

4.07 Ions in Aqueous Solution (5 points)

Outline

In this experiment, you will (i) determine molar conductivities of electrolyte solutions and see how they vary with concentration; (ii) measure transport numbers and use these to determine molar conductivities of individual ions, and (iii) appreciate the need for salt bridges in electrochemical cells, by observing liquid junction potentials (LJPs).

Safety

In this experiment you will be using solid cadmium and cadmium solutions. Cadmium is very toxic and you must wear gloves at all times when you might come into contact with cadmium-containing solutions. For more information, see the web page for this experiment: <http://ptcl.chem.ox.ac.uk/~hmc/tlab/experiments/407.html>.

Background

Relevant lecture courses: 1st year: Electrochemistry, States of matter. 2nd year Liquids and solutions.

Theory

When a potential is applied across two inert electrodes submerged in a fully dissociated electrolyte such as KCl [Fig. 1], it is found that:

- (i) the solution is an ohmic conductor, so that the potential difference (p.d.), V , across the electrodes is directly proportional to the current, I , passing through the solution: $V = IR$, where R is the resistance of the solution, and

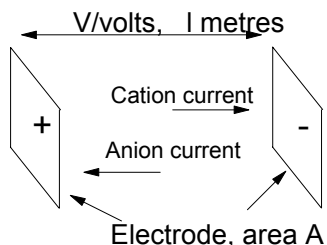


Fig. 1. Movement of ions in the presence of a potential difference.

- (ii) the cations and anions move essentially independently of each other. The conductivity, κ of such a solution is given by the expression

$$\kappa = l / RA$$

where l is the length of the solution and A is the exposed area of the inert electrodes. κ is measured in units of siemens per centimetre, $S\text{cm}^{-1}$. [Conductance (R^{-1}) is measured in Ω^{-1} siemens (S) (reciprocal ohms, formerly denoted mhos).]

The molar conductivity, Λ , of a solution is defined as $\Lambda = \kappa / c$ where c is the concentration of the solution. Λ is usually measured in units of $S\text{cm}^2\text{mol}^{-1}$. To a very good approximation, the conductivity is linearly dependent on the concentration of ions present (Fig. 2).

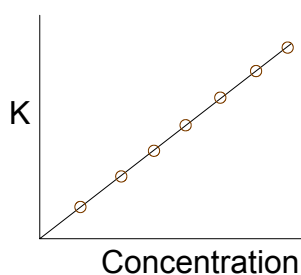


Fig. 2. The relationship between conductivity and ion concentration.

However, when careful measurements are made, the molar conductivity is seen to be slightly concentration-dependent:

$$\Lambda = \Lambda_0 - k \sqrt{c}$$

where $\{k \sqrt{c}\}$ is small compared with Λ_0 . This is the so-called *Kohlrausch Law*. Λ_0 is the limiting molar conductivity of the salt solution (ie. that at infinite dilution); c is

the concentration of the solution; and k is a solvent and temperature specific constant. Physically, this arises as a result of the following two effects:

(I) **The Relaxation Effect.** When an electric field is applied to a solution containing ionic species, the ionic atmosphere around each ion becomes slightly distorted, since the ions forming the atmosphere do not *instantaneously* respond when the central ion moves under the influence of the electric field, and, consequently, the ionic atmosphere is left momentarily incomplete in front of, and behind the central ion. The overall effect is that the centre of charge of the 'ionic atmosphere' is displaced behind the moving ion, and the movement of the ion is impeded.

(ii) **The Electrophoretic Effect.** The viscous drag on the moving ion, caused by friction with the solvent molecules (*vide infra*) is enhanced by ionic atmospheres, as the solvent molecules tend to move with ions that make up the ionic atmosphere in the *opposite* direction to that of the central ion.

Debye-Hückel-Onsager Theory takes these effects into account, and provides a theoretical expression for k . See Atkins, "Physical Chemistry", 5th edn, chapter 24, page 845 for further reading.

When the molar conductivity for each ion is known, the molar conductivity of any binary salt (M_aX_b) can be determined using the *Law of Independent Ion Migration*:

$$\Lambda_{\text{salt}} = a \Lambda_M^+ + b \Lambda_X^-$$

Note that this equation strictly applies only at infinite dilution.

3.1 Measuring Conductivities

Conductivities may be easily measured using a conductivity meter and the simple cell shown in Fig. 3. An a.c. supply is used, as dc would cause electrolysis of the electrolyte.

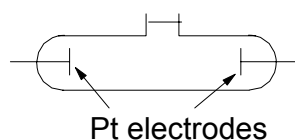


Fig. 3. A simple conductivity cell.

3.2 A Simple Model for Molar Conductivities

A crude model of the situation in Fig. 1 is shown in Fig. 4. The electrical force (F_e) of attraction between the ion and the electrolyte is opposed by the viscous drag (F_v) on the ion due to the movement of the ion through the solvent molecules.

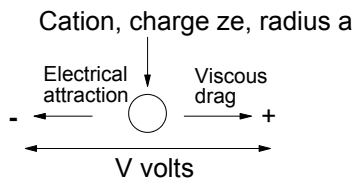


Fig. 4. Forces on a charged particle moving under the influence of an electric field.

Now $F_e = zeV / \ell$ F_v is given (to an approximation) by Stokes's Law

$$F_v = 6\pi a v \eta$$

where a is the radius of the ion; v is its velocity; and η is the solution viscosity. When the ion moves with a steady state velocity $F_v = F_e$, and therefore

$$zeV / \ell = 6\pi a v \eta$$

and the molar conductivity for the ion, $\Lambda \propto v / V \ell \propto ze / 6\pi a v \eta$ This predicts that Λ should be large for small ions, highly charged ions, and solvents of low viscosity.

$H^+(aq)$ and $OH^-(aq)$ ions have unusually large molar conductivities, as they do not have to move around water molecules - these ions can use the solvent molecules in a process known as the Grotthuss Mechanism (Fig. 5 below).

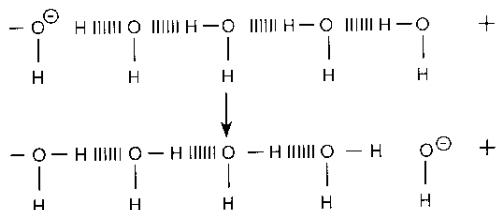


Fig. 5. The Grotthuss Mechanism for the transport of protons in aqueous solution.

3.3 Transport Numbers

The current that passes through an electrolyte solution is carried by solvated ions, positive cations moving towards the negative cathode, and negative anions moving towards the positive anode. However, the mobilities, and hence conductivities, of the cations and anions in an electrolyte solution are usually different. Consequently different fractions of the total current are carried by the different ions. These fractions are known as the transport numbers (or transference numbers) of the cations and anions. It will be appreciated that

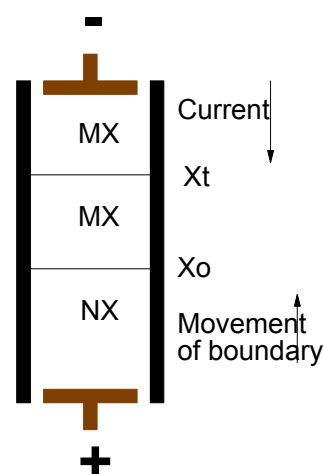
$$t_+ = \Lambda_+ / (\Lambda_+ + \Lambda_-) ; t_- = \Lambda_- / (\Lambda_+ + \Lambda_-)$$

where t_+ , t_- are the transport numbers of the cation and anion respectively, and Λ_+ , Λ_- are the molar conductivities of the cation and anion respectively. See Atkins, "Physical Chemistry", 5th edn., chapter 24, page 841, or Compton and Sanders "Electrode Potentials" chapter 3, page 59 for further reading.

Transport numbers are useful in that they can be used to calculate molar conductivities for *individual* ions once conductivity data is measured for any electrolyte.

There are various methods for determining transport numbers, the most direct being the 'moving boundary' method. Two electrolyte solutions containing a common anion or cation are placed in a tube to give a distinct, visible boundary between them. An electrode is positioned at each end of the tube. A known quantity of electricity is passed and, under suitable conditions, the boundary moves, but remains sharp. If one of the non-common ions is denser and less mobile than the other, there is a steeper potential gradient on the side of the boundary containing the less mobile species. If some of the relatively faster moving non-common ions diffuse or are carried by convection into the other electrolyte region, they encounter a higher potential gradient, and are sent forward to the boundary. On the other hand, if the slower non-common ions diffuse into the other electrolyte region, they will move more slowly than the faster non-common ions and are finally overtaken by the moving boundary. Hence, a sharp boundary is maintained. From the amount of electricity passed, and the extent of movement of the boundary, the transport number of the faster non-common ion may be found.

The figure to the right shows this in diagrammatic form. In a vertical tube a boundary at x_0 is formed by the juxtaposition of two solutions of electrolytes NX and MX. A current of I amps is passed through the tube for t seconds, corresponding to the passage of It coulombs. During time t , the boundary moves from x_0 to x_t . All the cations M in volume V dm³ of solution between x_0 and x_t must, during this time, have crossed the plane at x_t . If M is in the form of univalent cations of concentration c mol dm⁻³, the amount of electricity carried by them is cVF coulombs, where F is the Faraday constant (96,485 Cmol⁻¹). Then the transport number of the cations M^+ is given by



$$t_{M^+} = \{\text{current carried by } M^+ \text{ ions}\} / \{\text{total current}\} = \{cF/I\}dV/dt$$

It is important to ensure that the tube is regular (otherwise the rate of movement of the boundary is affected) and that a constant current is maintained. Thermal effects may also influence the boundary.

Salt Bridges and Liquid Junction Potentials

When two electrolyte solutions are in contact through a porous membrane (or even by using a piece of cotton wool soaked in one electrolyte), the ions of each solution will diffuse into the other solution. The rate of diffusion per unit area of the membrane (the flux, j_i / mol $\text{cm}^2 \text{s}^{-1}$) is given by Fick's First Law, which for one dimension is:

$$j_i = D_i \frac{\partial [I]}{\partial x}$$

The flux of species i will depend on its molar conductivity, since, by the Nernst-Einstein Equation, $\Lambda_i \propto D_i$. Hence, different ions will diffuse at different rates. Consider placing two solutions of HCl, with concentrations c_1 and c_2 in contact. The initial situation is shown in Fig. 7.

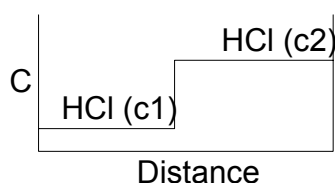


Fig 7. Initial concentration profile across a boundary.

There will be a large concentration gradient ($\frac{\partial [I]}{\partial x}$), and will thus cause diffusion of both H^+ and Cl^- from high concentration to low concentration. At the moment that the interface is formed, the concentration gradient of H^+ ions will equal that of Cl^- ions. Initially $D_{\text{H}^+} \gg D_{\text{Cl}^-}$, since H^+ ions can diffuse by the Grotthuss Mechanism, whereas Cl^- have to diffuse past water molecules. Thus a potential difference is set up across the interface, and the solution of lower concentration will become positively charged (see fig. 8). This p.d. causes the rate of proton transfer to be retarded, and will accelerate the transport of Cl^- .

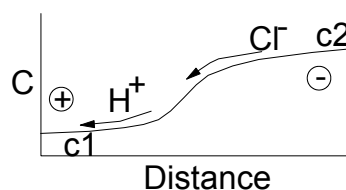


Fig 8. Steady state concentration across a boundary.

Ultimately, a steady state will be attained in which a potential difference will exist across the thin boundary region between the two solutions. This is known as a liquid junction potential. For 1:1 electrolyte solutions in concentration cells, the size of this potential difference (E_{LJP}) is given by

$$E_{LJP} = (t_+ - t_-) \{RT/F\} \ln \{c_2/c_1\}$$

where c_1 and c_2 are the different concentrations of the (same) electrolyte.

To overcome the problem of LJPs in electrochemical cells, we use a salt bridge that allows both solutions to be in contact with a third solution that gives rise to no LJP, e.g. KCl, KNO_3 , NH_4NO_3 . This is possible since in these electrolytes, $t_+ \approx t_- \approx 0.5$, and hence $E_{LJP} \approx 0$.

4 Experimental Procedure

1. For this experiment, use the conductivity meter specially designated for this experiment (marked with a large yellow spot to distinguish from other visually similar but inappropriate meters) along with the probe with BRIGHT Pt electrodes.

Using the 1.0M KCl solution provided, make up five solutions in the range of 0.001M to 0.1M. Store the solutions in a water bath thermostatted at 298K.

Wash the electrodes in the probe well with demineralised water before using it. Using the 0.01M KCl solution, calibrate the meter (see instructions below). Wash the electrodes well once more, and then record the conductivity of demineralised water at 298K. It is essential to take all measurements whilst the liquid is stirred with a magnetic flea.

Record the conductivity of the five KCl solutions in order of increasing concentrations, ensuring that you recalibrate the meter with 0.01M KCl and that you wash and dry the probe before taking any measurement.

Plot a graph of conductivity against concentration of KCl, and also of molar conductivity against the square root of the concentration of KCl, to determine the molar conductivity of the solution at infinite dilution.

(ii) Prepare 0.001M solutions of HCl, NaOH, LiCl, NaCl and $BaCl_2$ (TAKE CARE. The acid and base solutions are corrosive, and the barium solution is toxic). Measure the conductivity of each solution at 298K. **Recalibrate the meter with 0.01M KCl** before each measurement, wash and dry electrodes carefully before using them, and use the magnetic flea.

2. **Protective gloves must be worn at all times during this part of the experiment. Use the power supply provided for this experiment only.**

First prepare a silver/silver chloride electrode. Next lightly grease a cadmium electrode (taking care **not** to grease the flatish portion at the top of the electrode to be exposed to the liquid!) Fit this snugly into the ground glass socket of the moving boundary tube. Add just enough methyl violet to some 0.1M HCl for its colour to be clearly visible when the solution is in the narrow parts of the tube (you can check by partly filling a 1ml pipette). Rinse and then fill the tube with this solution, taking care no bubbles are trapped on the Cd electrode or in the tube; a hypodermic syringe with a long needle is useful for this operation (see technician). Fit the silver/silver chloride electrode into the top of the tube, and mount vertically in a clamp stand. Check that the seal at the cadmium is leak-proof.

Connect the electrodes, with the correct polarity (cadmium positive), and connect these to an output supply on the power unit. Adjust the power supply controls to the minimum current position (coarse and fine controls fully clockwise). Dry your hands, then switch on the unit (**the 200V power supply can give a severe shock - do not touch bare conductors**). Adjust the controls to obtain a current of about 5mA. Do not let the acid stand in prolonged contact with the electrode before starting.

When the boundary reaches the graduations, reduce the current to 2.0mA and keep it at this level throughout the experiment by adjusting the controls. Start the stop watch as soon as the boundary passes one of the calibration marks. Record the times taken for the boundary to move through successive volumes of 0.01cm^3 , until it has passed a total volume of 0.40cm^3 . **Dispose of the Cd-containing acidic solution in the Cadmium waste container. Cadmium wastes must NOT be washed down the sink.**

Plot a graph of volume against time and calculate the relevant transport numbers. Hence determine the molar conductivities for each ion mentioned in 1(i) and (ii), assuming 10^{-3}M approximates to infinite dilution.

3. Use the 0.1M zinc nitrate solution provided to make up 250cm^3 of 0.001M solution. Using the H-cell and clean zinc electrodes, set up the electrochemical cell as shown in fig. 9. Record the EMF of the cell. Note this is a cell with a LJP.

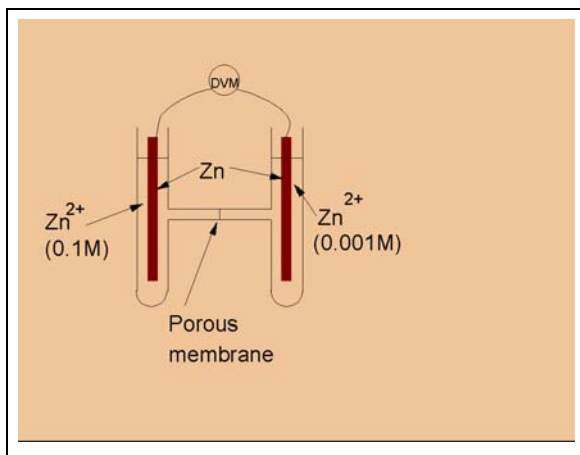


Fig 9. A zinc concentration cell.

Set up the concentration cell sketched in Fig. 10 which contains a salt bridge made using cotton wool soaked in saturated KCl.



Record the cell EMF, and contrast your two results.

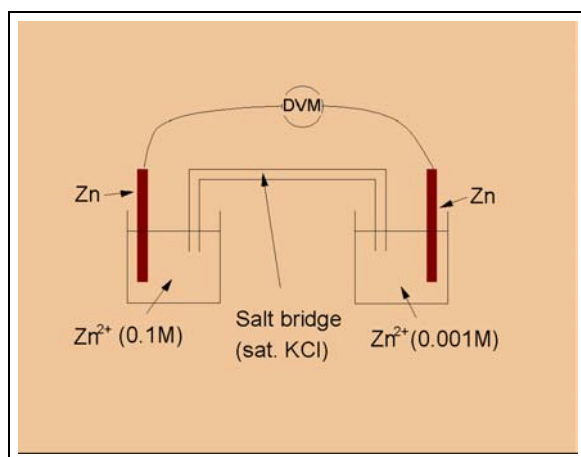


Fig. 10. A zinc concentration cell with salt bridge.