

Det Kgl. Danske Videnskabernes Selskab.

Mathematisk-fysiske Meddelelser. **X**, 8.

STUDIES OF CELLS WITH LIQUID-
LIQUID JUNCTIONS

PART III.

CELLS WITH A BRIDGE OF CONCEN-
TRATED POTASSIUM CHLORIDE

BY

A. UNMACK AND E. A. GUGGENHEIM



KØBENHAVN

HOVEDKOMMISSIONÆR: ANDR. FRED. HØST & SØN, KGL. HOF-BOGHANDEL

BIANCO LUNOS BOGTRYKKERI A/S

1930

In a recent paper BJERRUM and UNMACK¹ have published the results of measurements, extending over several years of numerous cells of the type



in which the solution S was either dilute hydrochloric acid, dilute alkali or a Sørensen buffer mixture, in each case made up to various total salt concentrations by the addition of alkaline chloride. The reproducibility of the E. M. F. measured varied from one or two tenths of a millivolt for most of the buffer solutions to about half a millivolt for some of the solutions of hydrochloric acid. For the latter cells this uncertainty was undoubtedly due to the non-reproducibility of the liquid-liquid junction. As, at the time these measurements were made, it was not known what factors determined the stability of the E. M. F. of cells with liquid-liquid junctions, all measurements were for the sake of consistency made as quickly as possible after making the junction.

Since the completion of these measurements a study has been made in the same laboratory by GUGGENHEIM² of the conditions for both the reproducibility and the stability of cells with liquid-liquid junctions. In these measure-

¹ BJERRUM and UNMACK, Kgl. Danske Vid. Selsk., Mat.-fys. Med. **9** (1) 1929.

² GUGGENHEIM J. A. C. S. **52** 1315 1930.

ments it was found convenient to use a calomel electrode in tenth normal hydrochloric acid and no special precautions were taken for the exclusion of air. For this reason the absolute values of the E.M.F.s measured are uncertain, although the conclusions regarding stability and reproducibility hold good because the electrodes used agreed amongst themselves.

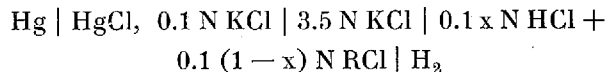
It seemed to us that it would be of interest to make some new measurements of the type of BJERRUM and UNMACK's in the light of GUGGENHEIM's conclusions and so find out to what extent, if any, the E. M. F. values are effected.

In BJERRUM and UNMACK's measurements the junction was made by dipping the side-tube of the hydrogen electrode vessel into a U-tube containing 3.5 N KCl, and in order to avoid contamination of the bridge solution, the liquid levels were so adjusted that on opening the tap between the electrode and the side-tube there was always an upward flow of liquid into the side-tube. Thus the junction was within the side-tube and not at its tip and so there was a fair approach to the cylindrical symmetry which GUGGENHEIM found to be such an important factor contributing not only to reproducibility but also to stability. In the present measurements the junction was made in the same manner except that extra care was exercised to get the junction about half way up the side-tube, so as more perfectly to obtain the desired cylindrical symmetry. It was found that the initial values of the E. M. F. agreed with those previously recorded by BJERRUM and UNMACK within their experimental uncertainty of several tenths of a millivolt, occasionally as much as half a millivolt. The E. M. F. however generally changed to the extent of a few tenths of a millivolt in the first fifteen to thirty minutes but always reached a steady

value reproducible to about one tenth of a millivolt and stable for a whole day. The sharper the initial junction the quicker was the steady state reached; the theoretical explanation of this has been given by GUGGENHEIM. In a large number of cases the junction was also made by means of the apparatus designed by GUGGENHEIM for making the junction which he calls of the "free diffusion type". For details of the various types of reproducible junctions the original paper must be referred to.¹ In all such cases the steady values obtained by the two arrangements agreed to within about one tenth of a millivolt. It is these stable reproducible values that are here recorded, as opposed to the initial values previously recorded by BJERRUM and UNMACK. It thus appears possible to obtain reproducibility and stability with a considerably simpler arrangement than GUGGENHEIM'S.

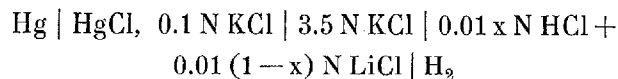
By way of contrast we made a few measurements with junctions in which cylindrical symmetry was deliberately avoided by making the junction where a narrow tube joined a wider one. There was no sign of stability and the E. M. F. values recorded were erratic to the extent of several millivolts.

The cells chosen for study may conveniently be divided into two classes A and B. The former were all of the type



where R denotes an alkali metal and x was varied from 0.05 to 1.00. This series was particularly suitable for comparison with BJERRUM and UNMACK'S measurements and for determining the reproducibility and stability of the liquid-liquid junction. The cells of class B were all of the type

¹ GUGGENHEIM J. A. C. S. 52 1315 1930.



were x was varied from 0.10 to 1.00. In these cells we may safely assume that any uncertainty due to the liquid-liquid junction will be no greater than in the type A cells and the accuracy is determined by the care in the preparation of the hydrogen electrode solutions. The primary object of these latter measurements was so far as possible to compare the observed values with those calculated theoretically. Why a similar calculation for cells of class A is not possible to the same degree of accuracy will be clear later.

For the hydrogen electrode solutions ordinary distilled water was used in the type A experiments, but conductivity water (specific conductivity less than 10^{-6} ohm $^{-1}$ cms $^{-1}$) for all the type B experiments. In all cases the hydrogen ion concentration was checked by titration. The hydrogen was prepared by electrolysis of a potassium hydroxide solution and freed from oxygen by passage over palladium at 300° C.

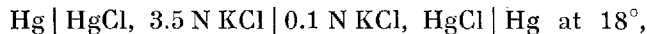
The calomel electrodes were prepared according to the directions of GJALDBAER¹, the calomel being made by precipitation from mercurous nitrate and hydrochloric acid. The potassium chloride was fused before weighing and the chloride content of the 0.1 N KCl solution checked gravimetrically. Ordinary distilled water was used.

We always had in use about ten calomel electrodes prepared at various times. The greatest deviation found at any time between two electrodes was about 0.3 millivolts. There was no definite systematic difference between freshly prepared and old electrodes. All measurements were there-

¹ GJALDBAER, Kgl. Danske Vid. Selsk., Mat-fys. Med. 5 (9) 1924.

fore corrected to correspond to the mean of the calomel electrodes. The probable error due to the calomel electrodes is thus not more than ± 0.15 millivolts.

We also prepared a number of Hg|HgCl, 3.5 N KCl electrodes and in agreement with BJERRUM and UNMACK found these to be less stable and slightly less reproducible than the Hg|HgCl, 0.1 N KCl electrodes. The E. M. F. found for the combination



as long as the left hand electrode was fairly newly prepared, was 83.1 ± 0.2 mv as compared with the values 83.13 found by GJALDBAEK¹ and 83.1 mv found by BJERRUM and UNMACK². The electrode vessels and electrical apparatus were the same as those used in the previous measurements³. All the measurements were made at 18.0° C. Incidentally it was discovered that the temperature regulation of the air-thermostat previously used by GUGGENHEIM was defective. It was by remedying this that we reduced the erratic fluctuations of the "free diffusion" measurements from about ± 0.25 mv to about ± 0.1 mv.⁴

The results of our measurements are recorded in table I. The first column gives the composition of the hydrogen electrode solution "S" and the second the value of E, the measured E. M. F. corrected to a hydrogen pressure of one atmosphere and to the mean of the calomel electrodes. Each cell was set up about five to ten times and readings taken over a period varying from two to twenty four

¹ loc. cit.

² loc. cit.

³ BJERRUM and UNMACK loc. cit.

⁴ cf. GUGGENHEIM loc. cit.

Table I.
 Hg | HgCl, 0.1 N KCl | 3.5 N KCl | Solution S | H₂ at 18° C.

Composition of S in moles litre ⁻¹	E and R. M. S. deviation in m. v.	$E - \frac{RT}{F} \log_e \frac{C_H}{C^+}$ in m. v.	$E_D + E_S$ in m. v.	E_D in m. v.	E_S in m. v.	$\frac{RT}{F} \log_e \frac{f_{\text{HCl}}^{(S)}}{f_{\text{HCl}}^{(\text{HCl})}}$ in m. v.	$2 \frac{RT}{F} \log_e \frac{f_{\text{HCl}}^{(S)}}{f_{\text{HCl}}^{(\text{HCl})}} - E_S$ in m. v.
Type A:							
.1000 HCl.....	-400.35 ± 0.25 ¹	-342.60	0.00	0.00	0.00	0.00	0.00
.0750 HCl + .0250 LiCl .	-406.95 ± 0.10	-342.00	+0.60	+1.10	-0.50	-0.01	..
.0500 HCl + .0500 LiCl .	-416.30 ± 0.07	-341.20	+1.40	+2.35	-0.95	-0.02	..
.0250 HCl + .0750 LiCl .	-432.60 ± 0.10	-340.10	+2.50	+3.80	-1.30	-0.03	..
.0100 HCl + .0900 LiCl .	-454.95 ± 0.10	-339.45	+3.15	+4.80	-1.65	-0.04	..
.0050 HCl + .0950 LiCl .	-471.95 ± 0.15	-339.10	+3.50	+5.20	-1.70	-0.04	..
.100 LiCl ²	-338.85	+3.75	+5.60	-1.85	-0.04	+1.77
.0500 HCl + .0500 NaCl.	-416.40 ± 0.10	-341.30	+1.30	+2.20	-0.90	-0.12	..
.0100 HCl + .0900 NaCl.	-455.30 ± 0.12	-339.80	+2.80	+4.55	-1.75	-0.22	..
.1000 NaCl ²	-339.35	+3.25	+5.30	-2.05	-0.24	+1.57

.0500 HCl + .0500 KCl ...	-416.85 ± 0.09	-341.75	+ 0.85	+ 2.10	- 1.25	- 0.25	..
.0100 HCl + .0900 KCl ...	-456.20 ± 0.07	-340.70	+ 1.90	+ 4.05	- 2.15	- 0.44	..
.1000 KCl ²	-340.40	+ 2.20	+ 4.70	- 2.50	- 0.49	+ 1.52
.0100 HCl + .0900 CsCl ...	-456.95 ± 0.08	-341.45	+ 1.15	+ 4.05	- 2.90	- 0.76	..
.1000 CsCl ²	-341.25	+ 1.35	+ 4.70	- 3.35	- 0.85	+ 1.65
Type B:							
.01000 HCl	-455.50 ± 0.07	-340.00	0.00	0.00	0.00
.00700 HCl + .00300 LiCl	-464.25 ± 0.05	-339.85	+ 0.15	+ 0.25	- 0.10
.00500 HCl + .00500 LiCl	-472.15 ± 0.08	-339.30	+ 0.70	+ 0.45	+ 0.25
.00100 HCl + .00900 LiCl	-511.50 ± 0.05	-338.30	+ 1.70	+ 0.80	+ 0.90
.01000 LiCl ²	-338.00	+ 2.00	+ 0.85	+ 1.15

¹ The cell where the solution S was .100 N HCl was measured at two periods several months apart. The values during each period agreed to within 0.10 millivolts. The somewhat larger R. M. S. deviation recorded is therefore presumably due to a change of 0.1 to 0.2 m. v. in the mean of the calomel electrodes during the interval and is not due to any difficulty in obtaining a satisfactory liquid-liquid junction.

² Values obtained by a slight extrapolation, vide Fig. 1.

hours. The values recorded are the mean of all readings, only excluding those in the first few minutes before the steady state was reached. The total number of readings for each cell varied from about 25 to about 150. The root mean square deviation of the individual readings from the mean is also recorded; the root mean square deviation, rarely exceeds one tenth of a millivolt. The values in the third column are obtained by subtracting from the measured E. M. F. $57.74 \log_{10} C_{H^+}$ millivolts¹ representing the effect of the hydrogen ion concentration on the E. M. F., salt effects being for the moment neglected. That the values in this column are not the same for all the cells is due partly to the liquid-liquid junction potential and partly to salt effects. These effects will be discussed in detail below and the remaining columns of the table explained. In Fig. 1 the values of $E - \frac{RT}{F} \log_e C_{H^+}$ have been plotted against the ratio of the hydrogen ion concentration to total cation

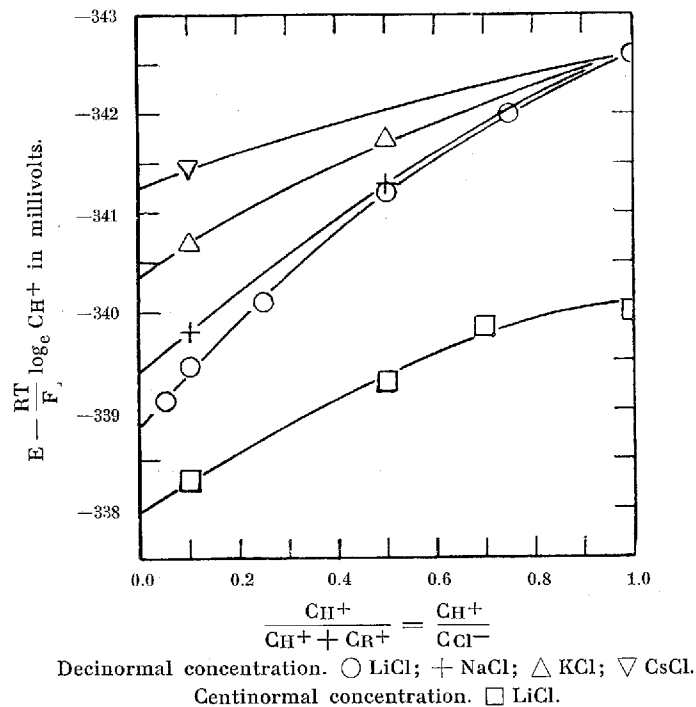
¹ The value 57.74×10^{-3} Int. Volts for $\frac{RT}{F} \log_e 10$ at 18°C. is obtained from the fundamental constants given in the Handbuch der Physik, Vol. II. In the International Critical Tables there is a slight inconsistency in the data:

- (1) 1.11800 mg Ag deposited per Int. Coulombs(a),
- (2) Atomic weight of Ag 107.880,
- (3) 1 Faraday = 96507 Int. Coulombs(a).

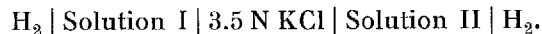
According to (1) and (2) 1 Faraday = 96494 Int. Coulombs(a). If we accept (1) and (2) and reject (3) the value obtained for $\frac{RT}{F} \log_e 10$ from the data of the International Critical Tables is identical with that given above. The true value of the fourth significant figure is not quite certain but for measurements, such as ours, confined to solutions containing HCl its effect on all computations fortunately corresponds to at most a tenth of a millivolt. Its effect is however appreciable on quantities obtained by combining measurements in alkaline solutions with measurements in acid solutions. For example the value of K_{H_2O} can be affected by about 1 to 2%.

or anion concentration. The regularity of the plots confirms the absence of any erratic fluctuations of more than 0.1 millivolts.

For a thermodynamic discussion of the significance of the E. M. F.s measured it is convenient to consider two of



the cells balanced against each other, the result being equivalent to the cell



It is well known that, if all mean activity coefficients were unity, the E. M. F. E' of such a cell containing only univalent ions could be written as

$$E' = E_{E1} + E_D \quad (1)$$

where E_{EI} denotes the difference in the "ideal" electrode potentials and E_D the "ideal" diffusion potential, these being given by

$$E_{EI} = \frac{RT}{F} \log_e \frac{C_{H^+}^{II}}{C_{H^+}^I} \quad (2)$$

and

$$E_D = -\frac{RT}{F} \int_I^{II} \sum_+ t_R d \log_e C_R + \frac{RT}{F} \int_I^{II} \sum_- t_X d \log_e C_X \quad (3)$$

where R denotes the gas constant, T the absolute temperature, F the Faraday, C_R , C_X the concentrations of each cation R and each anion X and t_R , t_X their transport numbers. \sum_+ , \sum_- denote summation for all cations or for all anions respectively. The integrals are to be evaluated through both transition layers from left to right. If the junctions are of the "continuous mixture type" the contribution of each junction to E_D is given by HENDERSON's formula.¹ Even if the junction is of the "free diffusion type", HENDERSON's formula will for the cells in question probably be accurate to within a few tenths of a millivolt.² Actually of course the mean activity coefficients of salts even in quite dilute solutions differ markedly from unity and so equation (1) is not applicable. It has been shown elsewhere that E' is given by the thermodynamically exact formula³

$$E' = E_{EI} + E_D + E_S \quad (4)$$

where E_{EI} and E_D are defined by equations (2) and (3), while E_S which may be called „the salt effect potential", is given by

¹ HENDERSON *Z. Ph. Ch.* **59** 118 1907.

² GUGGENHEIM *loc. cit.*

³ GUGGENHEIM *J. Ph. Ch.* **34** 1930.

$$E_S = \frac{RT}{F} \int_I^{II} \sum_+ 2t_R d \log_e \frac{f_{HX}}{f_{RX}} + \frac{RT}{F} \int_I^{II} \sum_- 2t_X d \log_e f_{HX} \quad (5)$$

f_{RX} denoting the mean activity coefficient of the salt RX . It will be seen that E_S is a function of the mean activity coefficients of all the salts present throughout the cell and of the transport numbers of all the ions at all parts of the cell. It is not possible physically to split up E_S between the electrodes on the one hand and the liquid-liquid junction on the other. This important fact is closely related to the principle, first unambiguously stated by TAYLOR, that the conception of an individual ionic activity coefficient is thermodynamically undefined.¹

It is not unusual to compute hydrogen ion activities by the formula

$$E' = E_{El} + \frac{RT}{F} \log_e \frac{f_{H^+}^{II}}{f_{H^+}^I} \quad (6.1)$$

or alternatively by the formula

$$E' = E_{El} + E_D + \frac{RT}{F} \log_e \frac{f_{H^+}^{II}}{f_{H^+}^I}. \quad (6.2)$$

These are equivalent respectively to two different conventional definitions of f_{H^+} , namely

$$\frac{RT}{F} \log_e \frac{f_{H^+}^{II}}{f_{H^+}^I} = E_D + E_S \quad (7.1)$$

and

$$\frac{RT}{F} \log_e \frac{f_{H^+}^{II}}{f_{H^+}^I} = E_S. \quad (7.2)$$

As pointed out by BJERRUM and UNMACK the system (6.1), (7.1) has the advantage over (6.2), (7.2) that, according to

¹ TAYLOR J. Ph. Ch. **31** 1478 1927. Cf. GUGGENHEIM J. Ph. Ch. **33** 842 1929.

the former but not the latter, when both the electrode solutions become infinitely dilute the ratio $f_{\text{H}^+}^{\text{II}}/f_{\text{H}^+}^{\text{I}}$ becomes unity. They therefore make use of the conventional definition (6.2) [or (7.2)].¹ Even with this definition, however, the individual ionic activity coefficients will not behave similarly to mean activity coefficients. Thus, as an approximation, setting the mean activity coefficients of all the salts at each part of the cell as equal, that is to say

$$f_{\text{RX}} = f_{\text{HX}} = f_{\pm} \quad (8)$$

(5) becomes

$$E_s = \frac{RT}{F} \int_{\text{I}}^{\text{II}} \sum 2t_x d \log_e f_{\pm} \quad (9)$$

and so according to (7.2), in general

$$\frac{f_{\text{H}^+}^{\text{II}}}{f_{\text{H}^+}^{\text{I}}} \neq \frac{f_{\pm}^{\text{II}}}{f_{\pm}^{\text{I}}}, \quad (10)$$

unless by chance $\sum t_x = \frac{1}{2}$ throughout the cell, that is to say unless the mean mobility of the cations is equal to that of the anions.]

In order to compare these conclusions with our experimental results let solution II be the same as solutions S and let solution I be the solution of HCl, without added salt, at the same total concentration. The values of $E_D + E_s$ in the fourth column of table I are then obtained by subtracting from those in the third column the corresponding values for the solutions containing only acid. In column five are given the [values of E_D computed by HENDERSON'S formula, the use of which involves two inexact assump-

¹ BJERRUM and UNMACK loc. cit.

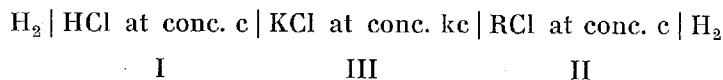
tions: firstly that the transition layers are of the "continuous mixture type" and secondly that from one part of the cell to another the mobilities of the various ions vary in a common ratio. Each assumption may involve an error of a few tenths of a millivolt but not more. Finally by subtracting these values from those in the fourth column the values of E_S recorded in the sixth column are obtained. According to the conventional definition (6.2) or (7.2) these are the values of $\frac{RT}{F} \log_e f_{H^+}^{(S)} / f_{H^+}^{(HCl)}$. For the sake of contrast we give in the seventh column for the type A experiments, the values of $\frac{RT}{F} \log_e f_{RCl}^{(S)} / f_{RCl}^{(HCl)}$ where $f_{RCl}^{(S)} / f_{RCl}^{(HCl)}$ is the ratio of the mean activity coefficient of the uni-univalent chloride RCl in the solution S and in 0.1 N HCl. That this ratio is the same for all uni-valent cations R there is abundant evidence both theoretical and experimental.¹ The values actually recorded are those obtained for HCl and for $[Co(NO_2)(SCN)(NH_3)_4]Cl$ in the very accurate experiments of GÜNTEMBERG.² It is clear that the conventional f_{H^+} ratios deviate from unity considerably more than the corresponding f_{RCl} ratios. This is particularly striking in the case of the solutions containing LiCl, for the ratio $f_{HCl}^{(LiCl)} / f_{HCl}^{(HCl)}$ differs from unity by less than 0.2 % while the conventional $f_{H^+}^{(LiCl)} / f_{H^+}^{(HCl)}$ differs from unity by 7 %. In this case the whole deviation of this ratio from unity or of E_S from zero is due to the difference in the mobilities of the H^+ and Li^+ ions and not at all to any difference in the thermodynamic properties of HCl and LiCl.

¹ BRØNSTED J. A. C. S. **44** 877 1922. BRØNSTED J. A. C. S. **45** 2898 1923. GÜNTEMBERG Z. Ph. Ch. **123** 199 1926. GUGGENHEIM Rep. of Scandinavian Science Congress Copenhagen 1929 p. 298.

² GÜNTEMBERG Z. Ph. Ch. **123** 199 1926.

It is unfortunately not practicable to compute E_S theoretically with any certainty for the type A experiments owing to our ignorance of the activity coefficients of HCl and RCl in the more concentrated parts of the transition layers. Such a computation is however possible with at least a moderate degree of accuracy in the case of the type B experiments, these having in fact been designed with this end in view. We shall now show how this computation can be carried out.

Let us consider the cell



We may, if desired, suppose that the RCl solution contains a trace of HCl to make the value of C_{H^+} definite. This value of C_{H^+} will of course determine E_{E1} but will clearly have no effect on E_S which according to (5) is given by

$$\begin{aligned} E_S = & \frac{RT}{F} \int_I^{II} 2t_R d \log_e \frac{f_{HCl}}{f_{RCl}} + \frac{RT}{F} \int_I^{II} 2t_K d \log_e \frac{f_{HCl}}{f_{KCl}} \\ & + \frac{RT}{F} \int_I^{II} 2t_{Cl} d \log_e f_{HCl} \end{aligned} \quad (11)$$

To evaluate these integrals we have to make use of certain approximations regarding the mean activity coefficients and mobilities. We therefore assume firstly that the mean activity coefficients of all chlorides are equal at each part of the cell, secondly that the ratios of the mobilities of the various ions are the same throughout the cell and thirdly that we

may treat the transition layers as of the "continuous mixture type". The first assumption, which may be written

$$f_{\text{HCl}} = f_{\text{RCl}} = f_{\text{KCl}} = f_{\pm}, \quad (12)$$

is certainly sufficiently accurate in the dilute parts of each transition layer and it is these that chiefly contribute to the integrals. For this very reason we shall eventually find that we may dispense with this assumption in the more concentrated parts of the transition layers, where it is least accurate. The first two assumptions are also involved in the application of HENDERSON'S formula to the evaluation of E_D .

By the first assumption (11) simplifies to

$$E_S = \frac{RT}{F} \int_I^{II} 2t_{\text{Cl}} d \log_e f_{\pm}. \quad (13)$$

According to the second assumption, since the mobilities of K^+ and Cl^- are so nearly equal, we may write

$$u_{\text{K}^+} = u_{\text{Cl}^-} = \frac{u_{\text{H}^+}}{\lambda} = \frac{u_{\text{R}^+}}{\lambda'}, \quad (14)$$

where u denotes a mobility and λ, λ' are constant throughout the cell. The third assumption then leads to

$$\begin{aligned} E_S = & \frac{RT}{F} \int_{x=0}^{x=1} 2 \frac{(1-x) + kx}{(\lambda+1)(1-x) + 2kx} d \log_e f \\ & + \frac{RT}{F} \int_{x=1}^{x=0} 2 \frac{(1-x) + kx}{(\lambda'+1)(1-x) + 2kx} d \log_e f' \end{aligned} \quad (15)$$

where f is the value of f_{\pm} for a mixture of $(1-x)$ parts of the electrode solution I and x parts of the bridge solution

III, while f' is the value of f_{\pm} for a similar mixture of solution II with the bridge solution III. In so far as f_{\pm} depends only on the total salt concentration f and f' are identical for equal values of x . Now it may be possible (this must be verified a posteriori) to split up the range of each integral into two parts $0 \leq x \leq x_1$ and $x_1 \leq x \leq 1$, such that in the first f_{\pm} is some simple function of the total concentration and in the second the HCl or RCl present is negligible compared with the great excess of KCl and so t_{Cl^-} is practically $\frac{1}{2}$. The contribution of the latter range to the first integral in (15) will thus approximately cancel its contribution to the second integral and there remains

$$E_s = \frac{RT}{F} \int_{x=0}^{x=x_1} 2 \frac{(1-x) + kx}{(\lambda+1)(1-x) + 2kx} d \log_e f$$

$$- \frac{RT}{F} \int_{x=0}^{x=x_1} 2 \frac{(1-x) + kx}{(\lambda'+1)(1-x) + 2kx} d \log_e f. \quad (16)$$

Let y^2c denote the total concentration of a solution consisting of $(1-x)$ parts of either electrode solution and x parts of bridge solution, so that

$$y^2 = (1-x) + kx \quad \text{or} \quad x = \frac{y^2-1}{k-1} \quad (17)$$

and let y_1 be the value of y corresponding to $x = x_1$. Let us now suppose that for all concentration y^2c less than y_1^2c the mean activity coefficient can be expressed in the form¹

$$\log_e f_{\pm} = -\alpha \sqrt{y^2c} + \beta y^2c \quad (18.1)$$

¹ BRØNSTED Trans. Far. Soc. 23 416 1927.

$$\text{or} \quad d \log_e f_{\pm} = -\alpha \sqrt{c} dy + \beta c 2y dy. \quad (18.2)$$

Then substituting from (17) and (18.2) into (16) we get

$$E_s = \frac{RT}{F} \int_1^{y_1} 2 \frac{(k-1) y^2 (-\alpha \sqrt{c} + 2\beta cy)}{k(\lambda-1) + (2k-\lambda-1)y^2} dy - \quad (19)$$

$$- \frac{RT}{F} \int_1^{y_1} 2 \frac{(k-1) y^2 (-\alpha \sqrt{c} + 2\beta cy)}{k(\lambda'-1) + (2k-\lambda'-1)y^2} dy.$$

As $\lambda > 1$ whilst we shall want to set $\lambda' < 1$, we express the two integrals in different forms to avoid imaginary quantities. We obtain finally

$$\begin{aligned} \frac{FE_s}{RT} = & \frac{2(k-1)}{2k-\lambda-1} \left[-\alpha \sqrt{c} \left\{ y_1 - 1 \right. \right. \\ & - \sqrt{\frac{k(\lambda-1)}{2k-\lambda-1}} \left(\arctan \sqrt{\frac{2k-\lambda-1}{k(\lambda-1)}} y_1 \right. \\ & \left. \left. - \arctan \sqrt{\frac{2k-\lambda-1}{k(\lambda-1)}} \right) \right\} + \beta c \left\{ y_1^2 - 1 \right. \\ & \left. \left. - \frac{k(\lambda-1)}{2k-\lambda-1} \log_e \frac{(2k-\lambda-1)y_1^2 + k(\lambda-1)}{(2k-\lambda-1) + k(\lambda-1)} \right\} \right] \quad (20.1) \\ & - \frac{2(k-1)}{2k-\lambda'-1} \left[-\alpha \sqrt{c} \left\{ y_1 - 1 \right. \right. \\ & - \sqrt{\frac{k(1-\lambda')}{2k-\lambda'-1}} \left(\operatorname{arctanh} \sqrt{\frac{2k-\lambda'-1}{k(1-\lambda')}} y_1 \right. \\ & \left. \left. - \operatorname{arctanh} \sqrt{\frac{2k-\lambda'-1}{k(1-\lambda')}} \right) \right\} + \beta c \left\{ y_1^2 - 1 \right. \\ & \left. \left. + \frac{k(1-\lambda')}{2k-\lambda'-1} \log_e \frac{(2k-\lambda'-1)y_1^2 - k(1-\lambda')}{(2k-\lambda'-1) - k(1-\lambda')} \right\} \right]. \end{aligned}$$

In the case that λ , λ' and unity are negligible compared with k , this simplifies to

$$\begin{aligned}
\frac{FE_S}{RT} = & \alpha \sqrt{c} \sqrt{\frac{\lambda-1}{2}} \left\{ \arctan \sqrt{\frac{2}{\lambda-1}} y_1 \right. \\
& - \left. \arctan \sqrt{\frac{2}{\lambda-1}} \right\} - \beta c \frac{\lambda-1}{2} \log_e \frac{2y_1^2 + \lambda - 1}{\lambda + 1} \\
& - \alpha \sqrt{c} \sqrt{\frac{1-\lambda'}{2}} \left\{ \operatorname{arctanh} \sqrt{\frac{2}{1-\lambda'}} y_1 \right. \\
& - \left. \operatorname{arctanh} \sqrt{\frac{2}{1-\lambda'}} \right\} - \beta c \frac{1-\lambda'}{2} \log_e \frac{2y_1^2 + \lambda' - 1}{\lambda' + 1}.
\end{aligned} \tag{20.2}$$

We shall now apply these formulae to the cell



Here $k = 350$, $\lambda = 5.0$, $\lambda' = 0.5$ so that the shorter formula (20.2) is almost as accurate as (20.1); we have however used the latter. We assign to α the value $0.50/\log_e 10$ corresponding to the DEBYE-HÜCKEL limiting law¹. For $\beta \log_e 10$ we have chosen the value 0.50 for the following reason. We shall find that almost the whole contribution to the integral comes from those parts of the transition layers where the concentration is less than 0.1 N. Up to this concentration the activity coefficients are given quite accurately by formulae of the type (18.1) with the following values of $\beta \log_e 10$: 0.40 for KCl in KCl, 0.60 for HCl or LiCl in HCl or LiCl and 0.50 for HCl or LiCl in KCl. Hence we have clearly to use a value between 0.40 and 0.60 and we have chosen the mean of these. Fortunately a difference of 0.10 in $\beta \log_e 10$ affects the final result by only 0.2 millivolts.

Finally remains the question what value to choose for y_1 and the verification of our assumption that practically the whole contribution to the integral comes from the

¹ DEBYE and HÜCKEL Ph. Z. **21** 185 1923.

Table II.

Computation of E_s for the cell $H_2 | 0.01 N HCl | 3.5 N KCl | 0.01 N LiCl | H_2$ at $18^\circ C$.

Value of y_1	3.0	3.5	4.0	6.0	7.0	8.5	$\sqrt{350}$
Conc at limit of integral = $.01 y_1^2$09	.12	.16	.36	.49	.72	3.50
t_{Cl^-} at limit of integral on HCl side411	.417	.447	.476	.483	.489	.500
t_{Cl^-} at limit of integral on LiCl side514	.510	.507	.503	.502	.501	.500
Term in E_s proportional to $\alpha \sqrt{c}$ in mv	+ 2.65	+ 2.92	+ 3.14	+ 3.64	+ 3.79	+ 3.95	+ 4.37
Term in E_s proportional to βc in mv	- 0.93	- 1.11	- 1.26	- 1.75	- 1.95	- 2.20	- 3.22
E_s in millivolts	+ 1.72	+ 1.81	+ 1.88	+ 1.89	+ 1.84	+ 1.75	+ 1.15

range $1 \leq y \leq y_1$ while the remaining range $y_1 \leq y \leq \sqrt{k}$ may be neglected. This is best tested by computing with a series of values of y_1 and seeing to what extent the computed value of E_s is independent of the value chosen for y_1 . The results of this computation are given in Table II, which explains itself. We see that the computed value of E_s does not vary more than two tenths of a millivolt in a range of $y_1^2 c$ values extending from 0.1 to 0.7. It must however be admitted that even at the concentration 0.7 N the transport number of the chloride ion still differs appreciably from $1/2$. For the concentration 3.50 N the formula assumed for f_{\pm} will be very inaccurate so that we must not attach too great importance to the calculation with $y_1^2 = 350$. However the result in this case also is only 0.6 mv less than that for the concentration $y_1^2 c = 0.7$. It therefore seems fairly safe to take as the computed value 1.5 ± 0.4 mv. As the experimental value, obtained by a slight extrapolation (see Fig. 1 and Table I), is 1.2 m. v. the agreement is

quite as good as could be expected in view of the unavoidably approximate nature of the whole computation. Expressed in terms of the conventional f_{H^+} scale we may say that for the deviation of $f_{\text{H}^+}^{(\text{LiCl})} / f_{\text{H}^+}^{(\text{HCl})}$ from unity experiment gives 5 % and computation 5 to 7 %. It is especially satisfactory that our computation is able to account for the greatness of this deviation, which is here due entirely to the difference in mobilities of H^+ and Li^+ , since at 0.01 N concentration all typical uni-univalent salts have the same mean activity coefficient at least to within a fraction of 1 %. For HCl and LiCl this equality in fact holds even at 0.1 N concentration.

Considering the difficulty of computing E_s for the type B cells, it seems hopeless to attempt a similar computation for the type A cells. It is however perhaps worth while trying to explain why E_s has opposite signs in the two cases. Now it will be observed that formula (20.2) is independent of k , except in so far as the value to be used for y_1 depends on k . For $c = 0.01$ and $k = 350$ formulae (20.2) and (20.1), as already mentioned, are practically indistinguishable. For $c = 0.1$ and $k = 35$ the two formulae will differ somewhat more and both may be very inaccurate. We shall nevertheless apply (20.2) to the cell



merely to obtain rough qualitative information of the behaviour of E_s . We see then that the term in E_s proportional to α/\sqrt{c} will be about 3 times greater than it was for the corresponding type B cell while the term proportional to βc will be about 10 times greater. Looking then at the figures given for these two terms in table II and remembering the extremely approximate nature of our

estimate, we find it at least reasonable to expect the negative βc term to be numerically greater than the α/\sqrt{c} term, in which case the sign of E_S will be reversed.

Remembering that according to BJERRUM and UNMACK'S conventional definition of f_{H^+} the values of E_S in the sixth column of table I may be regarded as values of $\frac{RT}{F} \log_e f_{H^+}^{(S)}/f_{H^+}^{(HCl)}$, by subtracting these from twice the values in the seventh column we obtain the corresponding conventional values of $\frac{RT}{F} \log_e f_{Cl^-}^{(S)}/f_{Cl^-}^{(HCl)}$, given in the eighth column. It is noteworthy that the values of f_{Cl^-} are the same within 1 % in the solutions of pure LiCl, NaCl, KCl and CsCl, but differ by no less than 6 to 7 % from its value in the solution of pure HCl. This again is in accordance with the fact that these conventional ionic activity coefficients are not purely thermodynamic functions, but depend largely on the transport numbers of the various ions present.

We have shown that the conventional ionic activity coefficients may remain extremely specific even at concentrations of the electrode solutions so low that the mean activity coefficients are given with 1 % accuracy by the non-specific limiting law of DEBYE and HÜCKEL, namely:

$$\log_{10} \bar{f}_{\pm} = -0.50 \sqrt{c},$$

for solutions containing only univalent ions. It might be argued that this effect is due to the exceptionally large proportion of hydrogen ions to other ions in one of the electrode solutions and that this complication would be absent as long as the electrode solutions were typical buffer solutions. This is indeed true as long as only univalent ions are present in the cell, for if they all have approxi-

mately equal mobilities E_D will be small and likewise the deviation of E_S from $\frac{RT}{F} \log_e \frac{f_{+}^{II}/f_{+}^I}{f_{-}^{II}/f_{-}^I}$. But there is no corresponding simple proposition holding for cells containing ions of several valencies. We shall refrain from giving here the more general formulae for E_D and E_S when ions of several valencies are present. If we make the simplest possible assumption namely that the KOHLRAUSCH mobilities are equal for all ions of the same valency and proportional to the valency for ions of different valencies, then the ideal liquid junction potential will be zero. But the further assumption that the activity coefficients at each part of the cell are the same for all salts of the same type is not sufficient to produce any notable simplification in the form of the "salt effect potential" E_S , except in the special case that in both electrode solutions the concentration of cations of each valency is equal to the concentration of anions of the same numerical valency. This last condition would in practice be difficult to fulfil in choosing a buffer solution owing to the general tendency of salts of symmetrical valence type to be insoluble except in the case of uni-univalent salts.

In conclusion we wish to express our gratitude to Professor BJERRUM for his friendly and helpful criticism. One of us (E. A. G.) is also indebted to the Rask-Ørsted Foundation for the award of a research grant.

Copenhagen March 1930.

The Royal Agricultural College Chemical Laboratory.