

RESEARCH ARTICLES

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On the thermodynamic activities of ions in aqueous solutions of electrolytes

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A strong electrolyte in a dilute aqueous solution of concentration m , completely dissociates into its ions, each individual ion having a concentration m , and each carrying a charge depending on its valency. The thermodynamic activity of each ion will depend on the charge it carries and on m , multiplied by a factor γ termed activity coefficient, to allow for the apparent reduction in concentration caused by mutually interacting different ionic species in the solution. Thus, the activity of an ion in a solution of m may be re-defined as the 'effective strength' of the ion and expressed by the term $z^2 \times m\gamma$, where z is the valency of the ion. It is not the 'effective concentration' or $m\gamma$ as it is now defined and generally assumed to be. Experimental data are presented to confirm this new definition. A reference electrode without liquid junction has been devised to measure single ion activities, using a solid ion-transmitting conductor of silver-chloride rod, which functions as a bridge between the reference and test cells.

Electrode potential, ionic activity and activity coefficient

WHEN a piece of an active metal, like zinc, is dipped in an aqueous solution, the metal acquires a potential, which is a measure of the tendency of the metal to release its ions into the solution and get negatively charged thereby. These ions, as well as the same ions already present in the solution, will tend to annul this

tendency of the metal, thereby controlling its potential with respect to the solution. The effectiveness or the strength of an ion in determining the potential of a reversible electrode depends on the concentration of ions of the same kind in the solution and also on the charge carried by the ion. Thus, a doubly-charged ion will be four times as effective as a singly-charged ion in this respect¹. The strength I_i of an ion in solution is, therefore, a product of its concentration and the square of its valence. However, with increasing concentration of ions in a solution, and with increase in the forces of attraction and repulsion among the charged particles, the free movement of the ion in the solution will be hampered, and its strength reduced to a fraction of its value. Thus, the activity of an ion in a solution of m may be re-defined as the effective strength of the ion expressed by the term $z_i^2 m\gamma_i$, where z_i is the valence of the ion, rather than the effective concentration signified by $m\gamma_i$. This fraction, termed the activity coefficient of the ion, γ_i , is dependent, according to Debye and Huckel, on the ionic strength I of the electrolyte solution as a whole, which takes into account both the concentration and charges of all ions in the solution and in very dilute solutions is given by the relation² $-\log \gamma_i = 0.509 z_i^2 \sqrt{I}$. In the case of solutions of concentrations of about 0.01 m , the relation

$$-\log \gamma_i = \frac{0.509 z_i^2 \sqrt{I}}{1 + \sqrt{I}}$$

holds good³. For more concentrated solutions of about 0.1 *m*, the activity coefficients are best calculated by the Davies' empirical equation

$$-\log \gamma_i = 0.509 z_i^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2 I \right)$$

which fits closely with experimental data⁴.

Experimental proof:

The activity can be experimentally derived by measuring the potential of an ion-responsive electrode dipping in the solution, by means of the Nernst Equation in the form

$$\log a_i = \pm \frac{n(E - E^\circ)}{0.05916}$$

where E is the observed potential of the electrode when E° is its potential in a solution of unit activity of the ion, i.e. the standard reduction potential of the electrode and n is the number of Faradays of charge carried by the ion in question. In this study, ionic activities in ZnCl_2 solutions of molality 0.1, 0.01 and 0.001 were determined by precision potentiometry and compared with calculated values and the results are given in Table 1.

Experimental

Zn electrode potentials:

The zinc electrode was a rod, 5 mm in diameter, cast from spec-pure zinc (Johnson Mathey); sleeved by a glass-tube and fixed with epoxy (araldite), with 1 cm length of the rod exposed and amalgamated with distilled mercury. The silver-silver chloride electrode (the thermal electrolytic type) was prepared according to procedure described elsewhere⁵.

Zinc chloride solutions were prepared by dissolving the exact weights of pure zinc in 1 : 1 HCl, evaporating to dryness and adding the requisite amount of deionized water. Any cloudiness in the solutions was cleared by adding one or two drops of 0.1 *m* HCl. The solutions were kept in a thermostat maintained at $25^\circ\text{C} \pm 0.1^\circ\text{C}$.

The potentials of the Zn electrode in ZnCl_2 solutions were derived by measuring the potential between the test half-cell Zn/ZnCl_2 and the reference half cell of SCE with a fixed potential of 0.2444 V at 25°C . The electrode reaction is represented in Figure 1a.

The net cell reaction is $\text{Zn} + \text{Hg}_2\text{Cl}_2 \rightarrow \text{ZnCl}_2 + 2\text{Hg}$. To complete this reaction, the 2Cl^- released in the reference cell moves to the test cell under the driving force of the potential difference between the cells.

Normally, this ion transport takes place through the liquid junction (LJ) between the solutions of the two

Table 1. Activities of ions in ZnCl_2 solutions with related data

Description	Symbol	Data	Data	Data	Remarks
Molality	<i>m</i>	0.1	0.01	0.001	
<i>Activity Coeff.</i>					
Zinc ion γ_+	+	0.2521	0.501	0.773	According to eqns. in references 2, 3 & 4 for the molality range
Chloride ion γ_-	-	0.709	0.841	0.938	
<i>Potentials (volts)</i>					
Cell:					
$\text{Zn}/\text{ZnCl}_2/\text{SCE}$	e_1	1.036	1.056	1.080	
Zn electrode	E_1	-0.7916	-0.8116	-0.8356	$0.2444 - e_1$
Cell:					
$\text{Zn}/\text{ZnCl}_2/\text{AgCl}, \text{Ag}$	e_2	1.082	1.157	1.237	
Ag/AgCl electrode	E_2	0.2904	0.3454	0.4014	$[e_2 + E_1]$
<i>Activity of Zn^{2+} ion</i>					
Observed	$a_{\text{Zn}^{2+}}$	0.0998	0.02120	0.0032	$\text{antilog} \frac{E_1 - E_{\text{Zn}}^\circ}{0.02958}$
Calculated	$a_{\text{Zn}^{2+}}$	0.1008	0.0200	0.0031	$4m\gamma_+$
By text-book method (eg ref 6)	$a_{\text{Zn}^{2+}}$	0.02521	0.005	0.000773	$m\gamma_+$
<i>Activity of Cl^- ion</i>					
Observed	a_{Cl^-}	0.0709	0.00833	0.00092	$\text{antilog} \frac{0.2224 - E_2}{0.05916}$
Calculated	a_{Cl^-}	0.0709	0.00841	0.00094	$m\gamma_-$
By text-book method	a_{Cl^-}	0.1418	0.01682	0.00188	$2m\gamma_-$
$E_{\text{Zn}}^\circ = -0.762 \text{ v}$		$E_{\text{Ag/AgCl}}^\circ = 0.2224 \text{ v}$		$E_{\text{SCE}} = 0.2444 \text{ v}$	

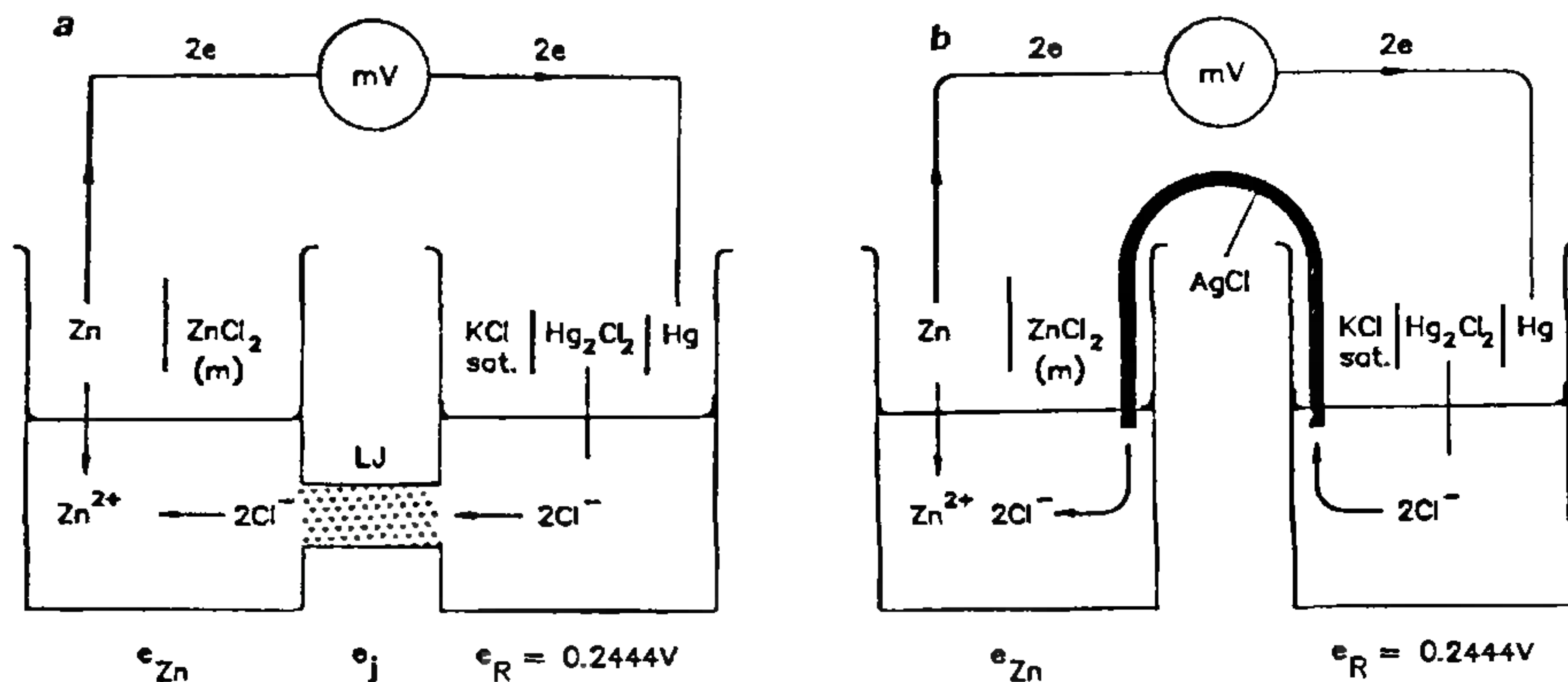


Figure 1. Cell reaction (a) with liquid junction and (b) without liquid junction

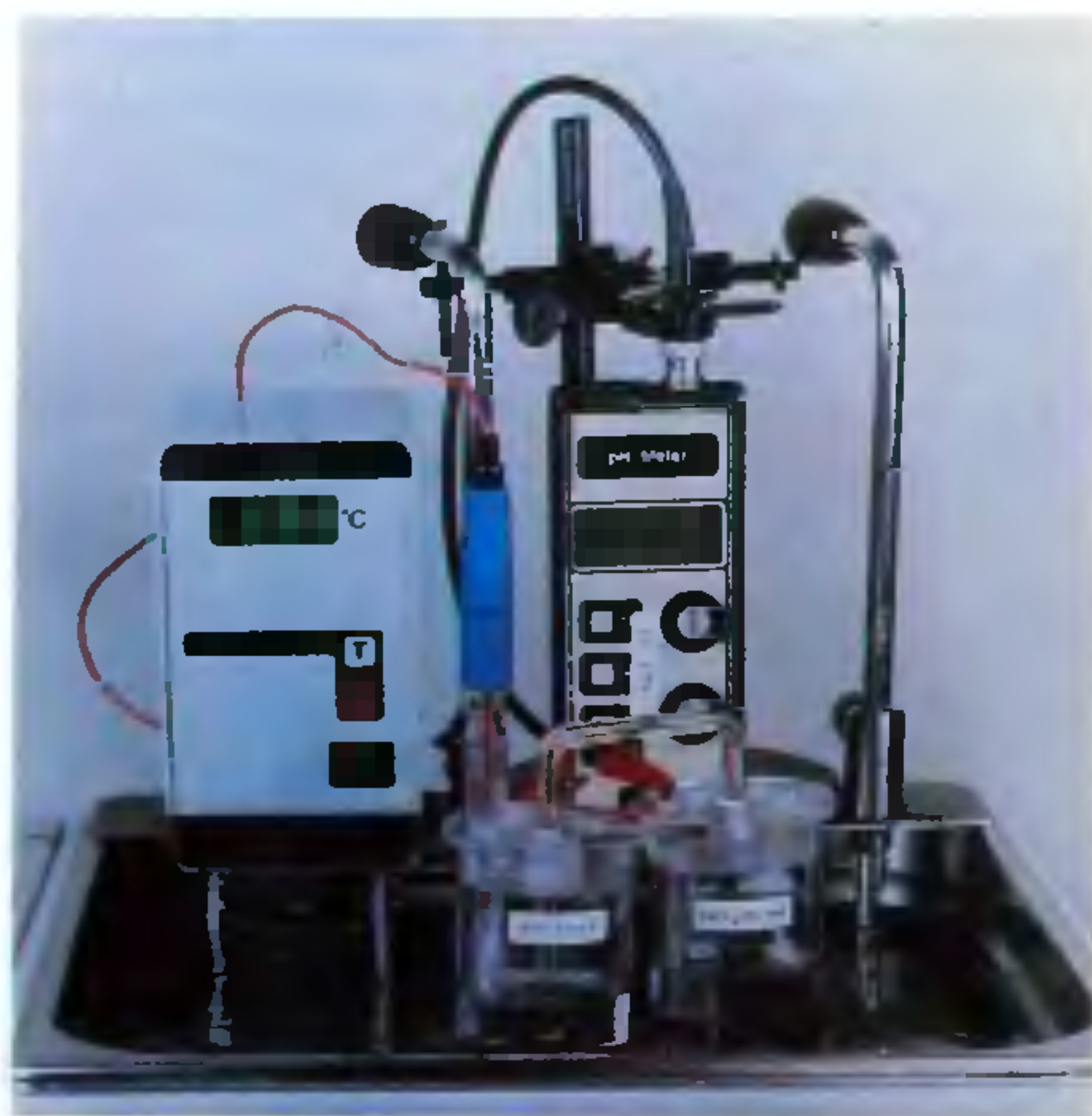


Plate 1.

half cells. Since the liquid junction allows free movement, both ways, of ions of different mobilities a separation of charges results and a potential e_j is built up around the junction which gets included as an error in the measured potential value. This error is avoided if the LJ is replaced by a solid ion-transmitting connector between the two separate half cells. Solid AgCl is found to act as Cl^- -ion conductor, when a potential difference

or potential exists across its two ends. Pure AgCl melted and cast as a thin rod of about 4 mm diameter and bent into the form of a 'U' was used as a bridge between the cells. The exposed portion of the bridge was protected from light by slipping an opaque sleeve over it. Since AgCl has a high ohmic resistance, it was necessary to use a voltage measuring instrument of very high input impedance for handling signals from high resistance sources, with negligible IR drop. The digital millivoltmeter used in this study was from Jenway Instruments, England, (model 3070) with an input impedance of 10^{13} ohms. Its calibration was checked against an NPL certified saturated Weston standard cell. The potential of the cell thus measured and the zinc electrode potential derived therefrom are absolute values, free from error, and are given in Table 1. The experimental set-up is as in Figure 1b (see also Plate 1).

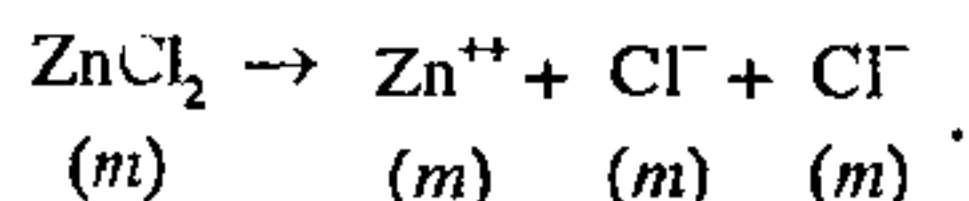
In the case of 0.001 m ZnCl_2 solution, the potential was slow to reach a final value. To remove any dissolved oxygen as a possible cause, when a drop of 0.1% ascorbic acid was added to the solution, equilibrium was quickly established and a steady, reproducible value was obtained.

The potentials of the zinc electrode in the different solutions having been determined with a high degree of accuracy and precision, it was used as a reference electrode for finding the potentials of the Ag/AgCl electrode, from the potential of the cell $\text{Zn}/\text{ZnCl}_2(\text{m})/\text{AgCl}, \text{Ag}$.

Discussion

As stated before, the thermodynamic activity of an ion

is expressed by the term $z^2 \times m \times \gamma$. In the case of a bi-univalent electrolyte like ZnCl_2 in aqueous solution of m , the electrolyte dissociates into three fragments, each of m . Thus,



The activities of these three ions calculated on the basis of the above expression work out to $2^2 \times m\gamma$ for Zn ion and $1^2 \times m\gamma$ for each of the chloride ions, i.e. $4m\gamma_+$, $m\gamma_-$ and $m\gamma_-$ respectively. The experimentally determined activities of these ions by potential measurements of the respective reversible electrodes are found to be in excellent agreement with their calculated values (Table 1) which provide a valid proof of the correctness of the expression for ionic activity. The activity of the electrolyte ZnCl_2 obtained experimentally by the emf measurement of the cell $\text{Zn}/\text{ZnCl}_2(m)/\text{Ag}/\text{AgCl}$, agrees in value with the product of the three calculated ionic activities or $4m^3\gamma^3$ where $\gamma = (\gamma_+ \times \gamma_- \times \gamma_-)^{1/3}$.

It may be mentioned in passing that the activity of an ion as defined hitherto⁶ and as generally assumed is the 'effective concentration' of the ion, and is expressed by the term $m\gamma$. According to this definition, in a ZnCl_2 solution of m , the activity of its three ions will be $m\gamma_+$ each, since each of these ions have the same m . Then the activity of ZnCl_2 which is the product of the three separate ionic activity terms, would work out to

$$a_{\text{ZnCl}_2} = a_{\text{Zn}^{++}} \times a_{\text{Cl}^-} \times a_{\text{Cl}^-} = m\gamma_+ \times m\gamma_- \times m\gamma_- = m^3\gamma^3$$

But the actual value of a_{ZnCl_2} is 4 times this value; it is $4m^3\gamma^3$. The discrepancy has been reconciled by replacing each chloride activity term $m\gamma_-$ by $2m\gamma_-$ which is the sum of two single quantities and the calculation of a_{ZnCl_2} is given as

$$\begin{aligned} a_{\text{ZnCl}_2} &= a_{\text{Zn}^{++}} \times a_{\text{Cl}^-} \times a_{\text{Cl}^-} \\ &= m\gamma_+ \times 2m\gamma_- \times 2m\gamma_- = 4m^3\gamma^3 \end{aligned} \quad (1)$$

which is clearly a serious mistake, as $2m\gamma_-$ cannot be a factor in the calculation of the activity of zinc chloride.

Further, it should be remembered that the total chloride concentration in a solution of ZnCl_2 of molality m is $2m$ and the activity $2m\gamma_-$ by reason of the fact that ZnCl_2 releases 2Cl^- ions in the solution on dissociation. Since $2m\gamma_-$ represents the activities of both Cl^- ions in solution, the activity of ZnCl_2 could then be defined as the product of just two factors only, viz. one zinc ion activity factor and one $2m\gamma_-$ factor. There is no stoichiometric need or scope for introducing the second $2m\gamma_-$ factor, in equation (1). But this is done presumably to match the observed value of $4m^3\gamma^3$ for the overall product, and is therefore not valid. Clearly, the activity values assigned to the three ions of ZnCl_2 in equation (1) are wrong. They have no experimental support; the experimentally determined zinc ion activity is $4m\gamma_+$ and not $m\gamma_+$, and the chloride ion activities are $m\gamma_-$ each and not $2m\gamma_-$ (Table 1). These errors are due to the omission of the factor of ionic charge in calculating its activity in solution.

Summarizing, the thermodynamic activity of an ion in a dilute aqueous solution of an electrolyte, is to be defined as the 'effective strength' of the ion and expressed by the term $z^2 \times m \times \gamma$. It follows that all electrolytes of the same valency type in solutions of the same concentration will have the same activity, irrespective of the nature of the ions⁷. Thus, all bi-univalent electrolytes in solutions of m will have the same activity $4m^3\gamma^3$, irrespective of whether the electrolyte is of the type MAB or MA_2 .

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