

Det Kgl. Danske Videnskabernes Selskab.

Mathematisk-fysiske Meddelelser. **X**, 14.

---

STUDIES OF CELLS WITH LIQUID-  
LIQUID JUNCTIONS

PART IV.

CELLS WITH NO BRIDGE SOLUTION

BY

E. A. GUGGENHEIM AND A. UNMACK



KØBENHAVN

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

BIANCO LUNOS BOGTRYKKERI A/S

1931

Pris: Kr. 1,20.

Det Kgl. Danske Videnskabernes Selskabs videnskabelige Meddelelser udkommer fra 1917 indtil videre i følgende Rækker:

Historisk-filologiske Meddelelser,  
Filosofiske Meddelelser,  
Mathematisk-fysiske Meddelelser,  
Biologiske Meddelelser.

Hele Bind af disse Rækker sælges 25 pCt. billigere end Summen af Bogladepriserne for de enkelte Hefter.

Selskabets Hovedkommissionær er *Andr. Fred. Høst & Søn*, Kgl. Hof-Boghandel, København.

---

Det Kgl. Danske Videnskabernes Selskab.  
Mathematisk-fysiske Meddelelser. **X**, 14.

---

STUDIES OF CELLS WITH LIQUID-  
LIQUID JUNCTIONS

PART IV.

CELLS WITH NO BRIDGE SOLUTION

BY

E. A. GUGGENHEIM AND A. UNMACK



KØBENHAVN

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

BIANCO LUNOS BOGTRYKKERI A/S

1931



### Introduction.

In the first paper of the present series<sup>1</sup> one of us gave a detailed discussion of the conditions for the reproducibility and stability of cells with liquid-liquid junctions and of how these factors depend on the nature of the junction. These theoretical considerations were substantiated by experimental measurements of cells of the type

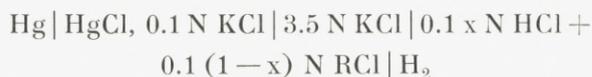


where the concentration  $c$  of the bridge solution was varied from 0.1 N to 3.5 N. Owing to the uncertainty of the effect of air on the calomel-hydrochloric acid electrode the absolute values of the E. M. F. measured were not reliable. But as the electrodes used agreed amongst themselves these measurements were sufficient to show that both reproducibility and stability over at least several hours were obtainable by junctions of two types, which were called respectively "free diffusion" and "continuous mixture layer", whereas junctions of a more indefinite type gave erratic fluctuations, sometimes amounting to as much as ten millivolts. The difference between the E. M. F.s given by the junctions of the "free diffusion" and "continuous mixture" types varied with the concentration of the "bridge" solution. There was a maximum difference of nearly one millivolt for a bridge concentration of 0.2 N. But for the

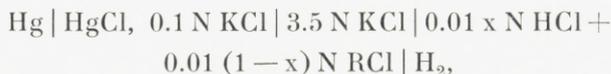
<sup>1</sup> GUGGENHEIM, *Journ. Amer. Chem. Soc.* **52**, 1315 (1930).

“bridge” concentration 0.1 N, and also for the most concentrated “bridge” solutions, the difference was of the same order as the experimental error.

In a more recent paper<sup>1</sup> an account was given of measurements of cells of the types



and



where R denotes an alkali metal.

Stability over several hours, or even days, and a reproducibility of about one tenth of a millivolt were obtained with junctions of the “free diffusion” type. It was also found that the same values for the E. M. F. were obtainable, also with a reproducibility of one tenth of a millivolt and a stability of several hours, by a considerably simpler technique, the junctions being prepared by simply sucking the bridge solution slowly about halfway up the side-tube of the electrode vessels and so ensuring the cylindrical symmetry, which appears to be such an important factor in determining the stability and reproducibility of the E. M. F.<sup>2</sup> Junctions prepared in this way may conveniently be referred to as “simple cylindrical”.

We shall now describe the results of a study of cells of the type



where R, R' represent two of the cations H<sup>+</sup>, Li<sup>+</sup>, K<sup>+</sup>.

<sup>1</sup> UNMACK and GUGGENHEIM, Kgl. Danske Vid. Selsk., Mat.-fys. Medd. **10**, No. 8. (1930).

<sup>2</sup> c. f. MAC LAGAN, Biochem. Journ., **23**, 309 (1929).

### Experimental technique and results.

The Ag - AgCl electrodes were essentially of the type used with such success by GÜNTEMBERG<sup>1</sup>, to whom we are indebted for valuable advice on the treatment of the electrodes. The electrode vessels were of the form shown in Fig. 1. At A was a cotton plug covered with a mixture B

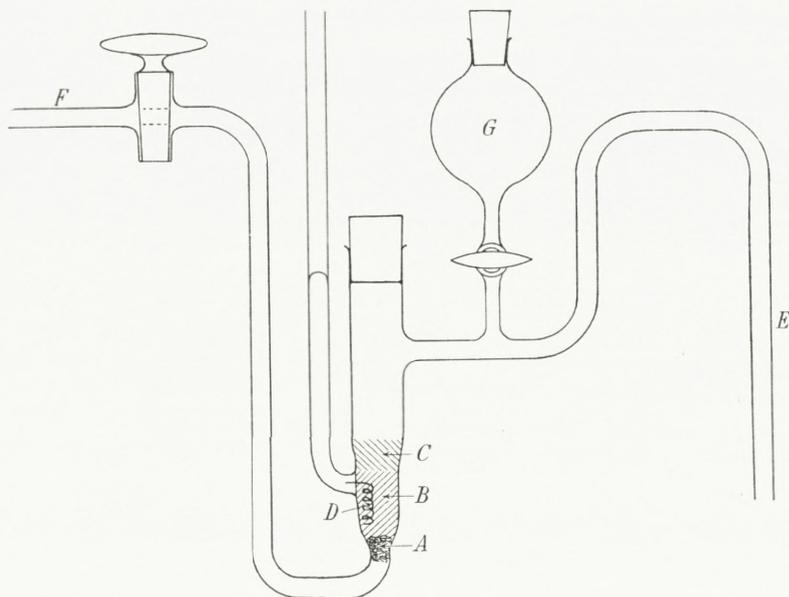


Fig. 1.

of silver (obtained by reduction of  $\text{AgNO}_3$  with  $\text{FeSO}_4$ ) and silver chloride (obtained by precipitation from  $\text{AgNO}_3$  with  $\text{HCl}$ ). Above this was a layer C of pure silver chloride. In some cases the platinum spiral D was silver plated, but it was found that this made no difference. The solutions were always pressed in through the side-tube E and out through the exit-tube F. The reservoir G was used only for rinsing the side-tube E before making a new junction. With this type of electrode vessel we could interchange

<sup>1</sup> GÜNTEMBERG, Z. physik. Chem. **123**, 199 (1926).

the electrode solutions, whilst using the same Ag-AgCl all the time. This seems to us far more satisfactory than using a different AgCl preparation for each new cell,<sup>1</sup> as for example by preparing the AgCl in situ by chloridising a silver electrode by electrolytic deposition. E. R. SMITH<sup>2</sup>, who amongst others used this procedure, emphasises that, in order to obtain reproducibility, he had to chloridise each electrode in a solution of the same composition as that in which it was to be used. This suspiciously suggest that the state of the AgCl, and so its chemical potential, differs according to what solution is used for its electric deposition or even that there may occur something irreversible. Furthermore SMITH's electrodes were presumably not stable, since he emphasises the necessity of preparing them just before use.

Our experience completely confirms that of GÜNTEMBERG<sup>3</sup> that, to obtain consistently reproducible results with these electrodes, it is essential rigorously to exclude access of oxygen. This we achieved by evacuating the space over each solution in its stock bottle until boiling commenced, cutting off the suction and allowing to stand several hours. The solution was next saturated with nitrogen, which had been passed over glowing copper filings. This whole procedure was repeated a second time. To fill an electrode vessel the air was first displaced by nitrogen and then the solution pressed over from the stock-bottle through the side-tube of the electrode vessel by means of nitrogen.

After standing twenty-four hours the electrodes prepared in this way were stable, anyhow for about a week. In

<sup>1</sup> c. f. BRØNSTED, Kgl. Danske Vid. Selsk., Mat.-fys. Medd. **3**, No. 9. (1920).

<sup>2</sup> SMITH, Bureau of Standards Journal of Research **2**, 1137 (1929).

<sup>3</sup> GÜNTEMBERG, Z. physik. Chem. **123**, 199 (1926).

contrast to calomel electrodes it is in acid solution that these electrodes seem least affected by the air. This may be connected with the impossibility of the existence of  $\text{Ag}_2\text{O}$  in the presence of acid.

The electrodes were entirely shielded from daylight, being prepared in a room lighted with electric light, then kept and used in a thermostat covered in with black cloth.

The hydrochloric acid solutions were prepared by dilution of a stock solution and the concentration controlled both by titration using  $\text{Na}_2\text{C}_2\text{O}_4$  as standard<sup>1</sup> and by gravimetric estimation of the chloride as  $\text{AgCl}$ . The sodium chloride and potassium chloride solutions were made up from weighed amounts of the salts, previously fused in platinum, and the concentrations checked by gravimetric estimation of the chloride as  $\text{AgCl}$ . A further check on these concentrations was the conductivity measurements described later. We used two sources of lithium chloride a) MERCK'S preparation b) a concentrated solution kindly given us by GÜNTEMBERG made from salt purified by him as described in his paper.<sup>2</sup> In each case we made up the solutions to a correct chloride concentration determined gravimetrically as  $\text{AgCl}$ . No difference could be detected between the solutions prepared from the two sources either by electrometric or by conductivity measurements.

The measuring apparatus was identical with that used previously. All measurements were made with the electrodes in a water-thermostat at  $18.0 \pm 0.02^\circ\text{C}$ , the junctions being either in the same thermostat or in an air thermostat also at  $18.0 \pm 0.1^\circ\text{C}$ , according to the type of

<sup>1</sup> SØRENSEN, *Oversigt over Kgl. Danske Vid. Selsk. Forh.* No. 3 (1900). SØRENSEN and ANDERSEN, *Z. anal. Chem.* **44**, 217 (1905).

<sup>2</sup> *loc. cit.*

junction. As a control over our electrodes we however measured the E. M. F. of the cell



both at 18°C and also at 20°C for direct comparison with GÜNTEMBERG'S value. We obtained the value  $352.95 \pm 0.1$  m. v. at 20°C as compared with GÜNTEMBERG'S value 353.05 m. v. (Actually he found 353.15 m. v. for a solution containing a deci-mole HCl in 1000 g H<sub>2</sub>O, whereas our solutions contained a deci-mole in 1 litre solution). Our value at 18°C was  $353.25 \pm 0.2$  m. v. The difference 0.3 m. v. for the range 18°C to 20°C is in good agreement with the results of NOYES and ELLIS<sup>1</sup>.

We experimented with altogether three types of junction. The "free diffusion" junctions were made in the air thermostat exactly as described in the previous paper<sup>2</sup>. A considerably simpler technique was however used for preparing junctions of the "continuous mixture" type. The vertical tube FG in the apparatus used for the "free diffusion" junctions<sup>3</sup> was replaced by a straight glass-tube of length about 30 cm and internal diameter 3 mm to 5 mm and this was filled by means of a capillary pipette with about a dozen successive portions each of 0.2 to 0.4 ccm of mixtures of the two electrode solutions, the compositions of the successive portions varying steadily from that of the one pure electrode solution to that of the other. It need hardly be mentioned that the electrode vessel with the denser solution was connected to the lower end of the vertical tube. In the case of the "free diffusion" junction

<sup>1</sup> NOYES and ELLIS, *Journ. Amer. Chem. Soc.* **39**, 2532 (1917).

<sup>2</sup> GUGGENHEIM, *Journ. Amer. Chem. Soc.* **52**, 1329 (1930).

<sup>3</sup> *Journ. Amer. Chem. Soc.* **52**, 1329, fig. 3. (1930).

there is a "lag" period before diffusion has annulled the inevitable irregularities associated with the initially "sharp" junction formed on opening the stopcock. In the case of the "continuous mixture" junctions there is no stopcock to open, but there is also a "lag" period before the temperature equilibrium is reached, as this is disturbed when the air-thermostat is opened to prepare the junction. In both cases however a steady value is reached after about half an hour, which is reproducible to within about 0.15 m. v. and stable for a whole day. For each cell set up readings were taken at irregular intervals spread over at least several hours.

The results are given below in table 1. The first column describes the nature of the cations R, R' in the two electrode solutions, the second gives the type of junction, "F. D." denoting "free diffusion" and C. M. "continuous mixture". The third column gives the mean of the values observed and the root-mean square deviation of the individual readings from the mean. The fourth column tells how often each cell was prepared and the fifth how many separate measurements made.

Owing to the great ease of preparing junctions of the "simple cylindrical" type and the conspicuous success obtained with them in the cells with a bridge of concentrated potassium chloride, it was natural to try to use them for the cells of the present type. It was however found extremely difficult to obtain consistent results when the two electrode solutions differ so little in density that only a very slight temperature difference is sufficient to start convection currents. By exercising great care one could generally obtain results agreeing with those given by the other two types of junction, but sometimes there were erratic

fluctuations of half a millivolt. We therefore cannot recommend this type of junction when the two solutions are so nearly of equal density and we are not giving the detailed results of these measurements.

Table 1.

Ag|AgCl, 0.1 N RCl|0.1 N R'Cl, AgCl|Ag at 18° C.

Nature of cations in electrode solutions		Type of junction	E. M. F. and R. M. S. deviation in m. v.	Number of cells	Number of readings
R	R'				
H	Li	F. D.	$34.85 \pm 0.15$	11	47
		C. M.	$34.85 \pm 0.15$	8	47
H	K	F. D.	$28.25 \pm 0.19$	8	38
		C. M.	$28.10 \pm 0.08$	3	12
K	Li	F. D.	$7.00 \pm 0.13$	12	50

We have a check on the consistency of our measurements, as follows.

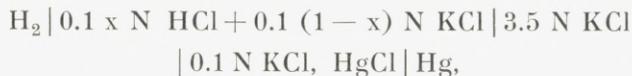
Firstly for the E. M. F. of the cell



we have

$$E = +28.2 \pm 0.15 \text{ m. v.} \quad (\text{a})$$

Secondly in our previous paper<sup>1</sup>, by a slight extrapolation from a series of cells of the type



we obtained for the cell



<sup>1</sup> UNMACK and GUGGENHEIM, Kgl. Danske Vid. Selsk., Mat-fys. Medd. **10**, No. 8 (1930).

$$E + \frac{RT}{F} \log_e c_{H^+}^{(KCl)} = +340.4 \pm 0.1 \text{ m. v.} \quad (b)$$

(R is the gas-constant, T the temperature, F the Faraday and  $c_{H^+}^{(RCl)}$  the hydrogen-ion concentration in the solution of R Cl).

Thirdly we have, from GÜNTEMBERG'S<sup>1</sup> measurements for the cell<sup>2</sup>



$$E - \frac{RT}{F} \log_e \frac{c_{H^+}^{(KCl)}}{c_{H^+}^{(HCl)}} = -1.0 \pm 0.0 \text{ m. v.} \quad (c)$$

Finally we have measured the E. M. F. of the cell



using the same electrodes as in our previous paper. We obtained the value  $-425.5 \pm 0.1$  m. v. Hence

$$E - \frac{RT}{F} \log_e c_{H^+}^{(HCl)} = -367.8 \pm 0.1 \text{ m. v.} \quad (d)$$

Adding the values (a), (b), (c), (d), we obtain

$$\begin{aligned} &+ 28.2 + 340.4 - 1.0 - 367.8 \pm \sqrt{0.15^2 + 0.1^2 + 0.0^2 + 0.1^2} \\ &= -0.2 \pm 0.2 \text{ m. v.} \end{aligned}$$

As this sum should theoretically be zero the agreement is within the experimental accuracy.

<sup>1</sup> GÜNTEMBERG, Z. physik. Chem. **123**, 199 (1926).

<sup>2</sup> GÜNTEMBERG'S measurements were at 20° C, but the correction to 18° C for this cell must be less than 0.01 m. v.

### Theoretical discussion.

Our measurements seem to establish definitely that the E. M. F.s given by the "free diffusion" junction and the "continuous mixture" junction are for these cells identical, at least to within an accuracy of 0.15 m. v. This is not altogether surprising, since it is just for cells of this type (two uni-univalent salts with one common ion both at the same concentration) that the ideal diffusion potential for the "continuous mixture" junction given by HENDERSON'S formula has identically the same value as the ideal diffusion potential given by PLANCK'S formula for yet another type of junction, namely the "constrained diffusion" type. As described elsewhere<sup>1</sup> this last type of junction is difficult to realise experimentally and the "free diffusion" type is mathematically intractable even in the simplest cases. P. B. TAYLOR<sup>2</sup> has attempted to compute approximately the concentration distribution for a "free diffusion" junction and in particular that between HCl and KCl of the same concentration. The accuracy claimed for this approximate computation has been challenged elsewhere by one of us<sup>3</sup>, but the distribution found by TAYLOR does at least give a qualitative picture of the deviations from a continuous mixture layer. As a final result he finds that these deviations cause a difference of only 0.3 m. v. in the computed diffusion potential, but this quantity is arrived at as the difference between two larger quantities contributed respectively by that part of the junction where the total concentration exceeds those of the electrode solutions and that part where the total concentration is less than those of

<sup>1</sup> GUGGENHEIM, *Journ. Amer. Chem. Soc.* **52**, 1315 (1930).

<sup>2</sup> TAYLOR, *Journ. Physic. Chem.* **31**, 1478 (1927).

<sup>3</sup> GUGGENHEIM, *Journ. Amer. Chem. Soc.* **52**, 1315 (1930).

the electrode solutions. It is therefore quite possible that the true residual difference is still less, if not exactly zero as it is known to be in the case of "constrained diffusion". The large irregular fluctuations in the values obtainable for the E. M. F., when an indefinite type of junction is made, for instance by merely dipping the end of one electrode vessel into a U-tube containing a solution, are then perhaps explicable as follows. Somewhere in the transition layer are places of concentration defects (or excess) as compared with a continuous mixture layer, whilst the corresponding concentration excess (or defect) may occur somewhere in the U-tube outside the direct circuit and so there is not compensation. On the other hand in the junction of the "simple cylindrical" type, this will not occur, as long as convection currents are absent.

We shall now see to what extent the E. M. F. of the present cells can be computed theoretically. We shall naturally assume a "continuous mixture layer" because of its mathematical simplicity. We denote by I and II the electrode solutions containing the cations R and R' respectively. We shall further use the following notation:  $c$  for concentration,  $f$  for activity coefficient of a salt,  $t$  for transport number,  $T$  for absolute temperature,  $R$  for the gas-constant,  $F$  for the Faraday. The lower suffices will refer to components, the upper to phases, e. g.  $t_{\text{Cl}^-}^{(\text{HCl})}$  is the transport number of  $\text{Cl}^-$  in a solution of HCl. Then, according to purely thermodynamic considerations and formulae given elsewhere<sup>1</sup>, the E. M. F. of the present cells may be regarded as the sum of three terms:

$$E = E_{\text{E1}} + E_{\text{D}} + E_{\text{S}} \quad (1)$$

<sup>1</sup> GUGGENHEIM, Journ. Physic. Chem. **36**, 1758 (1930).

where the "ideal electrode potentials"  $E_{E1}$  are given by

$$E_{E1} = -\frac{RT}{F} \log_e \frac{c_{Cl^-}^{II}}{c_{Cl^-}^I} \quad (2)$$

the "ideal diffusion potentials"  $E_D$  by

$$E_D = -\frac{RT}{F} \int_I^{II} t_R d \log_e c_R - \frac{RT}{F} \int_I^{II} t_{R'} d \log_e c_{R'} + \frac{RT}{F} \int_I^{II} t_{Cl} d \log_e c_{Cl} \quad (3)$$

and the "salt effects potential"  $E_S$  by

$$E_S = -\frac{2RT}{F} \int_I^{II} t_R d \log_e f_{RCl} - \frac{2RT}{F} \int_I^{II} t_{R'} d \log_e f_{R'Cl}, \quad (4)$$

each of the above integrals to be evaluated through the transition layer.

As the two electrode solutions are of equal concentration the "ideal electrode potentials"  $E_{E1}$  is here clearly zero. For these cells, in contrast to those with a bridge of concentrated KCl, the "salt effects potential"  $E_S$  can be much more accurately evaluated than the "ideal diffusion potential"  $E_D$ . We shall therefore consider  $E_S$  before  $E_D$ . According to the "principle of ionic strength"<sup>1</sup> the value of  $f_{RCl}$  in mixtures of RCl and R'Cl is approximately constant at constant total concentration. To this degree of accuracy  $E_S$  becomes zero. This approximation is however not accurate for deci-normal solutions. In fact the very accurate measurements of GÜNTEMBERG<sup>2</sup> completely con-

<sup>1</sup> LEWIS and RANDALL, *Journ. Amer. Chem. Soc.* **43**, 1137 (1921).

<sup>2</sup> GÜNTEMBERG, *Z. physik. Chem.* **123**, 199 (1926).

firm the more exact "principle of linear variation" put forward by BRÖNSTED<sup>3</sup>, according to which for mixtures of  $(1-x)$  parts of 0.1 N RCl and  $x$  parts of 0.1 N R'Cl the logarithms of the mean activity coefficients  $f$  vary linearly with  $x$ , so that

$$d \log_e f_{\text{RCl}} = d \log_e f_{\text{R'Cl}} = \beta \cdot dx. \quad (5)$$

where  $\beta$  is independent of  $x$ . We thus have

$$\frac{F}{RT} E_S = -2 \int_I^{II} (t_R + t_{R'}) \beta dx = -2 \beta \int_I^{II} (1 - t_{\text{Cl}}) dx. \quad (6)$$

Since transport numbers depend only on the ratios of the mobilities, we can for convenience take the mobility of the chloride ion as unity; in this scale we shall denote the mobilities of the other ions R and R' by  $\lambda$  and  $\lambda'$  respectively. Thus

$$t_{\text{Cl}} = \frac{1}{\lambda(1-x) + \lambda'x + 1} \quad (7)$$

and so finally

$$\begin{aligned} E_S &= -\frac{RT}{F} 2\beta \int_0^1 \left\{ 1 - \frac{1}{\lambda(1-x) + \lambda'x + 1} \right\} dx \\ &= -\frac{RT}{F} \cdot 2\beta \left\{ 1 - \frac{1}{\lambda - \lambda'} \log_e \frac{\lambda + 1}{\lambda' + 1} \right\}. \end{aligned} \quad (8)$$

In table 2 are given the data and results for the computation of  $E_S$ .

We have still to compute the integrals giving the "ideal diffusion potential"  $E_D$  and this is not so simple as might be supposed. As we are dealing with a "continuous mix-

<sup>3</sup> BRÖNSTED, Journ. Amer. Chem. Soc. **45**, 2898 (1923).

ture layer" we use HENDERSON'S formula<sup>1</sup>, which here takes the very simple form

$$E_D = \frac{RT}{F} \log_e \frac{\mathcal{A}_{RCl}}{\mathcal{A}_{R'Cl}} \quad (9)$$

where  $\mathcal{A}$  denotes equivalent conductivity. HENDERSON'S formula was originally derived on the assumption that each

Table 2.

Ag | AgCl, 0.1 N RCl | 0.1 N R'Cl, AgCl | Ag at 18°C.

Nature of cations:		Relative mobilities of cations:		$\frac{RT}{F} \cdot 2\beta$ in m.v.	$E_S$ in m.v.
R	R'	$\lambda$	$\lambda'$		
H	Li	5.0	0.5	-0.08	+0.05
H	K	5.0	1.0	-1.00	+0.7
K	Li	1.0	0.5	+0.92	-0.4

ion's mobility was independent of the composition of the solution in which it was present. If however one makes the less drastic assumption that the ratio of the mobility of a given ion in one solution to its mobility in another solution is the same for all ions, it follows at once, from the fact that transport numbers depend only on the ratios of the mobilities, that one obtains a formula identical with HENDERSON'S. But in this formula one must introduce values for the equivalent conductivities all corresponding to the same solution. That is to say in our present case we have

$$E_D = \frac{RT}{F} \log_e \frac{\mathcal{A}_{RCl}^{(RCl)}}{\mathcal{A}_{R'Cl}^{(RCl)}} = \frac{RT}{F} \log \frac{\mathcal{A}_{RCl}^{(R'Cl)}}{\mathcal{A}_{R'Cl}^{(R'Cl)}} \quad (10)$$

<sup>1</sup> HENDERSON, Z. physik. Chem. **59**, 118 (1907); **63**, 325 (1908).

It is inaccurate to use the expression  $\frac{RT}{F} \log_e \frac{A_{R'Cl}^{(R'Cl)}}{A_{RCl}^{(RCl)}}$  as is not

unusual<sup>1</sup>. Unfortunately data are scarce for the behaviour of conductivities in even the simplest mixtures. According to the measurements of STEARN<sup>2</sup>, for mixtures of the chloride, bromide or iodide of sodium with the corresponding potassium salt at decinormal concentration, deviations from the simple mixture law are always less than 0.2%. For various mixtures of 0.1 N NaCl and 0.1 N KCl the mixture law has been shown by MAC INNES, COWPERTHWAITTE and SCHEDLOWSKY<sup>3</sup> to hold good within 0.1%. We have ourselves verified that this also holds for each pair of the three salts LiCl, NaCl, KCl at a decinormal concentration, the deviations being in each case less than 0.1%. But for mixtures of each of these salts with HCl there are appreciably greater deviations. Our results are given in table 3 on a scale in which the specific conductivity of the KCl solution is taken as unity. The deviations with HCl might conceivably be due to the presence of a trace of alkali in the salt solutions, but we verified by titration that this was not the case. Moreover, if this had been the case, the deviations would have varied with the composition of the mixtures in quite another way. This may be seen from Fig. 2 in which the dotted curve shows the type of deviation one should expect due to alkali in the salt solutions. As may be seen from the third column of table 3 the relative conductivities of our solutions of single chlorides

<sup>1</sup> LEWIS and SARGENT, *Journ. Amer. Chem. Soc.* **31**, 363 (1909). MAC INNES and YEH, *Journ. Amer. Chem. Soc.* **43**, 2563 (1921). E. R. SMITH, *Bureau of Standards Journal of Research* **2**, 1137 (1929).

<sup>2</sup> STEARN, *Journ. Amer. Chem. Soc.* **44**, 670 (1922).

<sup>3</sup> MAC INNES, COWPERTHWAITTE, SCHEDLOWSKY, *Journ. Amer. Chem. Soc.* **51**, 2671 (1929).

are, except in the case of LiCl, in excellent agreement with the values found by Kohlrausch and his co-workers<sup>1</sup>.

As regards lithium chloride our value is somewhat higher than that given in LANDOLT-BÖRNSTEIN. This may have been due to the presence of a trace of a foreign salt, though this is rendered improbable by the fact that the

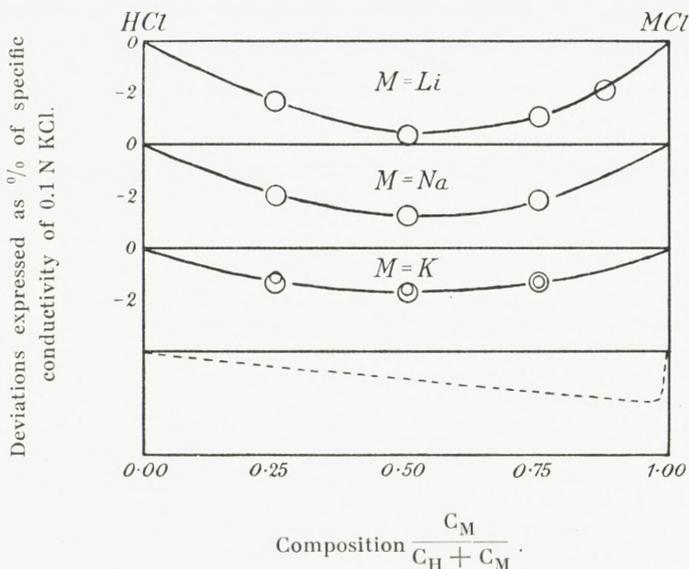


Fig. 2. Deviations of specific conductivities from mixture law in 0.1 N solutions. ○ Own measurements (18°C.). ◊ LONGSWORTH'S measurements (25°C.).

solutions made from the two different preparations were indistinguishable, both by electrometric and by conductivity measurements, when the chloride concentration was the same.

These measurements are of course not sufficient by themselves to determine the equivalent conductivities of the various components of the mixtures, but it seems plausible to expect a parallelism between on the one hand

<sup>1</sup> LANDOLT-BÖRNSTEIN, 5th edition p. 1079 (1923).

a lack of independence of the mobilities on the composition of the solution and on the other hand deviations from the simple mixture law for the conductivities.

Table 3.

Relative conductivities of mixtures of univalent chlorides at a total concentration 0.1 N and at 18° C.

Composition of solution.	Observed conductivity.	Conductivity according to Landolt-Börnstein.	Conductivity calculated according to mixture-law.	Deviation from mixture-law.
KCl	Unity	Unity		
HCl	3.133	3.133		
LiCl	0.740 <sub>8</sub>	0.735 <sub>7</sub>		
NaCl	0.821 <sub>3</sub>	0.821 <sub>4</sub>		
CsCl	1.017	1.014		
$\frac{1}{2}$ KCl + $\frac{1}{2}$ LiCl	0.869 <sub>6</sub>		0.870 <sub>4</sub>	-0.000 <sub>8</sub>
$\frac{1}{2}$ KCl + $\frac{1}{2}$ NaCl	0.910 <sub>4</sub>		0.910 <sub>7</sub>	-0.000 <sub>3</sub>
$\frac{1}{2}$ NaCl + $\frac{1}{2}$ LiCl	0.780 <sub>7</sub>		0.781 <sub>1</sub>	-0.000 <sub>4</sub>
$\frac{3}{4}$ HCl + $\frac{1}{4}$ KCl	2.587		2.600	-0.013
$\frac{1}{2}$ HCl + $\frac{1}{2}$ KCl	2.049		2.066	-0.017
$\frac{1}{4}$ HCl + $\frac{3}{4}$ KCl	1.520		1.533	-0.013
$\frac{3}{4}$ HCl + $\frac{1}{4}$ LiCl	2.512		2.535	-0.023
$\frac{1}{2}$ HCl + $\frac{1}{2}$ LiCl	1.901		1.937	-0.036
$\frac{1}{4}$ HCl + $\frac{3}{4}$ LiCl	1.310		1.339	-0.029
$\frac{1}{8}$ HCl + $\frac{7}{8}$ LiCl	1.021		1.040	-0.019
$\frac{3}{4}$ HCl + $\frac{1}{4}$ NaCl	2.536		2.555	-0.019
$\frac{1}{2}$ HCl + $\frac{1}{2}$ NaCl	1.950		1.977	-0.027
$\frac{1}{4}$ HCl + $\frac{3}{4}$ NaCl	1.378		1.399	-0.021

Just as these orientating conductivity measurements were completed, there appeared a paper by LONGSWORTH<sup>1</sup>

<sup>1</sup> LONGSWORTH, Journ. Amer. Chem. Soc. 52, 1897 (1930).

giving accurate data not only for the total conductivities, but also the various transport numbers and so the ionic conductivities in mixtures of HCl and KCl at a total concentration 0.1 N. These measurements were made at 25° C., but, as far as the conductivities of the HCl-KCl mixtures are concerned, the deviations from the mixture-law expressed as percentages of the conductivity of the KCl solution are in almost exact agreement with those found by us at 18° C. This is clear from Fig. 2, where LONGSWORTH'S measurements are included. For the determination of transport numbers the method used by LONGSWORTH was that of the moving boundary and his calculation involves the same assumption as that mentioned above as a condition for the application of HENDERSON'S formula, namely that the ratio of the mobility of a given ion in two different solutions is the same for the various ions. We shall hereafter for the sake of brevity refer to this as "LONGSWORTH'S assumption". The actual values found by LONGSWORTH for the transport numbers show that the assumption is not exact within his experimental accuracy, but the deviations are less than from the more drastic assumption of independent mobilities.

To compute the ideal "diffusion potential" we proceed as follows. We rewrite (10) in the form:

$$E_D = E_{L.S.} + E_A \quad (11)$$

where

$$E_{L.S.} = \frac{RT}{F} \log_e \frac{A_{RCl}^{(RCl)}}{A_{R'Cl}^{(R'Cl)}} \quad (12)$$

corresponds to the formula of LEWIS and SARGENT<sup>1</sup> and

$$E_A = \frac{RT}{F} \log_e \frac{A_{RCl}^{(R'Cl)}}{A_{RCl}^{(RCl)}} = \frac{RT}{F} \log_e \frac{A_{R'Cl}^{(R'Cl)}}{A_{R'Cl}^{(RCl)}} \quad (13)$$

<sup>1</sup> LEWIS and SARGENT, Journ. Amer. Chem. Soc. **31**, 363 (1909).

is the correction corresponding to the non-independence of the ionic mobilities and to the less drastic assumption of LONGSWORTH.

$E_{L.S.}$  can be calculated exactly from our own conductivity data. The values calculated are given in the second column of table 4. In view of the meagreness of the data

Table 4.

Ag | AgCl, 0.1 N RCl | 0.1 N R'Cl, AgCl | Ag at 18°C.

Nature of cations.	$E_{L.S.}$ in m. v.	$E_A$ in m. v.	$E_D$ in m. v.	$E_S$ in m. v.	$E_D + E_S$ in m. v.	$E$ in m. v.
R R'					calculated.	observed.
H Li	+ 36.3	- 1.3	+ 35.0	+ 0.05	+ 35.05	+ 34.85
H K	+ 28.6	- 0.65	+ 27.95	+ 0.7	+ 28.65	+ 28.2
K Li	+ 7.7	0.0	+ 7.7	- 0.4	+ 7.3	+ 7.0
(25°C)						(E. R. Smith)
H Na	+ 33.3	- 1.0	+ 32.3	+ 0.35	+ 32.65	+ 33.2

available, the correction term  $E_A$  can only be estimated roughly. We have to make two empirical assumptions:

- 1) For the HCl-KCl combination that  $\frac{E_A}{T}$  has the same value at 18°C as at 25°C.
- 2) For the three pairs of chlorides  $E_A$  is proportional to the maximum deviation of the conductivities from the mixture-law for mixtures of the respective pair of chlorides.

From LONGSWORTH'S data we have at 25°C

$$\begin{aligned} \mathcal{A}_{HCl}^{(HCl)} &= 391.28 & \mathcal{A}_{HCl}^{(KCl)} &= 379.75 \\ \mathcal{A}_{KCl}^{(HCl)} &= 131.82 & \mathcal{A}_{KCl}^{(KCl)} &= 128.89 \end{aligned}$$

from which

$$\log_{10} \frac{A_{\text{HCl}}^{(\text{KCl})}}{A_{\text{HCl}}^{(\text{HCl})}} = -.0130 \quad \log_{10} \frac{A_{\text{KCl}}^{(\text{KCl})}}{A_{\text{KCl}}^{(\text{HCl})}} = -.0098$$

the deviation between these corresponding to the inexactness of the assumption made by LONGSWORTH and ourselves. Using these same values at 18°C we obtain for the combination HCl - KCl

$$E_J = -0.75 \text{ m. v.} \quad \text{or} \quad E_J = -0.55 \text{ m. v.}$$

We choose the mean of these namely  $-0.65$  m. v.

For the combination HCl - LiCl by comparison of the deviations of the total conductivities from the mixture-law we estimate  $E_J$  to be  $-1.3$  m. v. For the combination KCl - LiCl we assume  $E_J$  to be negligible.

The final computation is summarised in table 4. The agreement between the calculated and observed values given in the last two columns is only fair. There is a general discrepancy of about 0.3 m. v., which we believe to be outside the experimental error. Presumably the greatest uncertainty is in the values computed for the correction term  $E_J$ . It is possible that at 18°C the ratios  $\frac{A_{\text{RCl}}^{(\text{RCl})}}{A_{\text{RCl}}^{(\text{R'Cl})}}$  differ more from unity than at 25°C. Moreover the assumption of LONGSWORTH that the ratios  $\frac{A_{\text{II}}}{A_{\text{I}}}$  are the same for all ions is known to be inexact, but without it one cannot compute transport numbers by LONGSWORTH'S method, nor can one use HENDERSON'S formula. We therefore do not see how we could dispense with this approximation.

We have included at the bottom of table 4 values for the combination HCl - NaCl at 25°C. The value of  $E_{\text{L.S.}}$  is computed from the data given in LANDOLT-BÖRNSTEIN<sup>1</sup>,

<sup>1</sup> LANDOLT-BÖRNSTEIN, 5th edition. Ergänzungsbd. p. 599 (1927).

$E_J$  is estimated by the method described above and  $E_S$  calculated from GÜNTEMBERG'S measurements as in the other cases. There is a discrepancy of about half a millivolt between the calculated value of  $E$  and that found by SMITH using the "flowing-junction". SMITH follows MAC INNES and SCATCHARD<sup>1</sup> in believing that the "flowing-junction", gives a continuous mixture layer, though, as admitted by SCATCHARD, there is no convincing evidence in favour of this belief. Further SMITH in his calculation assumes that the total E. M. F. is given simply by  $E_{L.S.}$  and he ignores both  $E_J$  and  $E_S$ . The excellent agreement claimed by him between calculated and observed values is therefore fortuitous, being due to the accidental balancing of two, if not three, errors.

In conclusion we take great pleasure in expressing our gratitude to Professor BJERRUM for his ever ready advice and his continuous interest in our work.

<sup>1</sup> Vide: GUGGENHEIM, Journ. Amer. Chem. Soc. **52**, 1323 (1930).

Copenhagen, October 1930.

