

IONIC SOLUTION CHEMISTRY

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AIMS

The aims of this examples class are:

- (1) To calculate the activity coefficients of ions at particular concentrations in ionic solutions using Debye-Hückel theory.
- (2) To calculate thermodynamic quantities, such as Gibbs' free energy, entropy, and enthalpy changes, activity coefficients, and solubility products, from measurements of cell potentials.
- (3) To calculate the limiting molar conductivities and transport numbers of ions in electrolytes, and the degree of dissociation of weak electrolytes, from measured conductivity data.

EXAMPLES

1. Show that the ionic strengths of solutions containing $c \text{ mol dm}^{-3}$ of K_2SO_4 , KNO_3 , and MgSO_4 , are $3c$, c , and $4c \text{ mol dm}^{-3}$, respectively.
2. Use (i) the Debye-Hückel Limiting Law, and (ii) the extended Debye-Hückel Law to calculate the mean activity coefficient for a 0.00913 M solution of HCl . (Take the values of the Debye-Hückel constants to be $A = 0.509$, and $Ba = 1.4$).
3. When 1.64 moles of a weak acid, HA , were dissolved in 1.000 dm^3 of water, the concentration of H^+ was found to be $0.040 \text{ mol dm}^{-3}$. Use the Debye-Hückel Limiting Law to estimate pK_a for the acid.
4. The solubility product, K_{sp} , for silver chloride, AgCl , is 1.20×10^{-10} at 298 K . Make use of the Debye-Hückel Limiting Law to estimate the solubility of AgCl in (i) pure water, (ii) $0.01 \text{ mol dm}^{-3} \text{ NaNO}_3$, and (iii) $0.01 \text{ mol dm}^{-3} \text{ NaCl}$.
5. Consider the electrochemical cell:
$$\text{Zn} | \text{ZnSO}_4(\text{aq}) || \text{CuSO}_4(\text{aq}) | \text{Cu}$$

Calculate $E^\ominus$ for the cell, and $\Delta G^\ominus$ and the equilibrium constant for the cell reaction.
 $[E^\ominus(\text{Zn}^{2+}, \text{Zn}) = -0.763 \text{ V}; E^\ominus(\text{Cu}^{2+}, \text{Cu}) = +0.337 \text{ V}]$.
6. The cell potential, E , of the cell,
$$\text{Pt}, \text{H}_2(1 \text{ atm}) | \text{HCl}(\text{aq}) | \text{AgCl}, \text{Ag}$$

was measured at 298 K as a function of the concentration, c , of the aqueous HCl solution, with the following results:

$c / 10^{-3} \text{ mol dm}^{-3}$	124	25.6	9.13	5.62	3.22	1.60
E / V	0.3420	0.4180	0.4683	0.4923	0.5200	0.5549

Estimate $E^\ominus$ for the cell. Deduce the value of the mean activity coefficient for the H^+ and Cl^- ions in a 0.00913 M HCl solution. Compare this experimental result with your values estimated from the Debye-Hückel laws in Question (2).

If, relative to the value at 298 K, the value of $E^\ominus$ increased by 3.32 mV at 293 K, and decreased by 3.13 mV at 303 K, deduce the values of $\Delta G^\ominus$, $\Delta H^\ominus$, and $\Delta S^\ominus$ for the cell reaction.

7. The standard cell potential, $E^\ominus$, of the cell,
 $\text{Pt}, \text{H}_2(1 \text{ atm}) | \text{HCl}(\text{aq}) | \text{KCl}(\text{sat.}) | \text{Hg}_2\text{Cl}_2(\text{s}), \text{Hg}(\text{l})$
 was found to vary with temperature as follows:

T / K	293	298	303
$E^\ominus / \text{V}$	+0.2699	+0.2684	+0.2669

Write down the cell reaction. Calculate $\Delta G^\ominus$ and the equilibrium constant for the cell reaction at 298 K. Estimate the corresponding values of $\Delta H^\ominus$ and $\Delta S^\ominus$ at 298 K.

What cell potential would be measured between the Pt and Hg(l) electrodes if the HCl(aq) solution had a concentration of $1.00 \times 10^{-4} \text{ mol dm}^{-3}$?

8. The cell,
 $\text{glass electrode} | \text{H}^+(\text{aq}) || \text{calomel electrode}$
 was found to have a cell potential, E , of +0.209 V when $\text{H}^+(\text{aq})$ solution was a buffer of pH 5.21. What are the hydrogen ion activities in solutions which result in cell potentials of +0.064 V and +0.329 V, respectively, in the same cell? What voltage would you expect to measure from a solution of pH 13.0?
9. Why is the cell potential of the cell,
 $\text{Ag} | \text{KI}(\text{aq}), \text{AgI}(\text{sat.}) || \text{H}^+(\text{a} = 1) | \text{H}_2(1 \text{ atm}), \text{Pt}$
 dependent on the iodide-ion activity, even though I is not involved directly in the reactions at either electrode? What is the cell potential if enough KI is added to create unit activity of iodide ions?
 $[E^\ominus(\text{Ag}^+, \text{Ag}) = +0.799 \text{ V}; K_{\text{sp}}(\text{AgI}) = 8.3 \times 10^{-17}]$
10. The limiting molar conductivities at 298 K of NaBr, NaNO_3 , and AgNO_3 are $128 \text{ S cm}^2 \text{ mol}^{-1}$, $122 \text{ S cm}^2 \text{ mol}^{-1}$, and $134 \text{ S cm}^2 \text{ mol}^{-1}$, respectively. Estimate the limiting molar conductivity of AgBr. Why might this be a difficult quantity to measure experimentally?
11. The autogenic moving boundary method was used to determine the transport number of the K^+ ion in a $0.01 \text{ mol dm}^{-3} \text{ KNO}_3$ solution. The boundary travelled a distance of 10.0 cm when a constant current of 0.965 mA was passed for a period of 33 minutes and 20 seconds. The cross-sectional area of the tube was 0.1 cm^2 . What is the value of t_+ for K^+ in this KNO_3 solution?

12. Use the following measurements of the molar conductivity, Λ_m , as a function of concentration, c , to estimate the limiting molar conductivity, Λ_m^0 , of sodium propanoate:

$c / 10^{-3} \text{ mol dm}^{-3}$	2.18	4.18	7.87	14.27	25.97
$\Lambda_m / \text{S cm}^2 \text{ mol}^{-1}$	82.5	81.3	79.7	77.9	75.6

Given that the limiting molar conductivities of HCl and NaCl are $426.2 \text{ S cm}^2 \text{ mol}^{-1}$ and $126.5 \text{ S cm}^2 \text{ mol}^{-1}$, respectively, deduce the limiting molar conductivity of propanoic acid.

If a 1.00 mol dm^{-3} solution of propanoic acid has a molar conductivity of $1.4 \text{ S cm}^2 \text{ mol}^{-1}$, what is the degree of dissociation of the acid in this solution?