Figure 5. Relationship between measured cell voltage ($V/\Delta\Phi$) and the ratio of the short-circuit response to the internal cell resistance (α).

reality with cells connected in series.

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Verification of the Approximate Equitransference of the Aqueous Potassium Chloride Salt Bridge at High Concentrations

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Use of chlorine electrodes in the transference cell Pt–Ir|Cl$_2$|KCl aq, m_2||KCl aq, m_1|Cl$_2$|Pt–Ir, whose electromotive force was measured at 298.15 K at various KCl molalities m_2 with fixed m_1, allowed the cation and the water transference numbers, τ_{K^+} and τ_w, respectively, to be determined up to the KCl saturation molality. The observed τ_{K^+} and τ_w values are in good accord with the overall and single-ion primary-hydration numbers of KCl. It turns out that τ_{K^+} is substantially constant at 0.486 in the usual molality range employed for KCl as a salt bridge in electrochemistry and electroanalysis. This imperfect equitransference of the popular, aqueous KCl salt bridge causes imperfect efficacy of the latter in minimizing liquid junction potentials and may, in turn, enlarge the uncertainty limits of analysis results. It is, thereby, suggested that when high-ionic-strength, strongly acidic or strongly alkaline samples are submitted to pH-metric, pIon-metric, or titrimetric analysis, the KCl salt bridge be replaced by the closely equitransferent (τ_{Cs^+} = 0.502) CsCl salt bridge, whose saturation molality is, furthermore, as high as 11.3 mol kg^{-1} at 298.15 K.

INTRODUCTION

Aqueous potassium chloride (KCl) at concentrations of 0.001, 0.01, 0.1, and 1 mol dm^{-3} is well-known as the standard material for reference in conductometric determinations. Yet, its greatest renown and popularity came from its applications as a salt bridge in pH-metric, pIon-metric, and titrimetric determinations where, however, it is normally used at higher concentrations (*1, 2*), e.g. 1, 1.75, 3.5, 4, and 4.804 mol kg^{-1}, the last figure denoting the saturated KCl at 298.15 K, so often associated with the equally popular Hg$_2$Cl$_2$ (calomel) reference electrode. The present widespread choice of aqueous KCl relies on the fact that it possesses to a good degree the essential qualifications of a salt bridge in terms of a *concentrated equitransferent* binary salt, a principle that rests on the evidence provided chiefly by Bjerrum's (*2, 3*) and Guggenheim's (*2, 4–6*) experiments.

The saturation concentration of KCl, though good, is not comparable with that of other equitransferent salts such as CsCl (11.3 mol kg^{-1} at 298 K) and constitutes a limitation to its use when in contact with sample solutions of high ionic strengths, especially strongly acidic or strongly basic.

It is, however, surprising and disturbing that the KCl equitransference, which also is good but not excellent, was hitherto ascertained only for the range of low concentrations, leaving the range from 1 mol kg^{-1} to saturation still unverified, in spite of the widespread and blindly confident use of KCl, taking for granted that KCl would become exactly equitransferent upon approaching its saturation concentration.

Such a verification is desirable and overdue, and it prompted the present investigation. The experimental basis was furnished by measuring the electromotive force (emf) E of the following concentration cell with transference

$$Pt-Ir|Cl_2|KCl\ (m_2)\|KCl\ (m_1)|Cl_2|Pt-Ir \qquad (1)$$
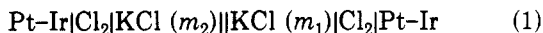
at various molalities, m_2 (up to KCl saturation), with fixed m_1. The chlorine electrodes are particularly suited to use in concentrated chloride solutions, and were chosen here to eliminate the drawback of the notoriously increasing solubility of the alternative AgCl or Hg_2Cl_2 electrodes in KCl with increasing concentration of the latter, a feature that may have discouraged this type of investigation prior to the availability of handleable and reliable chlorine electrodes (7).

Shedlovsky and MacInnes made accurate emf measurements on the parallel cell

$$Ag|AgCl|KCl\ (m_2)\|KCl\ (m_1)|AgCl|Ag \qquad (2)$$
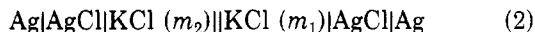
which has the same emf expression of cell 1, in the lower range of KCl concentrations (8). As a matter of fact, the present measurements and Shedlovsky and MacInnes's prove physically consistent; therefore, the two sets of measurements have been aggregated into one set to cover the whole concentration range in the further processing.

EXPERIMENTAL SECTION

Stokes and Levien's design (9–11) was used for cell 1, with appropriate modifications to allow entry and exit of chlorine gas. The structure of the chlorine electrodes was as described earlier by Faita, Longhi, and Mussini (7), the metal support chosen for the Cl_2/Cl^- redox system being a Pt-Ir 45% alloy on tantalum base, which was not corroded by the aggressive Cl_2/Cl^- couple. Chlorine was diluted with nitrogen at 1:99 pressure ratio, in order to make the occurrence of the reaction of Cl_2 with Cl^- to form Cl_3^- negligible. The KCl solutions were prepared by weight from reagent grade KCl and redistilled deionized water. The temperature control and the potentiometric measuring apparatus were exactly as described earlier (12).
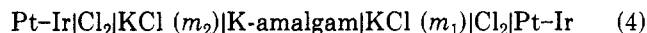
RESULTS AND DISCUSSION

The values of the emf, E, measured at 298.15 K at various KCl molalities (m_2) with fixed $m_1 = 0.100\,58$ mol kg^{-1}, are quoted in Table I.
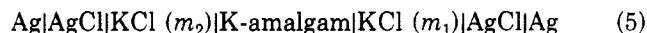
The basic thermodynamic equation linking E with the relevant transference parameters is (13–15)

$$dE/dE_{max} = \tau_{K^+} - \tau_w M_w m_2 \qquad (3)$$

where $M_w = 0.018$ kg mol^{-1} is the molar mass of water, τ_{K^+} and τ_w are respectively the transference numbers of the K^+ ion and of the water, and are defined as moles of species transferred per faraday through the cell from the anode (negative terminal) to the cathode (positive terminal) (16–20), and E_{max} is the emf of the corresponding concentration cell without transference, i.e.

$$Pt-Ir|Cl_2|KCl\ (m_2)|K\text{-amalgam}|KCl\ (m_1)|Cl_2|Pt-Ir \qquad (4)$$

or

$$Ag|AgCl|KCl\ (m_2)|K\text{-amalgam}|KCl\ (m_1)|AgCl|Ag \qquad (5)$$

The emf E_{max} need not be measured because it can be readily calculated by means of the equation

$$E_{max} = (2\ RT/F)\ \ln\ (m_2\gamma_2/m_1\gamma_1)_{KCl} \qquad (6)$$

where R is the gas constant, F is Faraday's constant, T is the absolute temperature, and accurate values for the required mean molal activity coefficients γ for KCl are available from the literature (10).

It is found that the E vs E_{max} relationship is best represented by the following straight line:

$$E = bE_{max} \qquad (7)$$

whose slope $b = dE/dE_{max} = 0.48839 \pm 0.00030$ turns out to be close to the infinite-dilution value of the transference number of K^+, $\tau_{K^+}^\circ = 0.48907 \pm 0.00007$. This result indeed constitutes a good first-stage confirmation for aqueous KCl as having an approximately constant equitransference over

Table I. Cation Transference Number (τ_{K^+}) and Water Transference Number (τ_w) for Aqueous KCl at Various Molalities m_2 (with Corresponding Mean Molal Activity Coefficients γ_2 (10)), as Obtained from the emf (E) of the Transference Cells (1) and (2) Processed through Equations 3 and 6–9, at 298.15 K[a]

$m_2/(mol\ kg^{-1})$	$(\gamma_2)_{KCl}$	E/V	τ_{K^+}	τ_w
0[b]	1.000[b]		0.4891[b]	-0.082[b]
0.005 023[c]	0.928[c]	-0.070 765[c]	0.4888	-0.082
0.010 035[c]	0.902[c]	-0.054 025[c]	0.4887	-0.082
0.010 085[c]	0.902[c]	-0.053 895[c]	0.4887	-0.082
0.020 072[c]	0.870[c]	-0.037 489[c]	0.4885	-0.082
0.020 073[c]	0.870[c]	-0.037 483[c]	0.4885	-0.082
0.030 114[c]	0.849[c]	-0.027 890[c]	0.4884	-0.082
0.030 400[c]	0.849[c]	-0.027 688[c]	0.4884	-0.082
0.040 163[c]	0.832[c]	-0.021 170[c]	0.4883	-0.082
0.050 325[c]	0.818[c]	-0.015 905[c]	0.4882	-0.081
0.060 274[c]	0.806[c]	-0.011 731[c]	0.4882	-0.081
0.080 423[c]	0.786[c]	-0.005 113[c]	0.4881	-0.081
0.100 58[c]	0.770[c]	0	0.4880	-0.081
0.201 74[c]	0.718[c]	+0.015 757[c]	0.4876	-0.080
0.508 80[c]	0.649[c]	0.036 453[c]	0.4871	-0.076
1.000 20	0.604	0.051 71	0.4867	-0.071
1.030 20[c]	0.604[c]	0.052 442[c]	0.4867	-0.070
1.033 00[c]	0.604[c]	0.052 508[c]	0.4867	-0.070
1.999 40	0.573	0.067 69	0.4863	-0.059
1.999 70	0.573	0.067 14	0.4863	-0.059
2.998 70	0.568	0.077 58	0.4860	-0.048
3.000 30	0.568	0.077 19	0.4860	-0.048
3.310 00[c]	0.569[c]	0.080 417[c]	0.4859	-0.044
3.993 70	0.576	0.085 11	0.4858	-0.037
4.000 90	0.576	0.084 95	0.4858	-0.037
4.799 90	0.589	0.090 11	0.4857	-0.028
4.800 90	0.589	0.090 11	0.4857	-0.027

[a] Probable errors: ±0.0001 for τ_{K^+}, and ±0.007 for τ_w. [b] Infinite dilution values. [c] Data from ref 8, but here requoted from molar to molal scale.

its whole concentration range. However, in principle, transference numbers depend on electrolyte concentrations and, for a critical verification, it is necessary to account for the simultaneous dependence of τ_{K^+} and τ_w on the KCl molality, as expressed by the key equation (3). To this purpose, Stoke's equation (10, 21)

$$\tau_{K^+} = \lambda_{K^+}/\Lambda_{KCl} = [\lambda_{K^+}^\circ - \tfrac{1}{2}f(I)]/[\Lambda_{KCl}^\circ - f(I)] =$$
$$[\tau_{K^+}^\circ - 1/2]/[1 - f(I)/\Lambda_{KCl}^\circ] + 1/2 \qquad (8)$$

where $f(I) = B_2 I^{1/2}/(1 + a_o B I^{1/2})$ with $I = m_2$ and $a_o = 0.38$ nm (22), and $\Lambda_{KCl}^\circ = 149.85$ S cm^2 mol^{-1} (10) was used to express τ_{K^+} in eq 3. In turn, τ_w was expressed by

$$\tau_w = \tau_w^\circ\ (1 - hm_2M_w) \qquad (9)$$

(where τ_w° is the limiting value of τ_w and h is the overall primary hydration number of KCl, assumed to be concentration independent within the range of concern), based on the assumption of constancy of the ratio of τ_w to the number of moles of unbound water (23). Upon combination of eqs 7–9 with eq 3, the three key parameters have been optimized by multiple nonlinear regression through the SAS statistical package (24), and the following results have been obtained: $\tau_{K^+}^\circ = 0.48907 \pm 0.00007$; $\tau_w^\circ = -0.082 \pm 0.007$; and $h_{KCl} = 7.5 \pm 0.5$.

Table I reports τ_{K^+} and τ_w as functions of m_2, as obtained through eqs 8 and 9 using the respective limiting values of $\tau_{K^+}^\circ$ and τ_w° above.

The following considerations apply:
(i) The value obtained for $\tau_{K^+}^\circ$ of KCl is in excellent agreement with the limiting ionic conductivity data in the literature (10).
(ii) The τ_{K^+} values are seen to decrease with increasing KCl molality, but just very slightly, and they keep substantially close to 0.486 over the whole KCl molality range. This

amounts to a 2.8% deviation from the exact equitransference ($\tau_+ = |\tau_-| = 0.5$) that would be desirable for a salt bridge.

(iii) The value obtained for the hydration number of KCl, $h_{KCl} = 7.5$, is in good accord with the sum of hydration numbers of the constituent ions, $h_{K^+} = 3.6$ and $h_{Cl^-} = 3.0$, as determined separately by independent methods (25–28). This substantial equality of h_{K^+} and h_{Cl^-} would, in terms of the Stokes–Robinson theory of ionic hydration (29, 30), point to the equality of the corresponding single-ion activity coefficients, $\gamma_{K^+} = \gamma_{Cl^-} = \gamma_{KCl}$, which is a useful feature when calculating reference electrode potentials.

(iv) The close-to-zero value obtained for the transference number of water for KCl within the whole molality range is, within experimental error, in accord with the fact that the two ions, K^+ and Cl^-, travel in opposite directions carrying a substantially equal number of moles of hydration water per faraday.

The good correlation of the results from i to iv substantiates the reliability of the present verification for the limits of equitransference of aqueous KCl, especially for the critical upper range of molalities up to saturation, hitherto unchecked. To give an idea of the "deficit of efficacy" of the KCl salt bridge is minimizing liquid junction potentials which is caused by the 2.8% deviation from exact equitransference mentioned above, let us consider the following cell at 298.15 K:

$$Pt\text{–}Ir|Cl_2|KCl \text{ (sat., } m_2 = 4.804)||KCl \ (m_1 = 1)|Cl_2|Pt\text{–}Ir \tag{10}$$
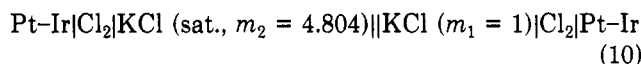
Now, integrating the general equation for the homoionic liquid junction potential E_J localized at the $||$ junction with the usual assumptions (here completely acceptable) of constant $\tau_{K^+} = 0.486$, as well as $\gamma_{K^+} = \gamma_{Cl^-} = \gamma_{KCl}$—see point iii above—and neglecting water transference (14), we obtain

$$E_J = (\tau_{K^+} - |\tau_{Cl^-}|) \ (RT/F) \ \ln \ (m_2\gamma_2/m_1\gamma_1)_{KCl} = -1.10 \text{ mV} \tag{11}$$

Now, a 1.10-mV unzeroed liquid junction potential would act as an additional error to the emf readout for the pIon-metric cell and would thus contribute an error of 4% to the measured concentration for a univalent ion or of 8% for a divalent ion. It is worthwhile here to contrast the KCl salt bridge with the recently described CsCl salt bridge (15), for which it was found that the τ_{Cs^+} value is close to 0.502 over the whole range of CsCl molalities, namely, up to 11.3 mol kg^{-1} at 298.15 K. If CsCl replaces KCl in the cell (11) still with $m_2 = 4.804$ and $m_1 = 1$ mol kg^{-1}, the E_J value calculated through eq 11 becomes +0.15 mV, i.e. just one-seventh of that for KCl, in absolute value.

CONCLUSIONS

From the foregoing results, the following conclusions can be drawn:

(a) Use of chlorine electrodes in KCl concentration cells avoids the drawback of the increasing solubility of the conventional AgCl or Hg_2Cl_2 electrode materials with increasing KCl concentration and permits a critical verification of the conditions of ionic equitransference for aqueous KCl up to saturation concentration of the latter. The observed good correlation between the relevant parameters (transference number of K^+ ion, transference number of water, and primary hydration number of KCl) confirms the reliability of the present analysis.

(b) Upon increasing KCl concentration up to saturation, the transference number τ_{K^+} (whose value at infinite dilution turns out to be 0.4891) undergoes a small decrease, however

with a substantial constancy at 0.486 in the usual molality range of KCl bridge operation.

(c) This 2.8% deviation of KCl from exact ionic equitransference may, when KCl bridges are used, leave junction potentials unzeroed by amounts of the order of 1 mV and thus introduce errors of several percent in the concentrations of the ions sensed.

(d) The imperfect equitransference of the KCl salt bridge, combined with its not high saturation concentration, may cause serious problems in the minimization of liquid junction potentials when the sample solution in contact with KCl is of high ionic strength and strongly acidic or strongly alkaline. In such a case, recourse should be made to the CsCl salt bridge, which shows nearly exact equitransference ($\tau_{Cs^+} = 0.502$) and a saturation concentration as high as 11.3 mol kg^{-1}.

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