with flowing electrodes, arrangements are made for bringing the amalgam to the same temperature before it enters the cell. This ensures that thermal equilibrium is maintained throughout an experiment. A little vacuum grease on all taps and joints prevents ingress of moisture without otherwise affecting the measurements.

The cell is first fitted with an appropriate capillary assembly and a reference electrode, normally a silver–silver-halide electrode. It is then attached to a delivery line (C in Figure 1), which supplies amalgam, mercury, or nitrogen, or connects to a vacuum line. The apparatus is twice evacuated and flushed with nitrogen, and by ordered manipulation of taps the amalgam electrode assembly

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[57] D. Feakins, A. R. Willmott, and A. S. Willmott, unpublished results.

[58] W. R. Carmody, *J. Amer. Chem. Soc.*, 1936, **58**, 2624.

is filled either with amalgam, for pool electrodes, or with mercury for flowing electrodes. The cell is now ready to receive the electrolyte solution. This is twice boiled under reduced pressure and saturated with an inert gas, *e.g.* nitrogen, before the flask containing it is connected to the appropriate delivery line. The solution is then gently pumped to the cell and at the same time dry nitrogen in the cell escapes from the outlets at D. Finally, nitrogen is slowly bubbled through the pre-saturators and cell compartments.

If the cell has a pool electrode, readings may be taken immediately after the cell has been filled. The e.m.f. usually reaches a steady value within 90 min, or less if the reference electrode has been pre-soaked in the cell solution or in a solution from a previous measurement. With a flowing electrode, two hours should be allowed for the reference electrode to reach equilibrium in the first measurement, and one hour for subsequent measurements in a series. The taps in the amalgam delivery line are then opened to supply amalgam to the cell, and the e.m.f. is monitored automatically. During measurements with streaming electrodes, nitrogen is by-passed over the solution in the cell compartment, so that the fine stream of amalgam is not disturbed. The e.m.f., recorded at 5—10 s intervals, is at first erratic as amalgam displaces mercury from the capillary, but within a few minutes reaches a steady value which may be maintained for up to twenty minutes. Spent amalgam is periodically drawn off from the base of the cell.

For saving time and effort a series of experiments is particularly valuable. With alkali-metal amalgams, pure mercury must be re-admitted to the capillary after each experiment so as to displace the amalgam remaining there. The cell is then emptied, washed, and refilled with a fresh solution in preparation for the next measurement. This procedure is not recommended in the case of an alkaline-earth amalgam, for the cell should be disconnected after each measurement to remove a solid layer of hydroxide from the inside of the cup. It is very practicable with class 'B' amalgams, which can often be left in the capillary between experiments. A series may be completed in a (long!) day after which the cell is detached for cleaning. Before and after a series of measurements it is important to compare the potential of the reference electrode with that of a duplicate. The change recorded is normally less than 0·1 mV and the work is then deemed satisfactory.

3. Discussion

The interpretation of data obtained from galvanic cells is well described in standard texts, but the examples which are cited are often restricted to the dependence of the e.m.f. upon electrolyte or electrode concentrations, or on the temperature. We now draw attention to some less well-known aspects of e.m.f. work which are nevertheless equally as important, and in Section C discuss some other topics which could be profitably developed.

A. Ion-Association.—Figure 2 shows the results of two independent investigations of the aqueous cadmium chloride system. E is the e.m.f. of a cell of type (I),

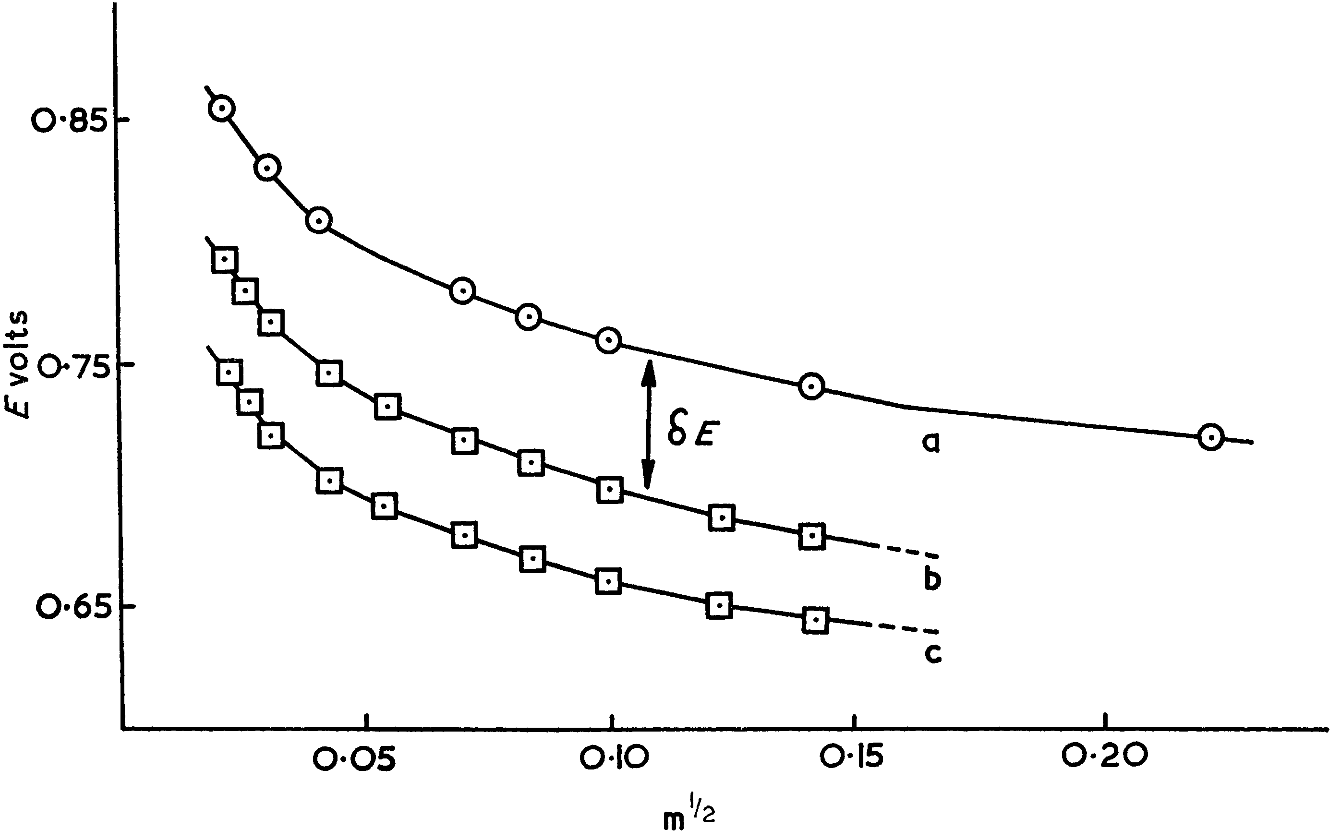

Figure 2 *E.m.f. readings for the cell* Cd(Hg) | CdCl$_2$ | AgCl–Ag
(amalgam) (solvent)
(a) *data for water, ref.* 59. (*two-phase amalgam*) (b) *data for water, ref.* 57. (***dilute amalgam***)
(c) *data for* 40 *wt* % *methanol, ref.* 57 (*dilute amalgam*)

given in one case[59] with a two-phase cadmium amalgam electrode, and in the other[57] with a dilute amalgam electrode. As the Figure shows, the measurements could be extended to very low concentrations of electrolyte in both studies. The voltage difference δE is consistent to within 0·1 mV, indicating the good agreement between the two sets of data; it measures the difference in the activities of the dilute and concentrated amalgams, and is equivalent to the e.m.f. of a cell of type (IV).

The Debye–Hückel theory fails to accommodate the raw data because appreciable concentrations of complex ions are present. When the chloride ion concentration is high, $CdCl_2$ and $CdCl_3^-$ are among the species formed in the solution, but in dilute aqueous solutions (<0·04 m) $CdCl^+$ and the free ions are the predominant ones. Allowance for the ion-association can be made, however, with the aid of iterative procedures, so as to give the best fit to a Debye–Hückel extrapolation function. The values of both the standard e.m.f. of the cell and K_d^o, the dissociation constant of $CdCl^+$, can then be determined. When methanol is added to the solution, K_d^o decreases from its value of $0{\cdot}11_{(4)}$ in water to a value $0{\cdot}0027_{(4)}$ in a 40 wt % methanol–water mixture, confirming the general picture from a polarographic study.[60] The value of K_d^o in water itself is in excellent agreement with the value $0{\cdot}011_{(8)}$ from recent measurements[55] with the cell (IX).

$$\mathrm{Cd(Hg)}\ \big|\ \mathrm{CdCl_2}(m_1),\ \mathrm{NaCl}(m_2)\ \big|\ \mathrm{AgCl\text{–}Ag} \qquad \text{(IX)}$$

Reilly and Stokes[55] have reviewed the results from the many studies of the aqueous system. They comment that 'the degree of complexing varies with the author'; thus although the agreement between values of K_d^o at zero ionic strength is good, the dissociation constants of the higher associated species remain uncertain. Inevitably, K_d is somewhat dependent on the precise form of the Debye–Hückel expression for the activity coefficient of the ionised fraction of the electrolyte.

Precise determinations of such dissociation constants are valuable not only for the intrinsic interest of the work,[61] but also because of its possible applications. Ion-pairing is sometimes relevant to the kinetics and mechanism of ionic reactions,[62] and it is useful to have an independent check on a particular value of K_d, though values are often assumed or calculated. For $CdCl^+$ a value $K_d = 0{\cdot}03$ has been inferred from ultrasonic absorption measurements,[63] which give rate constants for the conversion of 'outer-sphere' to 'inner-sphere' complexes. It is known that K_d increases with increasing electrolyte concentration, and the value $K_d = 0{\cdot}03$ from the relaxation studies (at high ionic strengths) is therefore not unreasonable.

[59] H. S. Harned and M. E. Fitzgerald, *J. Amer. Chem. Soc.*, 1936, **58**, 2624.

[60] I. Tur'yan and B. P. Zhantalai, *Russian J. Inorg. Chem.*, 1960, **5**, 848.

[61] J. E. Prue, *J. Chem. Educ.*, 1969, **46**, 12; 'Ionic Equilibria', Pergamon Press, Oxford, 1966, Chap. 10.

[62] F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions', John Wiley, New York, 1967, 2nd Edn.

[63] M. Eigen, *Pure Appl. Chem.*, 1963, **6**, 97.

B. The Solvation of Ions.—The practical advantages of 'double' cells have already been mentioned. Moreover, when ion–solvent interactions are the paramount interest, more information is gleaned from measurements with cells of type (V) than from 'single' cells. In the latter case the standard electrode potential (and the values of ΔG_{solv}, the conventional free energy of solvation calculated from them) vary greatly according to the ions taking part in the cell reaction, but are relatively insensitive to the nature of the solvent. In contrast, the standard e.m.f. ΔE_t° of the 'double' cell gives information about the ions in the dissolved state only, in terms of ΔG_t°, the standard free energy of transfer (see Section 1B). It is becoming generally recognised[15—17] that ΔG_t° is better than ΔG_{solv} as a probe for the ion–solvent interactions: in other words, to understand the rôle of the solvent it is the solvent itself which must be varied. This point is borne out in the following example.

Table 2 *Standard e.m.f.s* E°_{solv} *(in volts) for the cell*

$$\text{M} \;|\; \underset{\text{(solvent)}}{\text{MX}\,(m)} \;|\; \text{AgX–Ag}$$

M	X	$E^{\circ}_{H_2O}$*	E°_{NMF}†	ΔE_t°	$\Delta G_t^{\circ} = -nF\Delta E_t^{\circ}$ kJ mol^{-1}
Li	Cl	3·267	$3{\cdot}123_{(7)}$	−0·143	13·8
Na	Cl	$2{\cdot}935_{(3)}$	$2{\cdot}806_{(7)}$	$-0{\cdot}128_{(6)}$	12·4
K	Cl	3·146	$3{\cdot}021_{(2)}$	−0·125	12·1
Na	Br	$2{\cdot}785_{(1)}$	$2{\cdot}713_{(5)}$	$-0{\cdot}071_{(6)}$	6·9

* Values of $E^{\circ}_{H_2O}$ from the sum of the standard potentials of the metal (ref. 66) and the Ag–AgX electrode (refs. 1, 2, 3)
† Values of E°_{NMF} from the work of Luksha and Criss (ref. 65)

Table 2 lists the standard e.m.f.s of single cells containing alkali-metal chlorides in water and *N*-methylformamide (NMF),[65] together with values of ΔG_t° ($H_2O \rightarrow$ NMF) calculated from them. According to simple electrostatic theory[64] the transfer of any pair of ions from water to NMF is expected to be favoured, increasingly so the smaller the ion, because of the high dielectric constant of NMF (183) relative to that of water (78). The complete failure of this approach is evident in the positive sign of ΔG_t° and the nature of its dependence on the cationic radius, which is also the opposite of that predicted. These findings can only be explained by taking into account the short-range interactions between the ions and the solvent molecules.[28]

The conventional free energies of solvation calculated from $E^{\circ}_{H_2O}$ and E°_{NMF} could be accommodated by a modified Born equation in which adjustments are made to the values of the ionic radii. The apparent agreement of theory and experiment would, however, be misleading, for the values of ΔG_{solv} are

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[64] M. Born, *Z. Physik.*, 1920, **1**, 45.
[65] (*a*) E. Luksha and C. M. Criss, *J. Phys. Chem.*, 1966, **70**, 1496; (*b*) C. M. Criss, R. P. Held, and E. Luksha, *J. Phys. Chem.*, 1968, **72**, 2970.

dominated by gas-phase energies; they are relatively insensitive to a change of solvent, and can give us little detailed information about the ion–solvent interactions.* No such criticism can be levelled at the free energies of transfer. Indeed there is revealed in this case a striking difference between the cationic and anionic dependences of ΔG_t° on the ionic size. The transfer shows a marked difference between the chloride and bromide ions, a common feature of anionic solvation.

Table 2 highlights the need for precision in the e.m.f. measurements. The accuracy of ΔG_t° is limited particularly by $E^\circ_{H_2O}$ which is reliable, at best, to about a millivolt[66] (values for caesium are excluded as $E^\circ_{H_2O}$ is extremely uncertain). An analysis of the dependence of ΔG_t° on the size or on the electronic structure of the ions must wait on results of a greater accuracy, which could be attained with relative ease in e.m.f. measurements with cells of the type (V). In recent years there has been much interest[15–17] in the correlation of solvent effects on the kinetics and thermodynamics of ionic reactions with ionic free energies in solution.[67] For instance, the change of ionic free energy with a change of solvent may be expressed[67] in terms of a 'solvent activity coefficient', γ^s; single-ion values of γ^s are derived from approximate values of ΔG_t° by extra-thermodynamic assumptions. This method is promising, in that large solvation effects on kinetic behaviour can usually be predicted with confidence, but here too there is a need for greater accuracy in γ^s if this approach is to eventually give a more than semi-quantitative picture.

Similar standards of precision are desirable also for the transfer parameters ΔH_t° and ΔS_t°, analogous to ΔG_t°. Criss and Luksha[65] have been able to use their results from amalgam cells in a study of the partial molal ionic entropies of solution of simple salts in eight different solvents. Their results indicate that the entropy of transfer of a pair of ions from one solvent to another does not depend greatly on the pair of ions transferred. This important finding suggests that if the ions have a structural order in water,[68] then a similar order must exist in the other solvents; the modifications of liquid structure near an ion are apparently not unique to water.[69]

C. General.—The literature reveals many instances of e.m.f. studies where data are inconsistent and the experiments would bear repeating. The activity coefficients of sodium chloride, for example, appear to change curiously between 40 and 60 °C. The results at the lower temperature are from e.m.f. work (cell III), those above 60 °C from osmotic coefficients;[2] the discrepancy between them is unresolved, and has been hailed as possible evidence of a thermal anomaly[70] in the region 40—60 °C. Even in aqueous solutions there are still

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* See D. Feakins, ref. 17, p. 243.

[66] (*a*) W. M. Latimer, 'Oxidation Potentials', Prentice-Hall, New York, 1952, 2nd Edn.; (*b*) B. E. Conway, 'Electrochemical Data', Elsevier, Amsterdam, 1952.

[67] A. J. Parker, *Chem. Rev.*, 1969, **69**, 1.

[68] H. S. Frank and W.-Y. Wen, *Discuss. Faraday Soc.*, 1957, No. 24, p. 133.

[69] H. G. Hertz, *Angew. Chem.*, 1970, **9**, 124.

[76] W. Drost-Hansen, *Ann. New York Acad. Sci.*, 1965, **125**, 471.

many new systems to be explored. Rock[71] has discussed the design of cells without liquid junctions, some containing amalgam electrodes of the 'second kind'; thermodynamic studies of solutions containing ions such as $[Fe(CN)_6]^{3-}$ are feasible.[54]

Cells having amalgam pool electrodes would be suitable for high-pressure studies, which in principle can yield ionic partial molar volumes,[14,15,17] and metals other than mercury can support amalgam electrodes for work at high temperatures, where fused salts may form the electrolyte.[72] Many electrodes, including those which are difficult to operate in water, appear to function well in purified non-aqueous solvents, and await further application (see Table 1, ref. *g* and ref. *l*, in which some recent work is comprehensively reviewed).

Some of the amalgam electrodes may in time be replaced by the equivalent solid-state or glass electrodes ('ion-selective' electrodes[73]). These are more convenient to use but, despite their impact on analytical chemistry, have not been widely tested in precise comparisons with other electrodes. Glass electrodes sensitive to sodium ions give results that are in general agreement with those from amalgam cells, but are less precise.[74] They are in error at low concentrations, and do not afford accurate extrapolations to standard e.m.f. values. Both amalgam electrodes and glass electrodes have recently been used to study mixed electrolyte solutions.[13,74] The results agree with the predictions of the Brønsted–Guggenheim specific interaction theory,[75] and Harned's additivity rule[2] is confirmed. It is also found that a sodium amalgam electrode tends to behave irreversibly when in contact with a solution containing the closely-related ions Na^+ and K^+.

An amalgam, unused as yet in electrochemistry, is that of the ammonium ion.[76] It decomposes within minutes of preparation, puffing up spectacularly to release ammonia and hydrogen. There is a chance, a slight one, that under suitable conditions the quaternary ammonium amalgams[76,77] could provide electrodes reversible to the quaternary ammonium ions, which have lately attracted much attention.[16,17]

4 Conclusion

That after sixty years the standard electrode potentials of the alkali metals are still known only with millivolt accuracy, and that other metal electrode potentials are even less certain,[66] must be considered unsatisfactory. It is to be hoped that the compass of work will be extended to include a wider range of solvents, temperatures, pressures, and concentrations of electrolyte, so that structural theories of electrolyte solutions can be more broadly tested. This extension

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[71] P. A. Rock, *J. Chem. Educ.*, 1970, **47**, 683.

[72] N. W. Taylor, *J. Amer. Chem. Soc.*, 1923, **45**, 2865.

[73] (*a*) A. K. Covington, *Chem. in Britain*, 1969, **5**, 388; (*b*) R. E. Durst, ed., 'Ion-Selective Electrodes', NBS Special Publication 314, Washington, 1969.

[74] J. N. Butler, P. T. Hsu, and R. Huston, *J. Phys. Chem.*, 1970, **74**, 2976 and refs. therein.

[75] E. A. Guggenheim and J. C. Turgeon, *Trans. Faraday Soc.*, 1955, **51**, 747.

[76] G. B. Porter, *J. Chem. Soc.*, 1954, 760.

[77] J. D. Littlehails and B. J. Woodhall, *Discuss. Faraday Soc.*, 1968, No. 45, p. 187.

should now be possible with the help of modern techniques, which eliminate much of the tedium of the work.

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