Equitransferent Salt Bridge for Elimination of the Diffusion Potential Compared with Saturated Potassium Chloride Salt Bridge

K. V. GROVE-RASMUSSEN

Department of Inorganic Chemistry, Royal Danish School of Pharmacy, Copenhagen, Denmark

In a previous paper [1] it has been pointed out that an equitransferent solution of potassium chloride + potassium nitrate will probably be better suited for elimination of the diffusion potential than the saturated potassium chloride solution most frequently used for this purpose. The advantage by using an equitransferent reference solution * is that a convergence of the diffusion potential towards zero is obtained on increasing dilution of the test solution. Otherwise the diffusion potential will include a factor due to the difference of the ion mobilities in the reference solution as it is actually possible to regard the diffusion potential as consisting of two parts, one of which being due to differences between cation and anion mobilities in the test solution, and the other to differences between cation and anion mobilities in the reference solution. The latter part will be equal to zero if the reference solution is equitransferent. If this is not the case, it will increase proportionally with the logarithm of the degree of dilution. It will appear from the present paper that this part of the diffusion potential amounts to approximately 2, 3 and 4 mV for a saturated potassium chloride solution when the concentrations of the test solution are 0.1, 0.01 and 0.001 normal, respectively. This part of the diffusion potential has often been neglected because of wrong assumptions regarding the transference number of potassium chloride. However, this will not always involve that results obtained by the use of saturated potassium chloride on the basis of such assumptions include errors of the order of magnitude indicated, as in

---

* The word reference solution is used in this paper as a common designation for salt bridge and reference electrode solution.

practice the said part of the diffusion potential will very often occur twice with opposite signs in the experiments so that the error is cancelled out. The error will only be discernible in cases where a test solution is compared with a standard solution the conductance of which materially differs from that of the test solution, or where it is attempted to make extrapolations towards infinite dilution.

Another reason for trying to make the diffusion potentials as small as possible is, however, also that as a rule they are not particularly well defined. Even if it is possible to obtain comparatively reproducible results by observing particular experimental conditions in making the boundary, great diffusion potentials will always be a source of uncertainty as it may be taken for granted that the error which may be involved in an experiment by the diffusion potential must be proportional to the magnitude of same. This should hold in cases where it is tried to calculate the diffusion potential as well as in cases where two diffusion potentials of the same order of magnitude but of opposite directions are anticipated to cancel.

COMPUTED DIFFUSION POTENTIALS

The computations have been made on the basis of Henderson's formula. This formula has been deduced on the assumption of certain ideal conditions of which it can definitely be said that they do not exist in actual practice. The deviations occurring because these ideal conditions are not fulfilled can hardly be expressed by mathematical formulae. Consequently no absolute validity can be attributed to calculated diffusion potentials, they can only be regarded as an orientation about their order of magnitude.

In accordance with Guggenheim and Schindler [2] the ideal values for ion mobilities and activities have been used as the basis for the computations in the present paper. By this procedure the calculations are considerably simplified, and numerous table references are saved as compared with another procedure sometimes used (Bjerrum and Unmack [3]) to the effect of employing the stoichiometric ion concentrations in connection with the ion mobilities at the total ion concentration in question.

According to Henderson's formula the diffusion potential: reference solution/test solution is:

$$E_j = \frac{R\,T}{F\,\log e} \cdot \frac{(U - V) - (U_r - V_r)}{(\overline{U} + \overline{V}) - (\overline{U_r} + \overline{V_r})} \, \log \frac{(\overline{U_r} + \overline{V_r})}{(\overline{U} + \overline{V})} \tag{1}$$
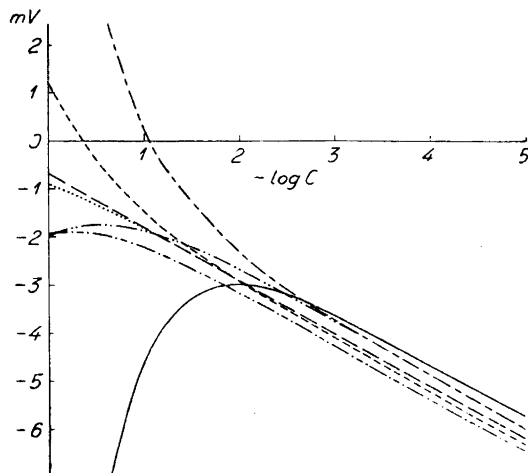
Fig. 1. The diffusionpotential: reference solution/test solution with 4.1 N potassium chloride as reference solution. c = molarity of test solution.

————————	HCl
— — — — —	$NaCl$
— — — —	KCl
— – — —	$NaOH$
··························	$KCl + KNO_3$
—— ·· —— ··	Na_2SO_4
—— · — · ——	CH_3COONa

where

$$U = \sum_t u_i\, c_i \qquad\qquad V = \sum_t v_j\, c_j$$

$$\overline{U} = \sum_t u_i\, z_i\, c_i \qquad\qquad \overline{V} = \sum_t v_j\, z_j\, c_j$$

$$U_r = \sum_r u_i\, c_i \qquad\qquad V_r = \sum_r v_j\, c_j$$

$$\overline{U}_r = \sum_r u_i\, z_i\, c_i \qquad\qquad \overline{V}_r = \sum_r v_j\, z_j\, c_j$$

u_i and v_j being mobilities of cations and anions, respectively, z_i and z_j their valence (taken positive) and c_i and c_j their molarities. Indices t and r refer to the test solution and reference solution, respectively. A positive value of E_j is concomitant with a positive test solution as compared with the reference solution.

If the values (taken from Harned and Owen [4]) for the ion mobilities of 4.1 N saturated potassium chloride and 3.6 N equitransferent solution of KCl + KNO$_3$, respectively, are inserted, the results obtained at 25° C are:
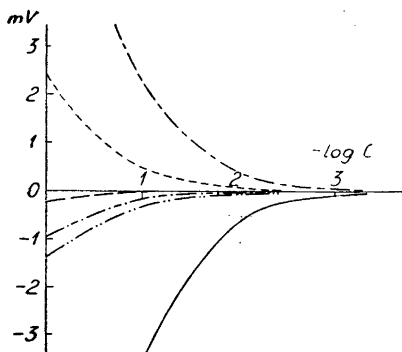
Fig. 2. The diffusion potential: reference solution/test solution with 3.6 N equitransferent solution of KCl + KNO₃. c = molarity of test solution.

————————— HCl

— — — — — — NaCl

—— —— —— KCL

—— — —— — NaOH

——··——·· Na₂SO₄

—— ·—· —— CH₃COONa

for 4.1 N KCl

$$E_j = \frac{0.05916 \; ((U - V) + 11.56)}{(\overline{\overline{U}} + \overline{\overline{V}}) - 614.4} \log \frac{614.4}{\overline{\overline{U}} + \overline{\overline{V}}}$$

or

$$E_j = \frac{0.05916 \; ((U - V) + 11.56) \; (2.7884 - \log \; (\overline{\overline{U}} + \overline{\overline{V}}))}{(\overline{\overline{U}} + \overline{\overline{V}}) - 614.4} \tag{2}$$

and for 3.6 N equitransferent solution of KCl + KNO₃

$$E_j = 0.05916 \; \frac{U - V}{(\overline{\overline{U}} + \overline{\overline{V}}) - 530.7} \log \frac{530.7}{(\overline{\overline{U}} + \overline{\overline{V}})}$$

or

$$E_j = \frac{0.05916 \; (U - V) \; (2.7248 - \log \; (\overline{\overline{U}} + \overline{\overline{V}}))}{(\overline{\overline{U}} + \overline{\overline{V}}) - 530.7} \tag{3}$$

Equations (2) and (3) are used for calculation of the curves in Figs. 1 and 2 giving a comparison of the diffusion potentials between a number of solutions and the two reference solutions under consideration.

In the calculations the following ion mobilities are used (after Harned and Owen [4]):

H 349.8; Na 50.11; K 73.52; Cl 76.34; OH 197.6; CH₃COO 40.9; NO₃ 71.44; ½SO₄ 80.

When the reference solution is 4.1 N KCl (Fig. 1), the diffusion potentials for the higher concentrations of the test solution assume values characteristic of the electrolytes concerned. With increasing dilution the curves take a
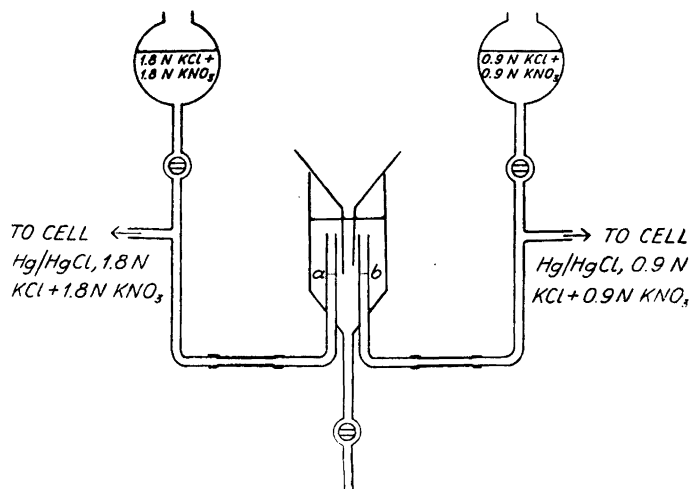
*Fig 3. Experimental arrangement. a and b boundaries corresponding
to equation (4).*

uniform course, the numerical value of the diffusion potential increasing
proportionally with the negative logarithm of the concentration.

If on the other hand the reference solution is a 3.6 N equitransferent
mixture of KCl + KNO$_3$ (Fig. 2), the diffusion potential for the higher concen-
trations will continue to be characteristic of the electrolytes concerned, but
with increasing dilution the curves will approach the abscissa asymptotically.

EXPERIMENTS

Measurements have been made in cells of the type:

Hg | HgCl, 1.8 N KCl + 1.8 N KNO$_3$ | test solut. | 0.9 N KCl + 0.9 N KNO$_3$, HgCl | Hg

a
b
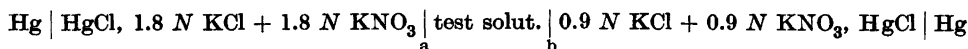
The diffusion potentials at a and b are not measurable, but if the difference
between the normal potentials of the two calomel electrodes is known, it is
possible by means of that difference to determine experimentally the differ-
ence between the two diffusion potentials. As the latter difference can also be
computed by means of Henderson's formula, this affords a possibility of check-
ing the results obtained by means of the formula.

If the diffusion potentials at a and b are denoted by $E_{3.6}$ and $-E_{1.8}$, $E_{3.6}$
will be given by equation (3) while the corresponding equation for $E_{1.8}$ will be:

$$E_{1.8} = \frac{0.05916 \; (U - V) \; (2.4237 - \log \; (\overline{U} + \overline{V}))}{(\overline{U} + \overline{V}) - 265.3} \tag{5}$$

The experimental arrangement is shown in Fig. 3. The two calomel electrodes were placed in a thermostat at 25° C. The remaining part of the apparatus was placed outside the thermostat. The room temperature was 25° C $\pm$ 0.3° C. The measurements were made on a measuring bridge with a mirror galvanometer as zero instrument. Readings were taken immediately after establishment of the boundaries. The measuring apparatus permitted readings with an accuracy of about 0.02 mV; for the weakest solutions it was, however, about 0.05 mV.

Before measurement the vertical tubes intended for the boundaries were washed with the pertinent reference solutions, and the test solution was filled in the vessel. In order to obtain cylindrical symmetry, the boundaries were established, as in previous experiments [1], by compression and subsequent expansion of the rubber tubing shown in the illustration so that the boundaries moved a few cms downwards in the tubes. Then the test solution rendered impure by mixture with the reference solution was removed from the vessel, and replaced by new test solution. Immediately afterwards the reading was taken. The results of the measurements are compared with the computed values of $E_{1.8} - E_{3.6}$ in Table 1.

The difference between the normal potentials of the two electrodes was determined from measurements in equimolar mixtures of potassium chloride + potassium nitrate. At the concentrations 0.001, 0.01, and 0.1 the values 19.91, 19.93, and 19.94, mV respectively, were obtained. The mean value 19.93 was used for determination of the experimental value of $E_{1.8} - E_{3.6}$, the measured potential difference being subtracted from the said figure.

It will appear from the table that there is no complete agreement between the computed and the measured values of $E_{1.8} - E_{3.6}$, a fact which may partly find its explanation in that the ideal conditions required for Henderson's formula are not satisfied. But apart from the results obtained with 1 N test solutions, there is a reasonable agreement for the other solutions. The experiments, moreover, confirm, as previously mentioned, that computed values of the diffusion potentials can only be in the nature of an orientation about their order of magnitude.

ON THE USE OF BJERRUM'S EXTRAPOLATION METHOD

The quantity $E_{1.8} - E_{3.6}$ dealt with in the preceding section is of particular interest as it may be compared with the so-called Bjerrum extrapolation. The extrapolation method for evaluation of the diffusion potential proposed by Bjerrum [5] in 1905 is based on the assumption that the diffusion potential of an arbitrary dilute solution and a 1.75 N potassium chloride solution will

Table 1. *Comparison of computed and measured values of* $E_{1.8} - E_{3.6}$. *mV.*

| | Measured potential difference | Computed values | | | Experimental values of $E_{1.8} - E_{3.6}$ |
		$E_{1.8}$	$E_{3.6}$	$E_{1.8} - E_{3.6}$	
1 N HCl	30.30	-20.71	-14.74	-5.97	-10.37
0.1 $-$ $-$	22.80	-5.77	-3.63	-2.14	-2.87
0.01 $-$ $-$	20.46	-1.11	-0.64	-0.47	-0.53
0.001 $-$ $-$	19.93	-0.17	-0.09	-0.08	0
1 N NaOH	12.90	14.76	10.20	4.56	7.03
0.1 $-$ $-$	18.25	3.74	2.30	1.44	1.68
0.01 $-$ $-$	19.70	0.67	0.38	0.29	0.23
0.001 $-$ $-$	19.95	0.10	0.05	0.05	-0.02
1 N NaCl	18.64	3.60	2.39	1.21	1.29
0.1 $-$ $-$	19.63	0.81	0.49	0.32	0.30
0.01 $-$ $-$	19.93	0.14	0.08	0.06	0
0.001 $-$ $-$	19.90	0.019	0.011	0.008	0.03
1 N KCl	19.38	0.36	0.24	0.12	0.55
0.1 $-$ $-$	19.84	0.83	0.050	0.033	0.09
0.01 $-$ $-$	19.96	0.014	0.0080	0.006	-0.03
0.001 $-$ $-$	19.92	0.0020	0.0011	0.0009	0.01
1 N CH$_3$COONa	19.97	-1.45	-0.95	-0.50	-0.04
0.1 $-$ $-$	20.01	-0.31	-0.018	-0.13	-0.08
0.01 $-$ $-$	19.95	-0.05	-0.03	-0.02	0.02
0.001 $-$ $-$	19.95	-0.007	-0.004	-0.003	0.02
0.5 M Na$_2$SO$_4$	21.53	-1.37	-0.98	-0.39	1.60
0.1 $-$ $-$	20.35	-0.50	-0.31	-0.19	-0.42
0.01 $-$ $-$	19.98	-0.09	-0.05	-0.04	-0.04
0.001 $-$ $-$	19.95	-0.014	-0.007	-0.007	-0.02

be double the quantity of the diffusion potential of the same solution and a
3.5 N potassium chloride solution. This is used in practice, for example in
a hydrogen ion measurement by measurements with 1.75 and 3.5 N
potassium chloride solutions as salt bridges. The difference between the two
measurements is put equal to the diffusion potential and used as a correction
for the measurement. The method was proposed on the assumption that a
potassium chloride solution is approximately equitransferent, and it is charac-
teristic that the extrapolations found decrease in magnitude with increasing

dilution of the test solution. As it is elucidated by the present findings this does not mean that the diffusion potential decreases with increasing dilution, but has its explanation in that the parts of the diffusion potentials $E_{1.75}$ and $E_{3.5}$ which are due to nonequitransference in the reference solutions are of the same order of magnitude. This again means that the experimental part of the present paper cannot be ascribed any significance for the purpose of an evaluation of the question whether the reference solutions used in the experiments are equitransferent. The assumption that this is approximately the case in an equimolar mixture of KCl + KNO$_3$ is, so far, exclusively based upon the paper by the present author [1] previously mentioned,

With regard to the applicability of Bjerrum's extrapolation for evaluation of the diffusion potential the above considerations imply that on condition of an equitransferent salt bridge — and only on this condition — the extrapolation will express the order of magnitude of the diffusion potential to the extent originally stated by Bjerrum [3,5] as it appears from the following quotation: ". . . es ist erlaubt anzunehmen . . ., dass man . . . aus dem Unterschiede zwischen den mit halbgesättigter und mit gesättigter Chlorkaliumlösung gefundenen Werten auf die Grössenordnung der Fehler schliessen darf, die man begeht, wenn man annimmt, dass eine gesättigte Chlorkaliumlösung das Diffusionspotential eliminiert. Und ich glaube weiter, dass man . . . durch die kleine Extrapolation etwas bessere Werte bekommen kann."

As previously mentioned Bjerrum's extrapolation will, however, be of value in many cases even if the salt bridge is not completely equitransferent. This will be the case for example if p$_H$ is measured in a given solution on the basis of a standard solution of the same conductance. Here the extrapolation will not be a function of the absolute magnitude of the diffusion potential, but it will be a measure of the error committed by not making allowance for the diffusion potential.

SUMMARY AND CONCLUSION

The diffusion potentials of some dilute solutions with saturated KCl and equitransferent 3.6 N KCl + KNO$_3$, respectively, as reference solutions are computed. With saturated KCl the diffusion potential increases with extreme dilution of the test solution proportionally with the logarithm of the degree of dilution. With equitransferent reference solution the diffusion potential converges towards zero on dilution of the test solution.

Some computed and experimental values of the quantity: $E_{1.8}$—$E_{3.6}$ for equitransferent reference solution are compared.

7

Bjerrum's extrapolation method for determination of diffusion potentials affords an orientation about the order of magnitude of the diffusion potential on condition that the reference solution is equitransferent, and only on this condition.

REFERENCES

1. Grove-Rasmussen, K. V. *Acta Chem. Scand.* **3** (1949) 445.
2. Guggenheim, E. A., and Schindler, T. D. *J. Phys. Chem.* **38** (1934) 533.
3. Bjerrum, N., and Unmack, A. *Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd.* **9** (1929) 1.
4. Harned, H. S., and Owen, B. B. *The physical chemistry of electrolytic solutions.* New York (1943).
5. Bjerrum, N. *Z. physik. Chem.* **53** (1905) 428.