

Scope of the Ionic Medium Method

On Measurements on Cells with Hydrogen Electrode-Silver-Silver Halogenide Electrodes in 3 M Media

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The emf of the cell $\text{Pt}(\text{H}_2)|\text{Solution}|\text{AgX},\text{Ag}$ has been measured at 25°C and 60°C. X stands for Cl or Br. The solution contained varying amounts of sodium, hydrogen, perchlorate, and chloride or bromide ions. The total concentration was kept constant at 3 M.

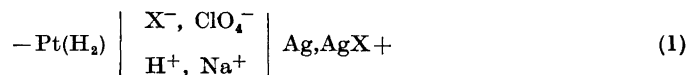
The standard emf's could be described by a simple linear equation (eqn. 7) which is an extension of Harned's rule.

This material gives support to the ionic medium method. By a suitable choice of reference electrodes and supporting electrolyte, the medium effects may be kept under control, even when large changes in the concentration of some species in the solution have to be undertaken. The disadvantages of liquid-junction cells are discussed.

One goal of coordination chemistry is to establish the complexes formed in a system and their stability constants. To do this, the composition of the solution has to be changed. Unfortunately, the measured effects are then partly due to "medium effects" and liquid-junction potentials. The latter are diminished by working in a "solvent" containing high and constant contents of neutral salts. This is the basis of the ionic medium method that has been used consistently in coordination chemistry since 1940.¹

The aim of the present paper is to study the medium effects in two model systems in some detail. One important requirement is that association or dissociation must not occur in the model system.

In this work the emf of the cell



has been measured. X stands for Cl or Br. The total equivalent concentration has been kept constant at $C_{\text{tot}} = 3 \text{ M}$:

$$C_{\text{tot}} = \frac{1}{2} \sum_i C_i \cdot |z_i| = [\text{X}^-] + [\text{ClO}_4^-] = [\text{H}^+] + [\text{Na}^+] \quad (2)$$

z stands for the charge of any of the ionic species of the solution and C for the corresponding concentration. Throughout this work the unit for concentration is mol dm⁻³ (M). Literature values given in mol/kg water have been recalculated to M.

Choice of standard state. The formulation of Nernst's law for the emf's of cell (1) calls for the definition of unit activity (*i.e.* the standard state) of the hydrogen and halogenide ions. The choice of standard state is arbitrary and is connected to the choice of a standard solvent. In the standard state, the hydrogen and halogenide ions have the same properties as if they had the concentrations given in the defined standard solvent, and they have a hypothetical unit concentration.

In the following, three standard solvents will be defined and Nernst's law will be formulated. The last definition will be adhered to in the remainder of the paper. The quantities E_{aq}° , E_{NaX}° , and E° stand for differently defined standard emf's of cell (1) and y and y' for mean activity coefficients.

i. The standard solvent is *water*:

$$E = E_{\text{aq}}^\circ - \frac{RT}{F} \ln [\text{H}^+][\text{X}^-] - \frac{2RT}{F} \ln y \quad (3a)$$

$$E_{\text{aq}}^\circ = \lim_{[\text{H}^+], [\text{X}^-], c_{\text{tot}} \rightarrow 0} \left(E + \frac{RT}{F} \ln [\text{H}^+][\text{X}^-] \right) \quad (3b)$$

This implies,

$$\lim_{[\text{H}^+], [\text{X}^-], c_{\text{tot}} \rightarrow 0} y = 1 \quad (3c)$$

This formulation is very common but it has serious disadvantages: the necessary extrapolation to pure water is difficult because the medium effects change very greatly at low concentrations. Furthermore, measurements at very low concentrations of hydrogen and halogenide ions will be accordingly uncertain.

ii. *Some solvent* with defined composition is chosen as standard solvent. For example, the standard solvent could be chosen as sodium halogenide with concentration C_{tot} :

$$E = E_{\text{NaX}}^\circ - \frac{RT}{F} \ln [\text{H}^+][\text{X}^-] - \frac{2RT}{F} \ln y' \quad (4a)$$

$$E_{\text{NaX}}^\circ = \lim_{\substack{[\text{H}^+], [\text{ClO}_4^-] \rightarrow 0 \\ [\text{X}^-], [\text{Na}^+] \rightarrow C_{\text{tot}}}} \left(E + \frac{RT}{F} \ln [\text{H}^+][\text{X}^-] \right) \quad (4b)$$

This implies,

$$\lim_{\substack{[\text{H}^+], [\text{ClO}_4^-] \rightarrow 0 \\ [\text{X}^-], [\text{Na}^+] \rightarrow C_{\text{tot}}}} y' = 1 \quad (4c)$$

This is the usual approach in coordination chemistry. The results obtained are extrapolated to the standard solvent chosen. Often, this extrapolation is

neglected and an average of determinations at low concentrations of the reacting species is given.

This is often permissible since the extrapolations are so short that the correction will be masked by the measuring errors.

iii. The *actual solvent* used is defined as the standard solvent:

$$E = E^\circ - \frac{RT}{F} \ln [H^+][X^-] \quad (5)$$

An extrapolation is necessary only when the reacting species are not constituents of the solvent. E° is a variable, contrary to the former two formulations, where E_{aq}° or E_{NaX}° have been assigned fixed values after a limit transition to a specific solvent.

The variation of E° is a direct measure of the variation of the medium effects. In the former two cases, the same variations can be studied in the terms $2RT/F \ln y$ and $2RT/F \ln y'$, respectively.

The formulation of eqn. (5) is more direct than those of eqn. (3) or eqn. (4). It should be preferred in those cases where a considerable part of the ions in the inert electrolyte has to be exchanged for reacting species. Two examples of this are: ligand exchange in the study of a weak metal complex; hydrogen ion exchange in the study of a strong acid.

E° according to eqn. (5) is often called the formal potential. It is to be observed, that E_{NaX}° or E° are as well thermodynamically defined as E_{aq}° .

Harned's rule. The rule is given for a specific example. If the solvent is changed from sodium chloride of concentration C_{tot} to hydrochloric acid of concentration C_{tot} , the logarithm of the activity coefficient (eqn. 3) varies linearly with the hydrogen ion concentration of the solution.

$$\log y = \log y_{\text{NaCl}} + \alpha \cdot [H^+] \quad (6)$$

This empirical law was first observed by Güntelberg² and has been used with great success in many systems.³

For a given value of C_{tot} , y_{NaCl} is a constant which denotes the mean activity coefficient of hydrochloric acid at infinite dilution in sodium chloride, if the standard state is chosen according to *i*. α is the slope of the linear variation.

An extension of Harned's rule. The experimental data of this paper indicate that E° according to eqn. (5) can be described by a linear equation, taking all the concentrations of hydrogen, sodium, halogenide, and perchlorate ions into account:

$$\begin{aligned} E^\circ = & \frac{[H^+][ClO_4^-]}{C_{\text{tot}}^2} \cdot E_{\text{HClO}_4}^\circ + \frac{[H^+][X^-]}{C_{\text{tot}}^2} \cdot E_{\text{HX}}^\circ + \\ & + \frac{[Na^+][ClO_4^-]}{C_{\text{tot}}^2} \cdot E_{\text{NaClO}_4}^\circ + \frac{[Na^+][X^-]}{C_{\text{tot}}^2} \cdot E_{\text{NaX}}^\circ \end{aligned} \quad (7)$$

E_{NaX}° has been defined in eqn. (4b) and $E_{\text{HClO}_4}^\circ$, E_{HX}° , and $E_{\text{NaClO}_4}^\circ$ are defined analogously.

The experimental condition for eqn. (7) to be valid is that the total equivalent concentration be kept constant at C_{tot} . According to eqn. (2),

$[\text{ClO}_4^-]$ and $[\text{Na}^+]$ are then $C_{\text{tot}} - [\text{X}^-]$ and $C_{\text{tot}} - [\text{H}^+]$, respectively, and E° is a function of $[\text{H}^+]$ and $[\text{X}^-]$ only.

A model of the three-dimensional function $E^\circ([\text{H}^+], [\text{X}^-])$ of eqn. (7) is illustrated in the stereoscopic Fig. 1. Sections through the model at constant $[\text{H}^+]$ or $[\text{X}^-]$ give linear variations of E° in accordance with Harned's rule, which may be readily verified from eqn. (7). In spite of this, the locus of E° is not planar but forms a "twisted plane".

The term "corner point" for the four solvents containing only perchloric acid, hydrochloric acid, sodium perchlorate, or sodium chloride will be obvious from Fig. 1.

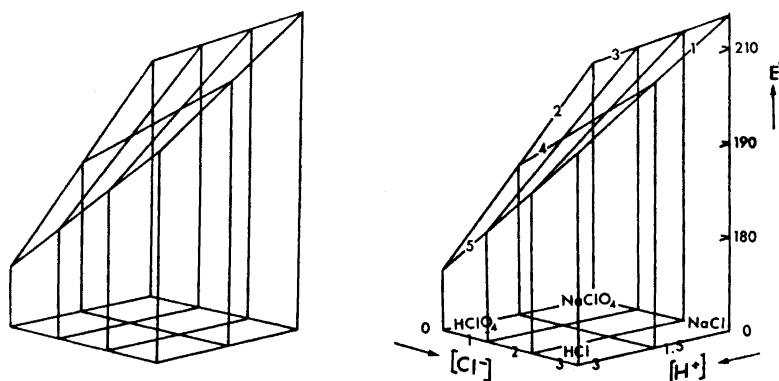


Fig. 1. A stereoscopic representation of the standard emf (mV) according to eqn. (5) (vertical axis) as a function of the hydrogen and chloride ion concentrations (M; the two horizontal axes). System: chloride at 25°C. The total concentration was held constant at 3 M by means of sodium ions and perchlorate ions. The lines marked (1) to (5) are illustrated in Figs. 2 and 3. The dimension perpendicular to the paper may be clearly seen by using a pocket stereoscope.

Harned's law is written in eqn. (6) for the special case, where $[\text{Cl}^-] = C_{\text{tot}}$ and sodium ions are exchanged by hydrogen ions. For comparison, eqn. (6) will now be derived from eqn. (7).

Since $[\text{ClO}_4^-] = 0$ and $[\text{Na}^+] = C_{\text{tot}} - [\text{H}^+]$, eqn. (7) will be simplified to:

$$E^\circ = E_{\text{NaCl}}^\circ + \frac{E_{\text{HCl}}^\circ - E_{\text{NaCl}}^\circ}{C_{\text{tot}}} [\text{H}^+] = E_{\text{NaCl}}^\circ + \frac{\partial[\text{H}^+]}{\partial E^\circ} [\text{H}^+] \quad (8)$$

Combination of eqns. (3a) and (5) will give $\log y$:

$$\log y = \frac{F}{2RT \ln 10} (E_{\text{aq}}^\circ - E^\circ) \quad (9)$$

Similarly, $\log y_{\text{NaCl}}$ can be solved from eqns. (3a) and (4b):

$$\log y_{\text{NaCl}} = \frac{F}{2RT \ln 10} (E_{\text{aq}}^\circ - E_{\text{NaCl}}^\circ) \quad (10)$$

Putting

$$\alpha = - \frac{F}{2RT \ln 10} \cdot \frac{E_{\text{HCl}}^{\circ} - E_{\text{NaCl}}^{\circ}}{C_{\text{tot}}} \quad (11)$$

and substituting (9), (10), and (11) into (8) will yield Harned's law, eqn. (6).

The important part of Harned's rule in conjunction with the ionic medium method is the slope α . According to eqn. (11) this slope may as well be studied through the standard emf E° (eqn. 5) directly and eqn. (8) is a more direct and easily defined and calculated form of Harned's rule. From this point of view, the use of a fixed standard state in a system is both unnecessary and unpractical.

EXPERIMENTAL

Chemicals. Reagent grade chemicals were generally used without further purification. Perchloric acid was from BDH and Baker (catalogue number 9652). Sodium perchlorate was from Merck (6564) and Fluka. Hydrochloric acid was from BDH. Sodium chloride was from Fisher (S-271) and Merck (6404). Hydrobromic acid was from Baker (6010) and Merck (307). Sodium bromide was from Baker (0271). The last reagent was further purified by two recrystallizations from water. No differences could be detected between different preparations of the same chemical.

Silver chloride and silver bromide were prepared by precipitation from reagent grade solutions of the sodium halogenides and silver nitrate. The substances were washed by decantation and dried.

3 M stock solutions were prepared with quartz-distilled water. The stock solutions were analyzed by acidimetric and argentometric titrations within 0.3 %. The measuring solutions were made up by mixing appropriate volumes of these stock solutions.

Impurities may have a very adverse effect on silver-silver chloride and silver-silver bromide electrodes.⁴⁻⁶ Therefore, all stock solutions were spot-tested with uranine for bromide⁶ (except hydrobromic acid and sodium bromide) and with nitrite and starch paper for iodide.⁷ No traces of bromide or iodide could be found. The limit of detectability was estimated to be 0.2 mM in both cases.

Hydrogen gas was taken from steel cylinders. It was deoxygenated with activated copper precipitated on kieselgur.⁸

Electrodes. Silver-silver chloride electrodes were prepared according to Brown.⁹ The base for the silver deposit was a small platinum disc, diameter 4 mm, thickness 0.2 mm, mounted on a platinum wire which was sealed to the glass stem. Fresh electrodes were used for each measuring solution and the average was taken from several electrodes.

Silver-silver bromide electrodes were prepared and used in a similar manner. The electrodes were brominated in 0.1 M sodium bromide solution of reagent grade quality. The current density was halved and the electrolysis time was doubled compared with the description of Brown.⁹

The solution in the silver-silver halogenide half cell was always saturated with silver halogenide, added in excess.

The hydrogen electrodes were of the Hildebrand type.¹⁰ Two independent platinum sheets (5 × 7 mm²) were mounted in the glass tubing. Platinization was performed in a solution of 2 g hexachloroplatinum(IV) acid and 40 mg lead acetate in 100 ml water with a current of 200 mA for a few seconds. Fresh electrodes were prepared for each measuring solution.

The glass tubing dipped in the measuring solution in the hydrogen half cell. The hydrogen gas filled this compartment and escaped through a piece of teflon tubing, coiled several times.

Cell. To avoid reduction of the silver halogenide by the hydrogen, the two half cells were constructed using titration vessels joined by a siphon fitted with a stopcock. The titration vessels were obtained from Ingold, Zürich, and consisted of a plastic cover with 5 standard bores NS 14 and a beaker with a threaded connection to the cover.

On the beaker a jacket for thermostated water was fastened. Magnetic stirring was employed.

Thermostating. A water stream of $25 \pm 0.1^\circ\text{C}$ or $60 \pm 0.1^\circ\text{C}$ was pumped through the jackets of the two titration vessels. In the same manner, a vessel for moistening the hydrogen gas was also thermostated. This vessel contained the same measuring solution as the rest of the cell.

At 60°C , it was necessary to place the whole cell in a large cabinet, where the air was maintained at $60 \pm 1^\circ\text{C}$. The gas was prethermostated and premoistened by bubbling through two washing bottles with water in the air thermostat. Then all effects due to condensation and evaporation of the solution were avoided.

Emf measurements. The emf's were measured with an HP 3420 B differential voltmeter to a precision of $10 \mu\text{V}$. The stopcock was closed all the time.

Calculations

Conversion from molality to molar concentrations. Quantities m given in the unit mol/kg water were converted to molar concentrations c with the unit mol dm^{-3} (M) by means of an empirical function

$$c/m = d_0 - Am + Bm^2 \quad (12)$$

taken from the textbook by Harned and Owen.¹¹ d_0 is the density of water, A and B are constants.

d_0 was taken as $0.9970 \text{ kg dm}^{-3}$ at 25°C and $0.9832 \text{ kg dm}^{-3}$ at 60°C .¹¹ The following values have been used for the constants A and B : [Substance, $t(^\circ\text{C})$, $A \times 10^2 (\text{kg}^2 \text{mol}^{-1} \text{dm}^{-3})$, $B \times 10^3 (\text{kg}^3 \text{mol}^{-2} \text{dm}^{-3})$], HCl, 25, 18.2, 0; HCl, 60, 18.05, 0; HBr, 25, 24.3, 0; HBr, 60, 24.4, 0; NaCl, 25, 18.3, 0; NaCl, 60, 19.3, 0; NaBr, 25, 24.8, 0.2; NaBr, 60, 26.2, 0.6; HClO₄, 25, 44.2, 1.8; HClO₄, 60, 47.0, 2.3; NaClO₄, 25, 43.6, 1.1; NaClO₄, 60, 46.9, 1.7.

The values for HCl, HBr, NaCl, and NaBr have been taken from Harned and Owen.¹¹ For NaCl and NaBr graphic extrapolation from 40°C has been employed.

For HClO₄ and NaClO₄ the constants A and B have been computed from density data found in the literature.¹²⁻²³ Extrapolation has been made from 50°C .

The molar concentration changes with temperature due to volume changes but the molality does not. To calculate the actual concentration of the measuring solutions at 60°C , two conversions have been made using eqn. (12), first from molar concentration at 25°C to molality and then back to molar concentration at 60°C .

The conversion factors for the actual measuring solutions, consisting of mixtures of up to four 3 M solutions, have been calculated by a linear combination similar to eqn. (5). Wirth *et al.*²⁴ have shown that the mean apparent molal volume for mixtures of any two of the electrolytes HClO₄, HCl, NaClO₄, and NaCl is a linear function of the two concentrations at total constant concentration within very narrow limits of error.

Treatment of literature values. The calculations were performed as follows:

i. Molalities were converted to molar concentrations (*cf.* above). *ii.* The emf's were adjusted. For older measurements the emf's were converted to absolute volts by dividing by 1.00034. If the mercury halogenide reference electrode was used, the emf was converted to the silver halogenide electrode (*cf.* below). *iii.* The standard emf E° was calculated according to eqn. (5). *iv.* The standard emf E° at total concentration 3 M was calculated by interpolation (or a short extrapolation) of the function $E^\circ = f(C_{\text{tot}})$. This was done graphically or, preferably, digitally. A second order polynomial was fitted to three adjacent points at a time and the value of this polynomial was calculated at $C_{\text{tot}} = 3$ M. In the same manner, the slope $\partial E^\circ / \partial C_{\text{tot}}$ at total concentration 3 M was calculated.

The potential difference between the mercury halogenide and silver halogenide electrodes. This difference is independent of the halogenide ion concentration. For chloride at 25°C , Pouradier and Chateau²⁵ have measured 45.50 mV (calomel positive). This agrees well with measurements by Gerke²⁶ and Brønsted²⁷ and with the difference between the standard potentials.²⁸

For bromide at 25°C , the difference between the standard potentials²⁹⁻³⁰ has been used. The mercury bromide electrode is 67.81 mV positive *versus* the silver bromide electrode.

Treatment of the measurements. The concentrations of hydrogen, halogenide, sodium, and perchlorate ions were calculated as described earlier.

The emf's were recalculated to a hydrogen partial pressure of 760 Torr, cf. below. The standard emf's were calculated by eqn. (5).

The emf's were corrected for the departure of the total concentration from 3 M by means of the simple formula $\Delta E^\circ = (C_{\text{tot}} - 3) \times \partial E^\circ / \partial C_{\text{tot}}$. The values of $\partial E^\circ / \partial C_{\text{tot}}$ for the "corner solutions" were taken from Table 2. For the measuring solutions, $\partial E^\circ / \partial C_{\text{tot}}$ was assumed to be a linear combination of the corner solutions, analogous to eqn. (7).

All the standard emf's of a measuring series were fitted at one time to eqn. (7) by means of a computer programme, Letagrop Vrid.³¹⁻³³ The programme determined the four constants $E_{\text{HClO}_4}^\circ$, E_{HX}° , $E_{\text{NaClO}_4}^\circ$, and E_{NaX}° so that the error square sum $U = \sum (E_{\text{calc.}}^\circ - E_{\text{meas.}}^\circ)^2$ was minimized. The programme also computed the standard deviation in each of these constants and in the whole material.³¹

The same constants resulted from an ALGOL-procedure.³⁴

The number of measuring points within a series has been divided between the corner standard emf's guided by the concentrations of each measuring point. For example, the number of determinations of $E_{\text{HClO}_4}^\circ$ is calculated by the formula:

$$N_{\text{HClO}_4} = \sum_1^N [\text{H}^+][\text{ClO}_4^-]/C_{\text{tot}}^2 \quad (13)$$

The concentration expression can be regarded as a weighting factor for the corner point and will be recognized in eqn. (7) also.

Correction for hydrogen partial pressure. To the measured emf was added a term $(RT/2F) \ln(p_{\text{H}_2}/760)$, where p_{H_2} is the partial pressure of hydrogen in Torr, which in turn is given by $p_{\text{H}_2} = B - p_{\text{aq}}$. The barometric pressure B was measured by a Paulin precision aneroid barometer. The vapour pressure p_{aq} of water over the measuring solution was taken as 21 Torr at 25°C for all solutions.

At 60°C the following round values of p_{aq} over the 3 M stock solutions were estimated from literature values: HClO_4 124 Torr; HCl 127 Torr; HBr 126 Torr; NaClO_4 132 Torr; NaCl 133 Torr and NaBr 131 Torr. p_{aq} was assumed to be a linear combination analogous to eqn. (7) over a composite measuring solution.

Stereo picture representation. Fig. 1 is a stereo (3-D) representation of the standard emf E° of the chloride system at 25°C as a function of both the chloride and hydrogen ion concentration. These concentrations are on the two horizontal axes while E° is on the vertical axis.

Fig. 1 has been drawn by a XY-plotter with data from a digital computer. The computer programme was based on a paper by Puckett.³⁵ Two figures are computed, to be seen by the left and the right eye, respectively. The diagonal in Fig. 1 is about 5 cm and the "computer's eyes" were 5 cm apart and 50 cm from the object.

Stereoscopy is a powerful tool for representing complicated functions. Three dimensions are usually represented on graph paper by having one dimension as parameter as in Figs. 2 and 3 of this paper. With stereoscopic representation, four dimensions may be unambiguously represented by having one dimension as parameter. Thus several surfaces may be visualized.

Computers used. The calculations were performed on a CDC 3600 computer or a CDC 3200 computer and/or an Olivetti Programma 101 programmable calculator. All steps were controlled by sample runs by hand.

RESULTS

The results for one of the measuring series, the chloride system at 25°C are given in detail to illustrate the fit between the experimental data and eqn. (7).

Small corrections to 3 M total concentration and to hydrogen partial pressure of 760 Torr were applied to the measured emf's. The standard emf E° has been calculated by eqn. (5). Finally, the material was fitted to eqn.

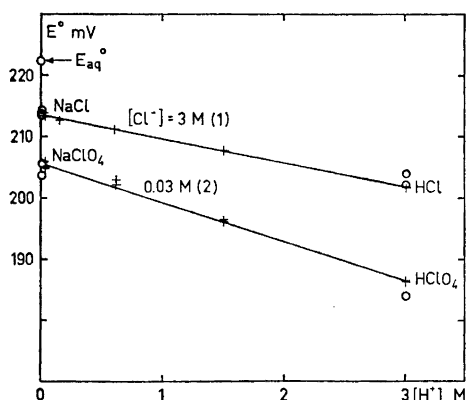


Fig. 2. The standard emf according to eqn. (5) of the chloride system at 25°C as a function of the hydrogen ion concentration. The chloride ion concentration was held constant at 0.03 and 3 M, respectively. The total concentration was held constant at 3 M by means of sodium ions and perchlorate ions. The straight lines were computed from eqn. (7). The four constants (E°) of eqn. (7) were computed to give the best fit to the whole material. Notations: + measured points from this work; \circ recalculated data from literature, taken from Table 2.

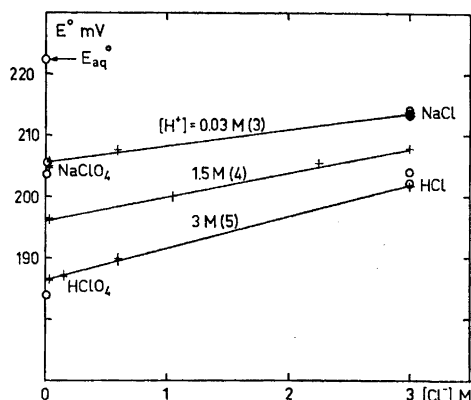


Fig. 3. The standard emf according to eqn. (5) of the chloride system at 25°C as a function of the chloride ion concentration. The hydrogen ion concentration was held constant at 0.03, 1.5, and 3 M, respectively. Otherwise as in Fig. 3.

(7) to yield the best values of the constants $E_{\text{HClO}_4}^\circ$, E_{HX}° , $E_{\text{NaClO}_4}^\circ$, and E_{NaX}° . For details see p. 881. These constants are called the standard emf's of the corner points (cf. Fig. 1).

The measured E° values are to be found in Figs. 2 and 3 as crosses together with straight lines calculated from eqn. (7). As can be seen, the material is well described by these straight lines, not only along the edges but also in the interior of the space. No systematic deviation can be seen. Literature determinations are marked with rings for comparison.

The results from the four measuring series are summarized in Table 1. For each corner point, a nonintegral number of determinations has been given. This is because the measurements have been divided between the corner points on foundation of the concentrations of the measurements. For details, see p. 881.

The measurements were performed during the course of a year. Somewhat different techniques and materials were used but no systematic trends could be found.

Literature data. Measuring series like those in Fig. 4 were chosen from literature. Suitable data are comparatively rare since many measurements have been done with liquid-junction cells and only few at sufficiently high total concentration.

Table 1. Summary of the measurements of the standard emf's of the corner points (i.e. the constants $E_{\text{HClO}_4}^\circ$, E_{HCl}° , $E_{\text{NaClO}_4}^\circ$, and E_{NaCl}° of eqn. 7).

System	Temp. (°C)	Corner point	E° (mV)	Standard deviation (mV)	Number of determinations
Chloride	25	HClO ₄	186.3	0.1	12.2
		HCl	201.8	0.2	6.3
		NaClO ₄	205.5	0.1	9.3
		NaCl	213.4	0.2	6.1
		Total	—	0.3	34
Chloride	60	HClO ₄	158.6	0.4	3.0
		HCl	180.8	0.5	2.7
		NaClO ₄	175.9	0.3	5.4
		NaCl	190.7	0.6	1.9
		Total	—	0.7	13
Bromide	25	HClO ₄	28.6	0.2	7.0
		HBr	36.8	0.2	9.9
		NaClO ₄	50.8	0.3	4.6
		NaBr	51.1	0.2	9.5
		Total	—	0.6	31
Bromide	60	HClO ₄	3.5	0.3	6.0
		HBr	17.1	0.3	8.1
		NaClO ₄	24.2	0.3	6.6
		NaBr	30.2	0.3	7.3
		Total	—	0.8	28

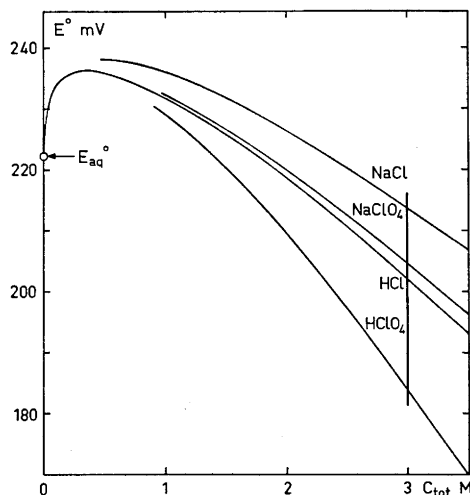


Fig. 4. The standard emf according to eqn. (5) of the cell $\text{Pt}(\text{H}_2)|\text{H}^+, \text{Cl}^-|\text{Ag}, \text{AgCl}$ at 25°C as a function of the total concentration in four different electrolytes. In the perchloric acid and sodium perchlorate solutions the chloride ion content was 0.01 mol kg⁻¹. In the sodium perchlorate and sodium chloride solutions the hydrogen ion content was 0.01 mol kg⁻¹. References: HClO₄,³⁶ HCl,³⁷ NaClO₄,³⁶ NaCl.⁴⁰⁻⁴²

Table 2. Survey of literature determinations of the standard emf's of the corner points (i.e. the constants $E_{\text{HClO}_4}^\circ$, E_{HCl}° , $E_{\text{NaClO}_4}^\circ$, and E_{NaCl}° of eqn. 7).

Ref.	System	Temp. (°C)	Corner point	Reference electrode	m_{H^+} (mol kg ⁻¹)	m_{Cl^-} (mol kg ⁻¹)	E° (mV) at $C_{\text{tot}} = 3 \text{ M}$	$\frac{\partial E^\circ}{\partial C_{\text{tot}}}$ (mV M ⁻¹) at $C_{\text{tot}} = 3 \text{ M}$		
36	Chloride	25	HClO ₄	Hg ₂ Cl ₂	1-6	0.01	184.4	26.8		
37			HCl	AgCl	0.004-4	0.004-4	202.2	17.7		
38			HCl	AgCl	0.005-9.3	0.005-9.3	204.0 ^a	21.8		
36			NaClO ₄	Hg ₂ Cl ₂	0.01	0.01	205.9	15.5		
39			NaClO ₄	AgCl	b	10 mM ^b	203.6	19.4		
38, 40, 41			NaCl	Hg ₂ Cl ₂ , AgCl	0.001-6 ^c	1-6 ^c	213.5	13.3		
42			NaCl	AgCl	0.01	0.01-3.01	213.7	14.1		
43			NaCl	Hg ₂ Cl ₂	0.001-0.01	0.5-4.0	214.2	13.6		
37			Chloride	60	HCl	AgCl	0.004-4	0.004-4	180.9	18.2
42					NaCl	AgCl	0.01	0.01-3.01	190.5	14.3
36	Bromide	25	HClO ₄	Hg ₂ Br ₂	1-6	0.01	24.6	30.0		
44			HBr	AgBr	0.001-3	0.001-3	34.5 ^d	25.6		
45			HBr	AgBr	0.06-5.6	0.06-5.6	37.1 ^a	23.8		
36			NaClO ₄	Hg ₂ Br ₂	0.01	0.01	50.8	17.3		
46			NaBr	AgBr	0.01	0.01-3.01	53.5	16.8		
47			NaBr	AgBr	0.01	0.01-3.01	51.5	17.6		
47			NaBr	AgBr	0.1	0.10-3.10	51.2	17.6		
45			Bromide	60	HBr	AgBr	0.06-5.6	0.06-5.6	17.0 ^a	23.8
46					NaBr	AgBr	0.01	0.01-3.01	37.3	16.3
48			Chloride	25	I→0	AgCl	→0	→0	222.24 ^e	
48	60	I→0		AgCl	→0	→0	195.44 ^e			
49	Bromide	25	I→0	AgBr	→0	→0	71.15 ^e			
49		60	I→0	AgBr	→0	→0	48.65 ^e			

^a Spread from a smooth curve ± 1 mV.

^b The solution was 1, 2, or 3 M NaClO₄ with 10 mM NaCl. Varying amounts of the sodium ion contents of the solution were exchanged by hydrogen ions. The results were extrapolated to $[\text{H}^+] = 0$.

^c The total concentration of NaCl and HCl was constant = 1, 3, 4, 5, or 6 m. The linear relationship between standard emf and molality of HCl has been extrapolated to $[\text{H}^+] = 0$.

^d The quantities used for calculation were: molality of HBr, activity coefficients, and standard emf.

^e The standard emf E_{aq}° .

The extracted values are to be found in Table 2. The agreement between values from different sources is poor.

For comparison purposes, the standard emf E_{aq}° (eqn. 3b) at infinite dilution in water has been introduced in Table 2 and Figs. 2–4. The values^{48,49} have been converted from molal to molar scale.

DISCUSSION

The agreement between this work and literature is fair with one exception: the measurements in sodium bromide at 60°C are 7 mV lower than the measurements by Harned and Hamer⁴⁶ in 1933. The reason for this poor agreement has not been elucidated, but it may be noted that the great importance of the absence of, for example, iodide^{4–6} was not recognized in 1933. Measurements in 1926 by Harned and James⁴⁷ at 25°C resemble the present measurements. Extended purification of the sodium bromide in this laboratory led to consistent results.

The influence of the solubility of silver halogenides has been neglected. The dominating species dissolved in the chloride system is AgCl_4^{3-} , with an estimated solubility of 3 mM in 3 M NaCl at 25°C.⁵⁰ The corresponding figure for AgBr_4^{3-} is 15 mM in 3 M NaBr.

The complex formation with silver has three consequences: *i.* The free chloride concentration is diminished. The chloride ion concentration in eqn. (5) should be corrected. *ii.* The solvent is not a single mixture of the four corner electrolytes. *iii.* There is a small liquid-junction potential at the reference cell-siphon interface.

The results of this work may be summarized in a few comments concerning the ionic medium method. What is reported here concerning emf's or standard emf's could in many instances be translated to other measured properties or equilibrium constants.

i. Investigate the medium effects in a model system. Measure the actual cell reaction as a similar exchange of ions is carried out or measure a similar cell reaction as the actual exchange is carried out. The conditions should be chosen where no association or dissociation occurs so that the measured effects are entirely due to medium effects. Determine the slope $\partial E^{\circ}/\partial C$ and compute the medium effect ΔE° in the actual system, when an exchange of ΔC is carried out:

$$\Delta E^{\circ} = \Delta C (\partial E^{\circ}/\partial C) \quad (14)$$

Under favourable conditions, the measured effects can be corrected for the medium effects.

Further, one important conclusion can be drawn from eqn. (14). Since E° is linear in C , the slope $\partial E^{\circ}/\partial C$ is constant and for a small exchange ΔC the medium effect ΔE° will be negligible.

The order of magnitude of the slope of Figs. 2 and 3 is 5 mV M⁻¹, corresponding to $\alpha=0.04$. Numerous examples found in literature^{3,51,56} also give slopes of this magnitude.

ii. Avoid too high concentration of inert salt. Several examples in Harned's and Owen's book³ show that the slope α is largely independent of C_{tot} provided

C_{tot} is larger than 0.3 M. From this point of view, C_{tot} should be chosen higher than 0.5 M only if there is a need for any species reaching a higher concentration. The impurity level grows with the concentration of neutral salt.

iii. *Consider the variations in total concentration.* Small variations in total concentration must always be considered. The errors from these variations depend on the slope of the standard emf with total concentration ($\partial E^\circ/\partial C_{\text{tot}}$). From Table 2 and Fig. 4 it appears that this slope is of the order of -20 mV M^{-1} at 3 M total concentration and approaches zero at around 0.5 M. At total concentrations below 0.1 M the activity coefficients may be roughly calculated from the Debye-Hückel limiting law.⁵⁷ Derivation and combination with eqns. (3) and (5) give for 1-1 electrolytes at 25°C:

$$\frac{\partial E^\circ}{\partial C_{\text{tot}}} = \frac{30}{\sqrt{C_{\text{tot}}}} \text{ (mV M}^{-1}\text{)} \quad (15)$$

These slopes are too large to be visualized in Fig. 4. Their high value is the main reason for using ionic media of high concentration. Preferably, the total concentration should be about 0.5 M. From measurements on systems other than hydrochloric and hydrobromic acid^{3,58} it can be concluded that very little is gained by increasing the total concentration beyond 1 M.

iv. *Make a suitable choice of reference electrode.* The electrode reaction should contain as few ionic species as possible and preferably ions of the same charge as the ion varied during the investigation. This is in accord with Brønsted's specific ion interaction theory,⁵⁹ which in short says that an ion is influenced by ions of opposite charge and not by ions of the same charge.

Two specific examples may illustrate this point: Zielen and Sullivan⁵¹ measured five different cells with only cationic species involved in the cell reaction. When the sodium ions of the 2 M sodium perchlorate medium were exchanged by hydrogen ions, the observed linear slopes of the standard emf's were found to be smaller than the slopes found in this paper.

Ginstrup and Leden^{60,61} measured cells with only the two anionic species PtX_6^{2-} and PtX_4^{2-} involved in the electrode reaction. When the sodium ions of the 3 M medium were exchanged by hydrogen ions the linear slope observed was -2 mV M^{-1} . When the perchlorate ions of the medium were exchanged by halogenide ions, the magnitudes of the slopes observed were less than 1 mV M^{-1} .

These two examples show that the ions are influenced mostly by ions of the opposite charge. By a suitable choice of cell reaction (by taking a suitable reference electrode) the slope of the standard emf may be diminished.

v. *Avoid liquid-junction cells.* The foregoing discussion deals entirely with cells without liquid-junction. In practice, potentiometric cells often contain one reference compartment with fixed solution composition and one compartment with variable concentrations.

If the sodium ions of sodium perchlorate are exchanged by hydrogen ions, the resulting liquid-junction potential E_j has been shown^{39,62,63} to be linear in the hydrogen ion concentration. The slope was found to be -17 mV M^{-1} at total concentration 3 M, -28 mV M^{-1} at 2 M and -63 mV M^{-1} at 1 M. This is the reason for using so high total concentration as 3 M in the majority of investigations.

In contrast to the medium effects, the liquid-junction potential is not thermodynamically defined. It depends on the construction of the liquid-junction and may thus be difficult to reproduce.

Biedermann and Sillén⁶² have attempted to separate the medium effects and the liquid-junction potential. They used a liquid-junction cell with 3 M sodium perchlorate and exchanged up to 0.6 M of the sodium ions by hydrogen ions. As measuring electrode they used a number of cation-sensitive electrodes or silver-silver chloride or silver-silver bromide electrodes.

With all the cation-sensitive electrodes the same slope was observed, *viz.* -17 mV M^{-1} . This was interpreted as change of the liquid-junction potential, *cf.* above. The cations were not affected by the cationic exchange of sodium ions for hydrogen ions.

With the two anion sensitive electrodes, the slope observed was -24 mV M^{-1} . This could be interpreted as the same change of liquid-junction potential plus medium effects acting on the chloride or bromide ions of -7 mV M^{-1} . This view is strongly supported by the good agreement with the slope of line 2 in Fig. 3, *viz.* -6.4 mV M^{-1} , or the corresponding slope in the bromide system, *viz.* -7.4 mV M^{-1} .

One disadvantage of diffusion-free cells is the necessity of working batchwise, when the chemicals of the two electrodes react with each other as in cell (1). The solutions both in the two half cell compartments and in the siphon have to be exchanged. With modern ion-specific electrodes this is of no concern because both electrodes may be situated in the same solution. For example, Zielen and Sullivan⁵¹ used a glass electrode as reference electrode with great advantage.

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