CXIV.—*Observations on Liquid Boundaries and Diffusion Potentials.*

By SYDNEY RAYMOND CARTER and FREDERICK MEASHAM LEA.

DURING an investigation (J., 1925, **127**, 487, 499) on the *E.M.F.* of systems involving potassium chloride and concentrated acid solutions, it was necessary to set up chains of connecting solutions having potentials which would be readily reproducible and be subject to the minimum fluctuation with time.

Various types of liquid junctions were studied, therefore, and the main results are collected in this paper. Thus in making up the oxidation cell (Pt)|Oxid. salts, xN-HCl|(*a*) . . . (*b*) N-KCl,Hg_2Cl_2|Hg or (Pt)|Oxid. salts, xN-HCl|(*a*) . . . (*b*) N-H_2SO_4,Hg_2SO_4|Hg the chain xN-HCl|(*a*) . . . (*b*)|N-KCl or xN-HCl|(*a*) . . . (*b*)|N-H_2SO_4 may be completed by connecting the points (*a*) and (*b*) in one of the following ways, (i) directly, (ii) through N-hydrochloric acid, (iii) through saturated potassium chloride solution.

A. *Acid–Acid Boundaries of the Type* xN-HCl|N-HCl.—This type of boundary occurred in scheme (ii), and two modes of formation of this boundary will be described.

(1) The connecting tube from (*a*) carries a tap and dips into hydrochloric acid of the same concentration (xN-HCl). Connexion is made to a vessel containing N-hydrochloric acid by means of an inverted **U** tube filled with N-hydrochloric acid and, as in other cases, plugged at the ends with filter-paper. It makes but little difference, however (about 0·001 volt), if this connecting tube be filled with the xN-hydrochloric acid. Diffusion potentials at boundaries so set up show little fluctuation with time.

(2) If the open end of the tube with tap from (*a*) is immersed directly in N-hydrochloric acid, complete mixing of the two acid solutions takes place as far as the tap and it is here that the actual liquid junction occurs. If the xN-hydrochloric acid be $5N$, this method gives diffusion potentials differing by about 0·006 volt from those obtained by method A (1).

In the work on the cupric–cuprous potentials, as well as that on the diffusion potentials, method A (1) was invariably employed.

B. *Acid–Salt Boundaries of the Type* HCl|KCl.—(1) Direct connexion between xN-hydrochloric acid and N-potassium chloride is equivalent to scheme (i) and leads to considerable fluctuations of *E.M.F.* when the value of x is high.

(2) An intermediate solution of N-hydrochloric acid between the

two solutions in (1) gives the combination xN-HCl|N-HCl|N-KCl, which is scheme (ii).

The xN-HCl|N-HCl boundary has already been described, and the N-HCl|N-KCl boundary is made as follows. The connecting tube is filled with N-potassium chloride, in which case the diffusion potential is constant to about 0·0010 to 0·0015 volt on standing. If the connecting tube be filled with N-hydrochloric acid, a divergence of about 0·002 volt from the above is observed. Our practice has been to use the potassium chloride solution.

Methods B (1) and (2) give values which differ considerably for the total diffusion potential between xN-hydrochloric acid and N-potassium chloride. For very strong hydrochloric acid solutions ($10N$—$11N$) this difference may amount to as much as 0·020 volt.

C. *Saturated Potassium Chloride Solutions.*—The interposition of a saturated potassium chloride solution between xN-hydrochloric acid and N-potassium chloride reduces the diffusion potential, but does not eliminate it completely for strong hydrochloric acid solutions. For concentrations of hydrochloric acid up to N, the conclusion of various workers is that saturated potassium chloride has no diffusion potential against the hydrochloric acid; but this does not hold for stronger hydrochloric acid solutions. Thus between $9N$-hydrochloric acid and N-potassium chloride the interposition of a saturated potassium chloride solution reduces the diffusion potential from approximately 0·090 volt to 0·050 volt. A direct connexion xN-HCl|N-KCl always gives a lower diffusion potential than that obtained when an intermediate N-hydrochloric acid is introduced; for $9N$-hydrochloric acid it is about 0·015 volt lower.

For $9N$-hydrochloric acid the approximate values of the following diffusion potentials are: xN-HCl|N-KCl, 0·090 volt; xN-HCl|N-HCl|N-KCl, 0·105 volt; xN-HCl|Sat. KCl|N-KCl, 0·050 volt.

D. *Liquid Junctions with Sulphuric Acid of the Type* xN-HCl|N-H_2SO_4.—Very little difference is observed if direct connexion be made between the xN-hydrochloric acid and N-sulphuric acid or N-hydrochloric acid be interposed, giving the xN-HCl|N-HCl|N-H_2SO_4 combination.

Variation of Diffusion Potentials.—For corresponding concentrations, an acid|salt boundary shows more variation with time than an acid|acid boundary. The latter, even for N-hydrochloric acid against $10N$-hydrochloric acid, shows little variation, in general not more than 0·001 volt and usually less. If, however, the xN-hydrochloric acid contains a high concentration of some salt in solution, then the xN-HCl|N-HCl boundary may show a fluctuation of several millivolts.

In making potential measurements, the most consistent results were obtained when fresh boundaries were used wherever possible, and this is the experience of other workers.

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UNIVERSITY OF BIRMINGHAM,
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