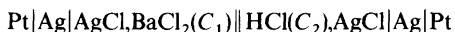


EMF of Concentration Cells with Liquid-liquid Junction Established by Free Diffusion. Part I. Experimental Results for HCl/BaCl₂ Junctions at Various Concentrations

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Emf's have been measured at 25 °C on the following cell:



where C_1 is ranging between 5.0×10^{-4} and 1.0 mol dm^{-3} and C_2 is ranging between 1.0×10^{-3} and $1.0 \times 10^{-1} \text{ mol dm}^{-3}$.

The liquid junction between the two half cells is established as free diffusion.

The results are compared with the simple model of Henderson. A detailed description for the preparation of reliable Ag/AgCl electrodes is given.

In a great number of potentiometric measurements the reference electrode is connected to the test solution by means of a salt bridge. In pH-measurements as well as in measurements with ion selective electrodes a calomel electrode together with a saturated KCl-solution is most often used as reference electrode. In such measurements it is postulated that the liquid junction potential created when the salt bridge is immersed in the test solutions containing different ions with different charges and concentrations is zero or at least constant from one test solution to another.

Surprisingly, only a limited number of important contributions to the understanding of this problem has been reported. The first contributions were given by Helmholtz¹ and Nernst,² who gave a description of electrolyte diffusion and pointed out that most often an electric diffusion potential is created when two electrolyte solutions are brought into contact. Two other important features of the liquid junction potentials were stated by Cumming

and Gilchrist³ in their study of KCl/HCl and HCl/HCl liquid junction potentials: (1) The emf-values are affected by variations in the nature of the liquid boundary and (2) the potentials of KCl/HCl solutions varied with the time the two solutions had been in contact with each other. Guggenheim,⁴ Guggenheim and Unmack,⁵ and MacInnes⁶ pointed out the importance of controlled experimental conditions and reported values for two different 1:1 salts measured under different boundary and initial conditions.⁷ A more detailed description of the most commonly used liquid junctions was given by Smyrl and Newman.⁸ Among the recent contributions to the understanding of 1:1 liquid junction potentials we must mention the paper of Lindeberg and Østvold⁹ treating a mixed boundary between HCl and KCl, the paper of Spiro¹⁰ dealing with a Henderson model for completely dissociated univalent electrolyte solutions, and the book of Newman¹¹ containing numerous – mostly theoretically calculated – values of liquid junction potentials and literature references. Only very few experimental results of emf's with liquid junction potentials caused by other electrolytes than 1:1 salts are reported in the literature. Those reported by Henderson¹² are of questionable value, since the experimental conditions were not properly stated. Jones and Doyle¹³ have computed the transference number of BaCl₂ at various concentrations from emf measurements on concentration cells with liquid junctions. However, in such cases with only a single electrolyte present it is well known that the liquid junction potentials are independent of the initial conditions.

Obviously, there is a lack of reliable data on emf

measurements on cells with liquid junctions between two electrolytes where at least one is not a 1:1 electrolyte. In the present paper we intend to amend the present lack in knowledge. Emf measurements have been carried out on the following cell:



where C_1 is ranging between 5.0×10^{-4} and 1.0 mol dm^{-3} and C_2 is ranging between 1.0×10^{-3} and $1.0 \times 10^{-1} \text{ mol dm}^{-3}$. The electrolytic contact was established with "free diffusion" boundary conditions. The technique is described in detail in the experimental section. The reason why the BaCl_2/HCl system was selected can be summarized in the following points:

(1) To support previous investigations carried out in this institute.¹⁴

(2) This system is used as example in the calculations made by Pleijel.¹⁵ His model gives a theoretical treatment of liquid junction potentials between two electrolytes of different valence types during steady interdiffusion in a fixed layer.

(3) Activity coefficients of BaCl_2/HCl mixtures are reported in the literature.¹⁶

(4) Due to the common ion in the BaCl_2/HCl system, the same type of measuring electrode – i.e. Ag/AgCl – can be used in the two electrolytes. This enables us to correct for inevitable asymmetric potentials between the two Ag/AgCl -electrodes.

(5) To the best of our knowledge, apart from in this institute,¹⁴ no experimental values for the BaCl_2/HCl system with specified boundary conditions have been reported.

(6) Due to the great difference in mobility of the H^+ -ion and the Ba^{2+} -ion, it is to be expected that BaCl_2/HCl junction potential contributes reasonably to the total cell-emf and therefore the possibilities of estimating the liquid junction potential with reasonable accuracy are enhanced.

In this paper we shall limit ourselves to give a brief theoretical introduction, a more detailed experimental description, and to report the experimental values together with preliminary calculations. As liquid junction potentials in principle are immeasurable with ordinary electrochemical devices, the results will be presented as total emf-values.

In a subsequent paper the BaCl_2/HCl system will be treated theoretically. New models for liquid junction potentials will be developed and compared with those of Planck, Pleijel, Henderson and others.

THEORY

Assuming one dimensional diffusion the liquid junction potential between two electrolyte solutions of arbitrary compositions can be written:

$$\Delta\phi = -\frac{RT}{F} \int_{x=-\delta_1}^{x=+\delta_2} \sum_i \frac{t_i}{z_i} \frac{\partial \ln a_i}{\partial x} dx \quad (2)$$

where δ_1 and δ_2 indicate the boundary of the diffusion zone (see Fig. 1), t_i is the transport number, a_i is the activity and z_i is the valency of the i th ion.

The conditions pertaining to emf-measurements in cells with liquid junctions are: (1) the electric current density is zero and (2) the liquid junction potentials are created due to concentration gradients in the cell. Since transport numbers are defined according to the conditions (1) electric current is passing through the cell and (2) there are

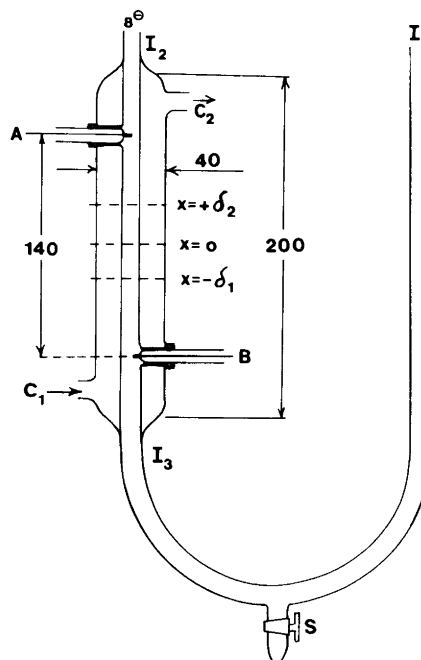


Fig. 1. Diffusion column with attached plastic tubes. Dimensions in mm. The free diffusion junction established at $x=0$. Distance from $x=-\delta_1$ to $x=+\delta_2$ indicates length of diffusion zone at the time $t=\tau$. Emf measured between the two Ag/AgCl electrodes A and B. C_1 : thermostated water inlet, C_2 : thermostated water outlet. I_1 and I_3 : inlet of lower electrolyte. I_2 : inlet of upper electrolyte. S: cock for connection to water pump.

no concentration gradients in the cell, the interpretation of eqn. (2) is far from simple. This equation cannot be derived by simple arguments about "passing a Faraday through the cell". Although such arguments are the ones most frequently found in textbooks they are of the "quasithermostatic" type analogous to the arguments of Thomson²⁸ in connection with thermo emf.

In connection with liquid junction potentials, Helmholtz¹ was the first to apply quasi-thermostatic arguments. However, Onsager²⁶ realized that the correct proof of such methods rested on extra-thermostatic principles, *viz.* the reciprocal relations. Therefore, the identity of transference numbers measured by means of the Hittorf method and the transference numbers obtained by emf-measurements in liquid junctions can be taken as an experimental proof of the validity of Onsager's reciprocal relations. See for example Miller (Ref. 17, p. 395, eqn. (11.59)). See also Wagner²⁷ for a careful comparison between the "quasi-thermostatic" method and the method of "irreversible thermodynamics".

In the single-electrolyte case — for example when the two electrolytes both are BaCl₂ at various concentrations — eqn. (2) yields:

$$\Delta\phi = \frac{RT}{F} \ln \frac{a_{\text{Cl}^-}(1)}{a_{\text{Cl}^-}(2)} - \frac{RT}{F} \int_{\ln a_{\text{BaCl}_2(1)}}^{\ln a_{\text{BaCl}_2(2)}} \frac{t_{\text{Ba}^{2+}}}{2} d \ln a_{\text{BaCl}_2} \quad (3)$$

The liquid junction potential cannot be measured directly due to the first term in eqn. (3). This term can be eliminated by measuring the total emf of the following cell:



including the liquid junction potential under examination. The expression for EMF of cell (4) has the form:

$$\text{EMF} = \frac{RT}{2F} \int_{\ln a_{\text{BaCl}_2(2)}}^{\ln a_{\text{BaCl}_2(1)}} t_{\text{Ba}^{2+}} d \ln a_{\text{BaCl}_2} \quad (5)$$

Because $t_{\text{Ba}^{2+}}$ is a function of a_{BaCl_2} only, the integral in eqns. (3) and (5) can be calculated numerically from table-data of $t_{\text{Ba}^{2+}}$ and $\ln a_{\text{BaCl}_2}$ as functions of concentration. This means that emf's of concentration cells including liquid junctions with only

one electrolyte present are invariant with time and therefore independent of the manner in which the liquid junctions are formed.

If we have simultaneously two different electrolytes in the junction — for example when cell (1) is examined instead of cell (4) — the emf expression takes the form:

$$\text{EMF}_{t=\tau}^{(1)} = -\frac{RT}{2F} \int_{x=-\delta_1}^{x=+\delta_2} t_{\text{Ba}^{2+}} + \left(\frac{\partial \ln a_{\text{BaCl}_2}}{\partial x} \right)_{t=\tau} dx - \frac{RT}{F} \int_{x=-\delta_1}^{x=+\delta_2} t_{\text{H}^+} + \left(\frac{\partial \ln a_{\text{HCl}}}{\partial x} \right)_{t=\tau} dx \quad (6)$$

Although eqns. (5) and (6) are very much alike some difficulties — not existing in eqn. (5) — arise when eqn. (6) is applied. Due to the fact that both the two transport numbers and the two activities are functions of *two* concentrations — *i.e.* C_{BaCl_2} and C_{HCl} — it is necessary to know how the concentration profiles vary with time along the diffusion zone, *i.e.* the path of integration in C_{BaCl_2} – C_{HCl} space must be known. This is normally not known and can only be simulated by using a specific model of electrodifusion.¹⁸

After some time the concentration profiles have in practice reached their final pattern. In the free diffusion case the diffusion profiles only become functions of time *through* the Boltzmann parameter x/\sqrt{t} , where t is the time elapsed from a hypothetical "infinitely sharp" step in the concentrations around $x=0$. When those "Boltzmann-profiles" have been reached the liquid junction potential (or cell emf) can be shown again to be independent of time (but *not* of the profiles).¹⁸

Even when the concentration profiles have reached their final pattern it is only possible to calculate those profiles by numerical calculations. The period of building up the concentration profiles will experimentally be observed as a drift in the measured emf (eqn. (6)). The dependence of the profile-pattern on the *boundary conditions* is observed as a variation in the (stable) measured emf.⁷

EXPERIMENTAL

Chemicals. The hydrochloric acid solutions were made from Titrisol ampullas containing 1.0 mol HCl by dilution. The barium chloride solutions were made from analytical grade BaCl₂·2H₂O (Riedel-de Haen), predried for one week at 50 °C. The silver plating solution was made of analytical grade

$\text{KAg}(\text{CN})_2$ (Merck) used without further purification. For all solutions distilled and deionized water was used.

Apparatus. The diffusion column was made of Pyrex glass. The column consists of a tube with circular cross section – inside diameter 8 mm – covered with a water jacket in which the temperature was kept at 25 ± 0.1 °C. For further details see Fig. 1.

Measuring devices. For the preliminary measurements the cell emf was measured with a Hewlett-Packard 3420 A DC differential voltmeter to which a Radiometer recorder, REC 61, was connected. With this experimental set-up it should be possible to measure potentials with an accuracy down to ± 1 μV . We experienced that the measured potentials were affected by the choice of sensitivity ranges on the instruments. With two different HP 3420 A DC/ REC 61 instruments we found it impossible to measure the asymmetric potential (the potential developed when two Ag/AgCl electrodes are placed in the same chloride solution) with an accuracy greater than ± 0.2 – 0.3 mV, and we also observed that the voltmeter and the recorder affected well prepared Ag/AgCl electrodes so that the asymmetric potentials during the measurements became time dependent and instable, even if in all measurements the electrodes were connected to the voltmeter with

shielded cables connected to earth. Based on the above observations we decided to give up the possibility of continuous recording of emf, and measure the potential only by means of a single digital mV-meter. We found that with a high impedance Data Technology $3\frac{1}{2}$ digits millivoltmeter (input impedance = 10^9 Ω for 500 mV full scale) the asymmetric potentials could be reproduced within ± 0.05 mV.

Preparation of silver-silver chloride electrodes. In order to be able to obtain emf-values with an accuracy and reproducibility of 0.1 mV it is absolutely necessary to have reliable electrodes with short response time. Numerous different methods for electrolytic preparations of Ag/AgCl electrodes can be found in the literature.^{19–23} We have tried some of these methods, but did not succeed in preparing electrodes with the required qualifications. Many of the reported methods are so troublesome, that in practice it is almost impossible to control all the parameters during the preparation. Besides this we found the electrodes were slow to come to equilibrium and to give different asymmetric potentials when placed in different chloride solutions. Furthermore we found that the electrodes were greatly affected by the daylight as visualized in Fig. 2. We have therefore developed our own method for electrolytic preparations of Ag/AgCl

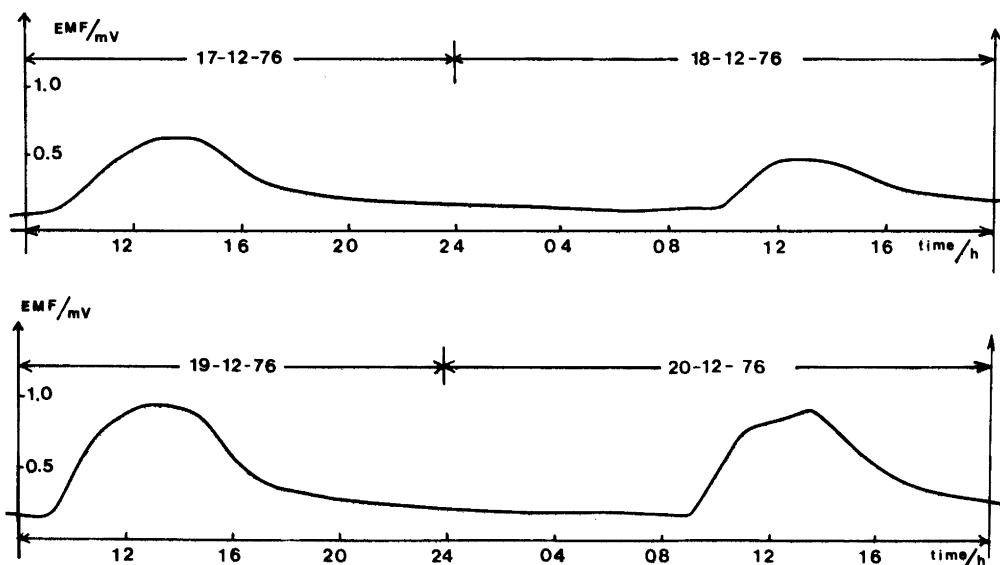


Fig. 2. Illustration of light dependence on Ag/AgCl electrode potentials. Continuous registration of emf between A and B (Fig. 1) in four subsequent days and nights with diffusion column filled with 0.1 mol dm^{-3} HCl. Hours and dates are read on figure. The Ag/AgCl electrodes were prepared according to Güntelberg.²⁰ Although the electrodes were not exposed to direct sunshine the influence from daylight on the measured EMF is clearly illustrated.

electrodes. Also, we decided to carry out all measurements in darkness in order to insure no influence from daylight on the silver-silver chloride electrodes. The electrodes were prepared as follows: A Radiometer platinum electrode, P 1312, was placed in concentrated nitric acid. In this solution the electrode was cleaned with electrolytic H₂ and O₂ evolution on the electrode, 10 min as cathode and 10 min as anode. This procedure was followed twice. The Pt electrode was rinsed for about 1 min in running distilled water and surrounded by an Ag-spiral in a distance of 2–3 mm. Immediately afterwards the Pt electrode and the Ag-spiral were placed in a well-stirred aqueous KAg(CN)₂-solution, 10 g dm⁻³, through which purified nitrogen had been bubbled for at least 1 h in advance. The Pt-electrode was cathodically electrolyzed at a current density of 5 mA cm⁻² for 60 min. The Ag-spiral served as anode. The Pt-electrode was rinsed for another minute in running distilled water. A part of the silver layer on the Pt electrode was electrolytically converted into AgCl in an aqueous 0.1 mol dm⁻³ HCl-solution with a current density of 5 mA cm⁻² for 2 min. The silver-silver chloride electrode was now ready for use.

The Ag/AgCl electrodes prepared as described above have asymmetric potentials rarely exceeding 0.05 mV, (A potential between +0.05 mV and -0.05 mV is indicated on the Data Technology voltmeter by the reading .0000 V with a fluctuating + and - sign). The useful life is somewhat uncertain. We made the observation, that generally an electrode pair may be used for five to fifteen experiments in a period of one to two months, and, generally, equilibrate with the cell solutions within half an hour. Failure of an electrode pair is indicated by increasing values in asymmetric potential and longer equilibration periods.

Measuring technique. A plastic tube was connected to the bottom of the diffusion column at I₃ (Fig. 1). Before each experiment the whole system was thoroughly rinsed several times with distilled and deionized water. Then the system was rinsed twice with absolute ethyl alcohol and allowed to dry under suction at least one hour. The screw-cock, S, was closed, the two Ag/AgCl electrodes were mounted in the diffusion column, and the lower part of the diffusion column was filled with the more dense electrolyte through inlet I₃ via I₁. The walls of the plastic tubes were pressed together with two screw-taps in order to close the connection between I₃ and I₁ and the surface of the more dense electrolyte was then at the position $x=0$ (Fig. 1). Very carefully the second electrolyte was then placed on top of the first one by means of a semi-automatic burette adjusted to give a flow of 4.5 ml h⁻¹. Except for the cases where the densities of the two electrolytes were approxi-

mately equal, the liquid junction could in this way be formed with a sharp boundary as could be observed by means of the difference in the refraction index of the two electrolytes. Electrode A was covered with electrolyte approximately half an hour after the formation of the liquid junction. From this time emf of the cell was measured during a period of at least 24 h. Before and after each emf measurement on the concentration cell the asymmetric potential was measured in one of the two electrolytes used in the experiments.

Further, before each experiment the electrodes A and B were allowed to equilibrate at least one hour in the electrolytes applied to the measurements.

RESULTS AND DISCUSSION

Fig. 3 shows the time dependence of emf from four experiments carried out on cell (1). The time $t=0$ is selected when the first drop of the upper electrolyte was placed on the lower one. The first measuring points on the upper, middle and lower figures refer to the time when electrode A was covered with electrolyte. The individual curves in Fig. 3 can be roughly divided into three sections. In section one a variation in the measured emf is observed during the first 3–4 hours of the experiment. Section two is characterized by constant emf values, and in section three a continuous fall in the measured emf is observed. We assume that the emf variations in section one are mainly due to variations in the potential of electrode A. At the time when electrode A is covered with the upper electrolyte, electrode B has been covered with the lower electrolyte and the diffusion zone has been developed so long that both the potential of electrode B and the concentration profiles in the diffusion zone have most probably been well established. Experiences from measurements of asymmetric potentials show that at least the electrode potential of electrode B should be stable, when electrode A is covered with electrolyte. However, although the emf variations are different from experiment to experiment and although duplicate experiments on the same HCl–BaCl₂ solutions give different curves, it is seen from the upper Fig. 3 that the constant emf value can be reproduced and determined with a few tenths of millivolts. This constant emf value is selected as the true emf of cell (1). The emf fall shown on the right-hand side of Fig. 3 shows that the diffusion zone now has reached at least one of the measuring electrodes.

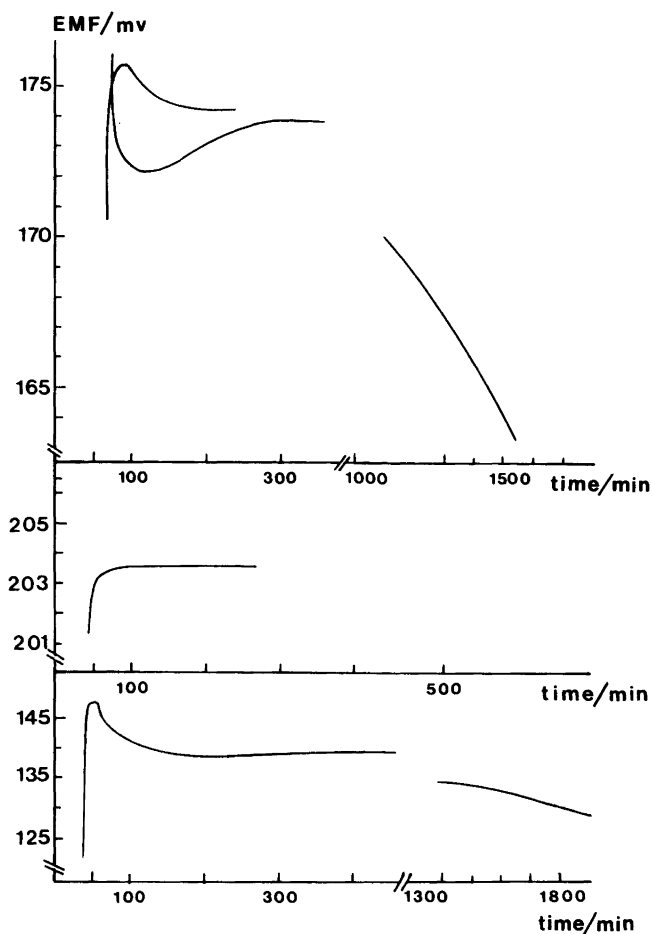


Fig. 3. Measured emf on cell (1) versus time. Emf measurements were performed on the diffusion column at 25 °C. Upper curves: $C_1 = 0.001 \text{ mol dm}^{-3}$, $C_2 = 0.1 \text{ mol dm}^{-3}$ (duplicate experiments). Middle curve: $C_1 = 0.0005 \text{ mol dm}^{-3}$, $C_2 = 0.1 \text{ mol dm}^{-3}$. Lower curve: $C_1 = 0.001 \text{ mol dm}^{-3}$, $C_2 = 0.05 \text{ mol dm}^{-3}$.

Emf values from different HCl–BaCl₂ pairs, determined as described above, are collected in Table 1. The integers (in parenthesis) indicate the number of emf determinations.

Due to complex formation between Cl⁻ ions and crystalline AgCl²⁴ it was impossible to exceed $C_{\text{HCl}} = C_{\text{BaCl}_2} \cong 0.1 \text{ mol dm}^{-3}$ with electrodes prepared as described above. Some experiments have been carried out with $C_{\text{BaCl}_2} = 1.0 \text{ mol dm}^{-3}$. In these experiments it was necessary to cover the Ag/AgCl electrodes with ten times the amount of AgCl as described earlier. Similar experiments with $C_{\text{HCl}} = 1.0 \text{ mol dm}^{-3}$ have not been performed until now.

The ./ signs in Table 1 indicate HCl/BaCl₂ ratios when the densities of the two electrolytes are so much alike that we found it impossible to establish a free diffusion zone. Further in Table 1 is shown [in parenthesis] the corresponding emf-values from Sørensen.¹⁴ As these measurements all were carried out at 17 °C, it is not directly possible to compare our results with those made by Sørensen, but generally it is shown that his values are smaller than ours. To our knowledge, besides Sørensen, only Henderson¹² has reported experimentally emf-values from cells with HCl/BaCl₂ liquid junctions. Since Henderson indicates almost no experimental details and since he further in two papers gives two

Table 1. Experimental emf-values of cell (1) together with the estimated accuracies. (Temp. 25.0 ± 0.1 °C). The integers in parenthesis indicate the number of experiments. The corresponding values from Ref. 14 are given in brackets [] (Temp. 17.0 ± 0.1 °C).

C _{HCl}	C _{BaCl₂} 0.0005	0.001	0.005	0.010	0.050	0.100	1.000
0.001		-5.3 ± 0.5 (2)		43.7 ± 0.4 (5)		86.8 ± 1.0 (2)	126.4 ± 1.0 (3)
0.005	·/·	-54.8 ± 0.1 (1)					
0.010	-111.2 ± 0.1 (2)	·/·	-30.2 ± 0.1 (2)	-15.8 ± 0.6 (2)		40.7 ± 0.2 (2) [37.7 ± 1.0]	82.9 ± 1.0 (2) [79.2 ± 1.5]
0.050		-138.9 ± 0.1 (1)	·/·	-61.7 (1)			
0.100	-203.3 ± 0.2 (2)	-174.0 ± 0.1 (3)	-113.6 ± 0.1 (2)	·/· [-92.4 ± 0.7]	-32.7 ± 0.1 (2)	-16.3 ± 1.0 (2) [-22.2 ± 1.8]	40.6 ± 0.2 (2)

different values for the same experiment, we are unable to compare our results with his.

Probably the most simple model for calculating the liquid junction potential of, for example, cell (1) is the one given by Henderson.¹² This model, combined with the ideal Nernst equation for electrode potentials, gives the following equation for the total emf of cell (1):

$$\text{EMF} = \frac{RT}{F} \left[\frac{2C_1(U_{\text{Ba}^{2+}} - U_{\text{Cl}^-}) - C_2(U_{\text{H}^+} - U_{\text{Cl}^-})}{2C_1(2U_{\text{Ba}^{2+}} + U_{\text{Cl}^-}) - C_2(U_{\text{H}^+} + U_{\text{Cl}^-})} \right. \\ \left. \ln \left(\frac{2C_1}{C_2} \times \frac{U_{\text{Cl}^-} + 2U_{\text{Ba}^{2+}}}{U_{\text{H}^+} + U_{\text{Cl}^-}} \right) + \ln \frac{2C_1}{C_2} \right] \quad (7)$$

where C_1 is the concentration of BaCl₂, C_2 is the concentration of HCl. U_i is the mobility of the i th specie, $i = \text{H}^+$, Ba^{2+} , Cl^- . For $C_1 \ll C_2$ eqn. (7) gives:

$$\text{EMF}_{C_1 \ll C_2} = \frac{RT}{F} \left[\left(\frac{U_{\text{H}^+} - U_{\text{Cl}^-}}{U_{\text{H}^+} + U_{\text{Cl}^-}} + 1 \right) \ln \frac{2C_1}{C_2} + \right. \\ \left. + \frac{U_{\text{H}^+} - U_{\text{Cl}^-}}{U_{\text{H}^+} + U_{\text{Cl}^-}} \ln \left(\frac{U_{\text{Cl}^-} + 2U_{\text{Ba}^{2+}}}{U_{\text{H}^+} - U_{\text{Cl}^-}} \right) \right] \quad (8)$$

and for $C_2 \ll C_1$

$$\text{EMF}_{C_2 \ll C_1} = \frac{RT}{F} \left[\left(\frac{U_{\text{Ba}^{2+}} - U_{\text{Cl}^-}}{2U_{\text{Ba}^{2+}} + U_{\text{Cl}^-}} + 1 \right) \ln \frac{2C_1}{C_2} + \right. \\ \left. + \frac{U_{\text{Ba}^{2+}} - U_{\text{Cl}^-}}{2U_{\text{Ba}^{2+}} + U_{\text{Cl}^-}} \ln \left(\frac{U_{\text{Cl}^-} + 2U_{\text{Ba}^{2+}}}{U_{\text{H}^+} - U_{\text{Cl}^-}} \right) \right] \quad (9)$$

In Fig. 4 eqn. (7) is plotted together with our experimental results. As in the Henderson model it is

assumed that the ionic mobilities were independent of concentration and the values at zero concentration were used to make the plot. These values were calculated from the corresponding ionic equivalent conductivities taken from Robinson and Stokes.²⁵ It is seen that there is only a rough agreement between the experimental data and data calculated from the model, *i.e.* by means of the model an experimental result can be calculated only with an accuracy of about 10 mV. Another comparison between calculated and experimental results is made in Fig. 4. Eqn. (7) predicts linear dependence of emf *vs.* $\log \frac{C_1}{C_2}$ when $C_2 \gg C_1$ [eqn. (8)] and when $C_1 \gg C_2$ (eqn. (9)). As seen in the figure also the experimental results fit a straight line under these conditions.

Another more general conclusion can be drawn. If a liquid junction is established between two electrolytes, both consisting of one salt and the conditions from eqn. (8) or (9) are fulfilled, then the liquid junction potential between the two electrolytes is determined only by the ionic mobilities – or ionic transport numbers – of the more concentrated electrolyte. This situation is approximately obtained in practical emf measurements in dilute solutions with a saturated calomel electrode as reference electrode. Here the liquid junction potentials are impressed by the saturated KCl-salt bridge.

More detailed discussions concerning comparison of experimental results with results calculated from theoretical models will be given in part II.

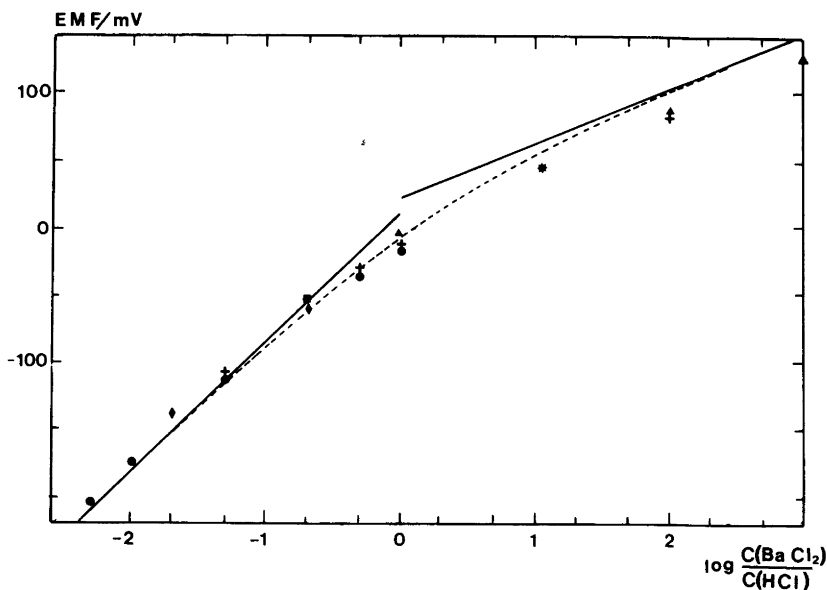


Fig. 4. Measured emf on cell (1) as function of $\log \frac{C_{\text{BaCl}_2}}{C_{\text{HCl}}}$. Emf measurements were performed on the diffusion column at 25 °C. $C_{\text{HCl}}/\text{mol dm}^{-3}$: 0.1 (●), 0.01 (+), 0.001 (▲), 0.05 (■), 0.005 (◆). In cases where the experimental values coincide, the symbol * is used. The dotted curve is a plot of eqn. (7). The straight lines indicate the two asymptotes to the dotted curve. The mathematical expressions of these asymptotes are given by eqns. (8) and (9).

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