Lecture 8 ELECTROLYTE SOLUTIONS

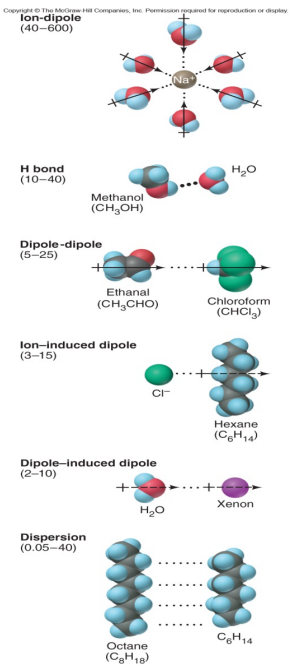
WHICH OF THESE ARE ELECTROLYTE SOLUTIONS:

SOLUTIONS:

- Solutions are homogeneous mixtures of two or more pure substances.
- In a solution, the solute is dispersed uniformly throughout the solvent.

State of Solution	State of Solvent	State of Solute	Example
Gas	Gas	Gas	Air
Liquid	Liquid	Gas	Oxygen in water
Liquid	Liquid	Liquid	Alcohol in water
Liquid	Liquid	Solid	Salt in water
Solid	Solid	Gas	Hydrogen in palladium
Solid	Solid	Liquid	Mercury in silver
Solid	Solid	Solid	Silver in gold

The major types of intermolecular forces in solutions.



LIKE DISSOLVES LIKE

Substances with similar types of intermolecular forces dissolve in each other.

When a solute dissolves in a solvent, solute-solute interactions and solvent-solvent interactions are being replaced with solute-solvent interactions. The forces must be comparable in strength in order for a solution to form.

Hydration shells around an aqueous ion.

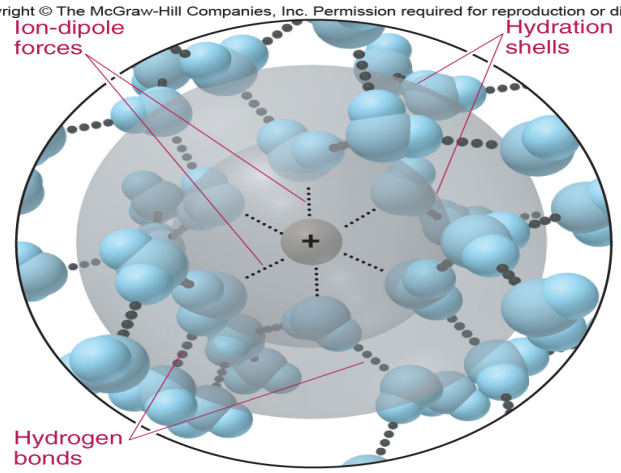
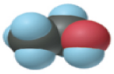
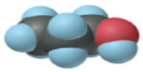
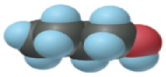
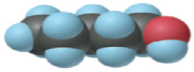
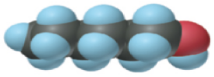
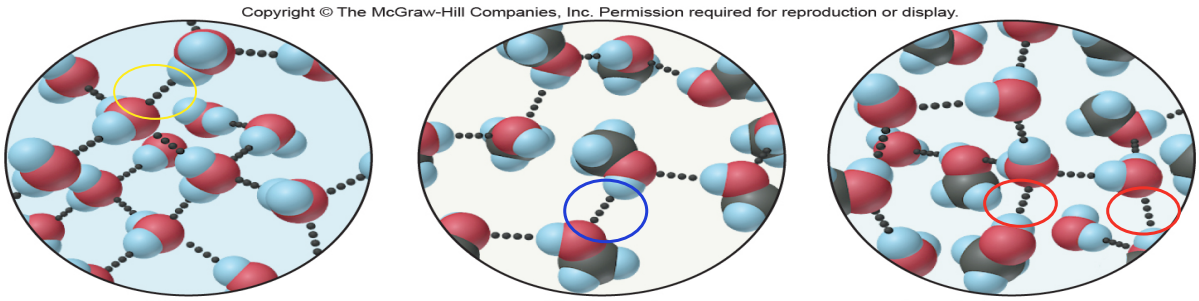


Table 13.2 Solubility* of a Series of Alcohols in Water and Hexane

Alcohol	Model	Solubility in Water	Solubility in Hexane
CH_3OH (methanol)		∞	1.2
CH_3CH_2OH (ethanol)		∞	∞
$CH_3(CH_2)_2OH$ (1-propanol)		∞	∞
$CH_3(CH_2)_3OH$ (1-butanol)		1.1	∞
$CH_3(CH_2)_4OH$ (1-pentanol)		0.30	∞
$CH_3(CH_2)_5OH$ (1-hexanol)		0.058	∞

*Expressed in mol alcohol/1000 g solvent at 20°C.

Figure 13.3 Like dissolves like: solubility of methanol in water.



Water | Methanol | A solution of water and methanol

SAMPLE PROBLEM: PREDICTING RELATIVE SOLUBILITIES OF SUBSTANCES

Predict which of the given solvent will dissolve more of the given solute:

(a) Sodium chloride in methanol (CH_3OH) or in 1-propanol ($CH_3CH_2CH_2OH$)

(b) Ethylene glycol ($HOCH_2CH_2OH$) in hexane ($CH_3CH_2CH_2CH_2CH_2CH_3$) or in water.

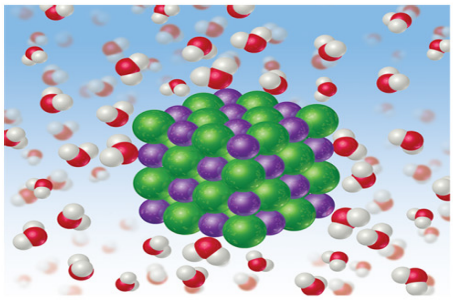
(c) Diethyl ether ($CH_3CH_2OCH_2CH_3$) in water or in ethanol (CH_3CH_2OH)

ELECTROLYTE SOLUTIONS:

How does a solid dissolve into a liquid?

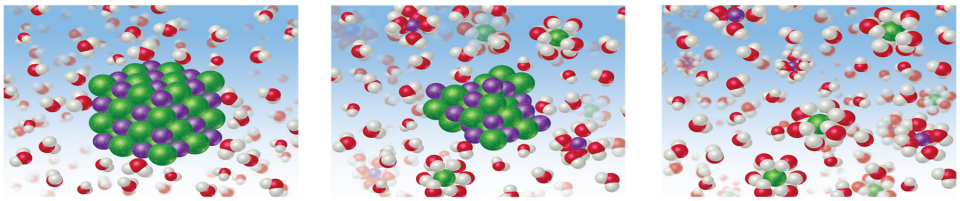
What 'drives' the dissolution process?

What are the energetics of dissolution?



HOW DOES SOLUTION FORM?

1. Solvent molecules attracted to surface ions.
2. Each ion is surrounded by solvent molecules.
3. Enthalpy (ΔH) changes with each interaction broken or formed.



Ionic solid dissolving in water

HOW DOES A SOLUTION FORM?

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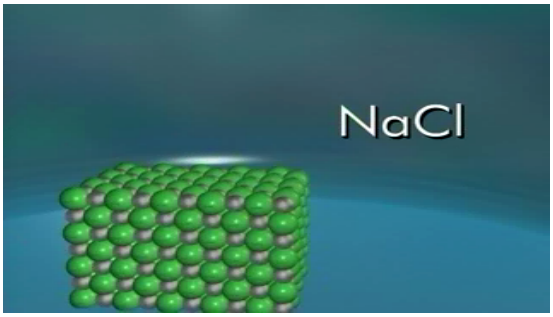
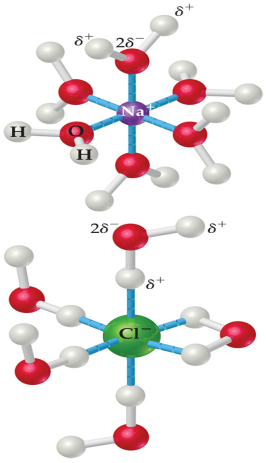


HOW DOES SOLUTION FORM?



The ions are **solvated** (surrounded by solvent).

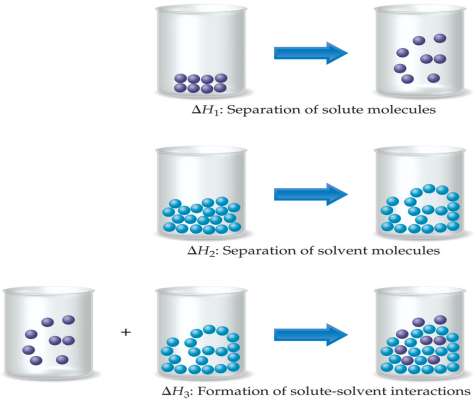
If the solvent is water, the ions are **hydrated**.

The intermolecular force here is ion-dipole.

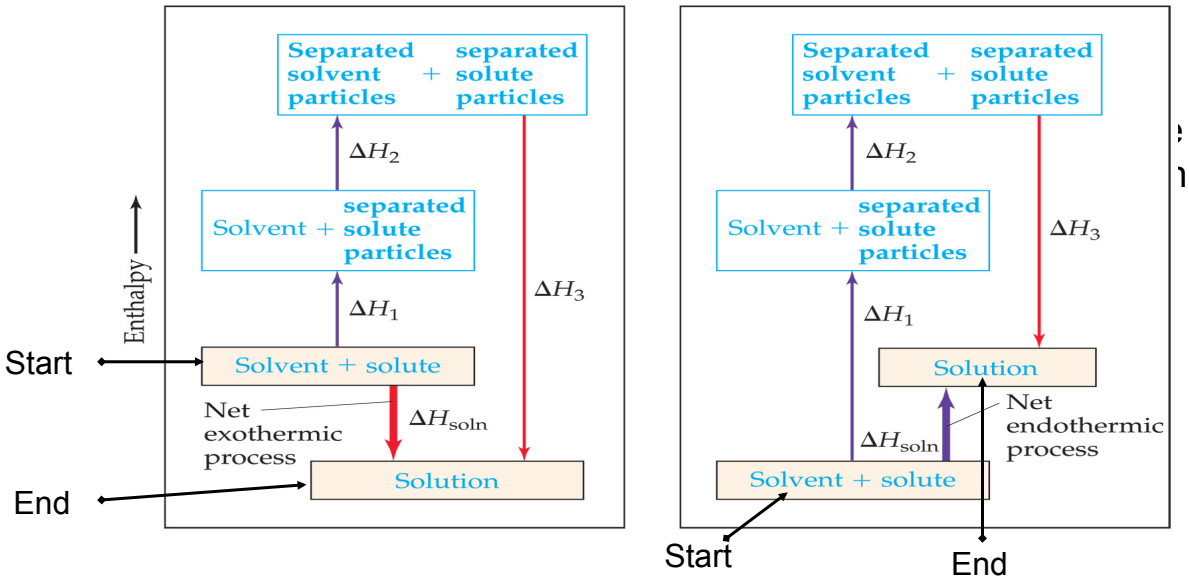
ENERGY CHANGES IN THE SOLUTION PROCESS:

To determine the enthalpy change, we divide the process into 3 steps.

1. Separation of solute particles.
2. Separation of solvent particles to make 'holes'.
3. Formation of new interactions between solute and solvent.

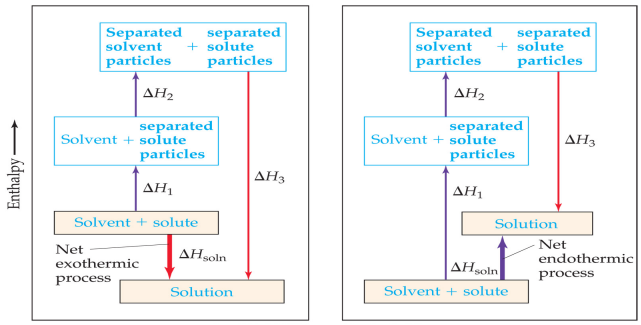


ENTHALPY CHANGES IN SOLUTION



ENTHALPY CHANGES IN SOLUTION

$$\Delta H_{soln} = \Delta H_1 + \Delta H_2 + \Delta H_3$$

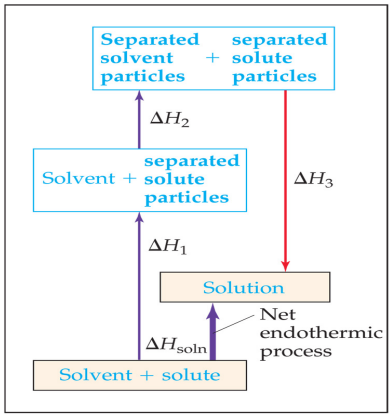


The enthalpy of solution, ΔH_{soln}, can be either positive or negative.

ΔH_{soln} ($MgSO_4$) = -91.2 kJ/mol --> exothermic

ΔH_{soln} (NH_4NO_3) = 26.4 kJ/mol --> endothermic

WHY DO ENDOTHERMIC PROCESSES SOMETIMES ARE SPONTANEOUS?



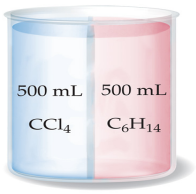
Some processes, like the dissolution of NH_4NO_3 in water, are spontaneous at room temperature even though heat is absorbed, not released.

ENTHALPY IS ONLY PART OF THE PICTURE

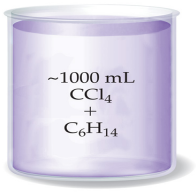
Entropy is a measure of:

- Dispersal of energy in the system.
- Number of microstates (arrangements) in the system.

b. has greater entropy,
∴ is the favored state



(a)

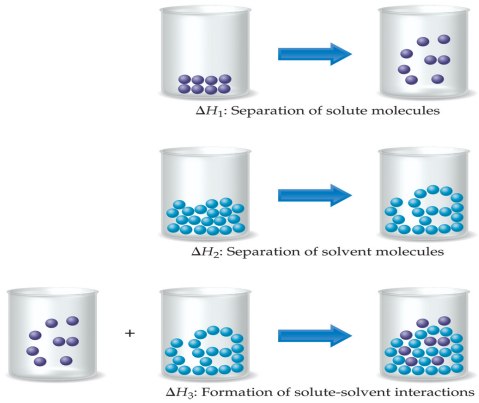


(b)

ENTROPY CHANGES DURING DISSOLUTION

Each step also involves a change in entropy.

1. Separation of solute particles.
2. Separation of solvent particles to make 'holes'.
3. Formation of new interactions between solute and solvent.

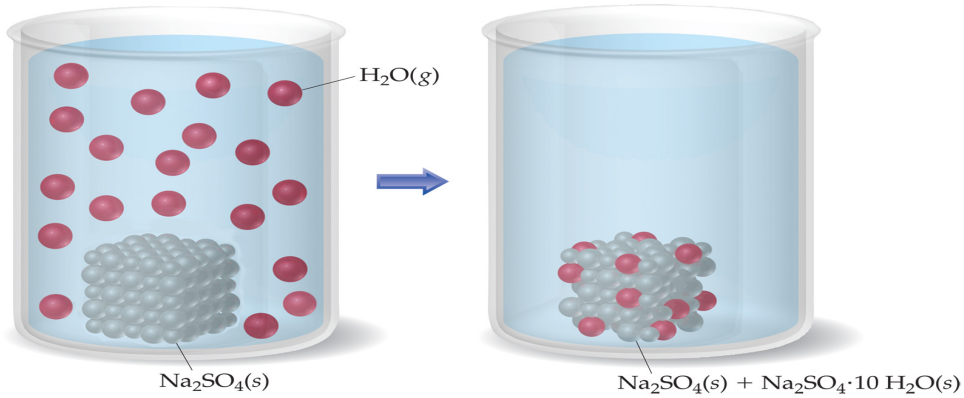


SAMPLE EXERCISE Assessing Entropy Change

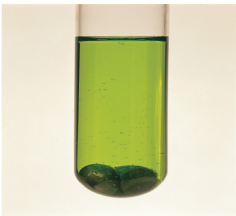
In the process illustrated below, water vapor reacts with excess solid sodium sulfate to form the hydrated form of the salt. The chemical reaction is

$$Na_2SO_4(s) + 10\ H_2O(g) \longrightarrow Na_2SO_4 \cdot 10\ H_2O(s)$$

Does the entropy of the system increase or decrease?



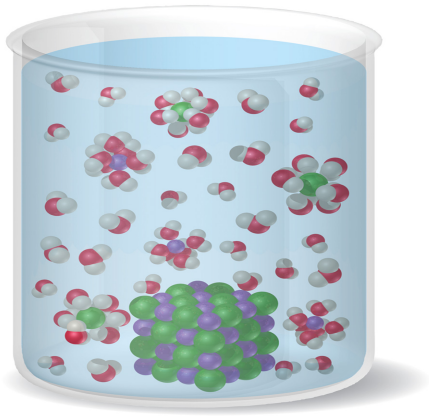
DISSOLUTION vs. REACTION




$$Ni(s) + HCl(aq) \longrightarrow NiCl_2(aq) + H_2(g) \xrightarrow{dry} NiCl_2(s)$$

- Dissolution is a physical change—you can get back the original solute by evaporating the solvent.
- If you can't, the substance didn't dissolve, it reacted.

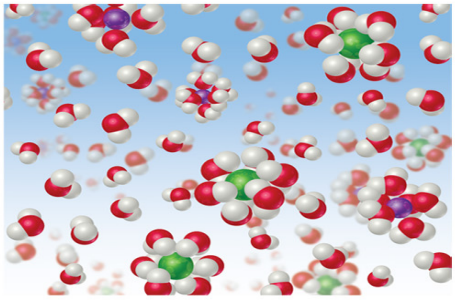
DEGREE OF SATURATION



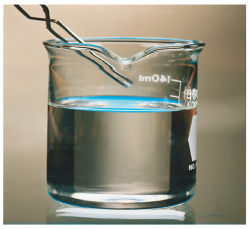
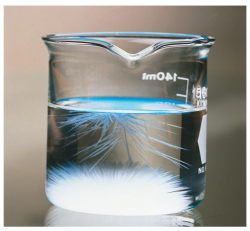
- Saturated solution
  - Solvent holds as much solute as is possible at that temperature.
  - Undissolved solid remains in flask.
  - Dissolved solute is in dynamic equilibrium with solid solute particles.

DEGREE OF SATURATION

- Unsaturated Solution
  - Less than the maximum amount of solute for that temperature is dissolved in the solvent.
  - No solid remains in flask.

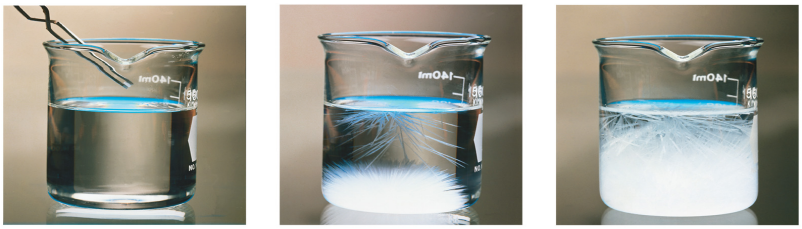


DEGREE OF SATURATION:


- Supersaturated
  - Solvent holds *more* solute than is normally possible at that temperature.
  - These solutions are unstable; crystallization can often be stimulated by adding a “seed crystal” or scratching the side of the flask.

DEGREE OF SATURATION:



Unsaturated, Saturated or Supersaturated?

⇒ How much solute can be dissolved in a solution?

More on this in Ionic Equilibria)

ELECTROLYTE SOLUTIONS:

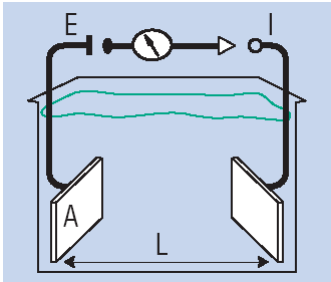
An electrolyte is any substance that when dissolved in a solvent produces a solution that will conduct electricity.

An electrolyte can be an acid, a base or a salt.

ELECTRICAL CONDUCTION IN SOLUTION:

Ohm's Law:

The current (I) flowing through a particular medium is directly proportional to the voltage or the electrical potential difference (V) across the medium and indirectly proportional to the resistance of the medium (R).



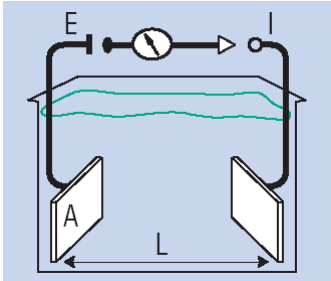
$$I = \frac{V}{R}$$

I in amperes, V in volts, and R in Ohms (Ω)

ELECTRICAL CONDUCTION IN SOLUTION:

RESISTANCE (R):

Is directly proportional to the length and inversely proportional to the cross section area of the medium.



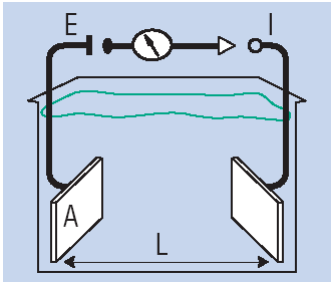
$$R \propto \frac{V}{R}$$

$R = \rho \frac{l}{A}$, ρ *is specific resistance or resistivity*

ELECTRICAL CONDUCTION IN SOLUTION:

CONDUCTANCE (C):

Is the reciprocal of resistance where κ is the specific conductance, or conductivity equal to $1/\rho$.



$$C = \frac{1}{R} = \frac{1}{\rho}\frac{A}{l} = \kappa\frac{A}{l}$$

Sample Problem:

The conductance of a solution is 0.689 Ω^{-1}. Calculate the specific conductance if the cell constant is 0.225 cm^{-1}.

MOLAR CONDUCTANCE:

Expressing conductance as a molar quantity:

$$\Lambda_m = \frac{(1000 cm^3 L^{-1})\kappa}{c}$$

c is the concentration of solution in mol L^{-1}

$\Lambda = \Lambda_o - B\sqrt{c}$, *where Λ_o is the equivalent conductance at infinite dilution.*

Sample Problem:

The conductance of a cell containing an aqueous 0.0560 M KCl is 0.239 Ω^{-1}. When the sample cell is filled with an aqueous 0.0836 M NaCl solution, its conductance is 0.0825 Ω^{-1}. Given the equivalence conductance of KCL is 134.5 Ω^{-1} $equiv^{-1}cm^2$, calculate the equivalent conductance of NaCl solution.

Degree of dissociation

At certain concentration, an electrolyte maybe only partially dissociated.

At infinite dilution, any electrolyte is completely dissociated.

$$\alpha = \frac{\Lambda}{\Lambda_o}$$

$$K_a = \frac{c\Lambda^2}{\Lambda_o(\Lambda_o - \Lambda)}$$

Ostwald Dilution Law ⟶

$$\frac{1}{\Lambda} = \frac{1}{K_a \Lambda_0^2}(\Lambda c) + \frac{1}{\Lambda_o}$$

SAMPLE PROBLEM:

The equivalent conductance of an aqueous acetic acid solution, concentration 0.10M, is $5.2\Omega^{-1}$ equiv^{-1} cm^2 at 298 K. Calculate the dissociation constant of acetic acid.

APPLICATION OF CONDUCTANCE MEASUREMENTS

Acid Base Titration:

- Conductance of H^+ and OH^- ions are considerably higher than those of other cations and anions.

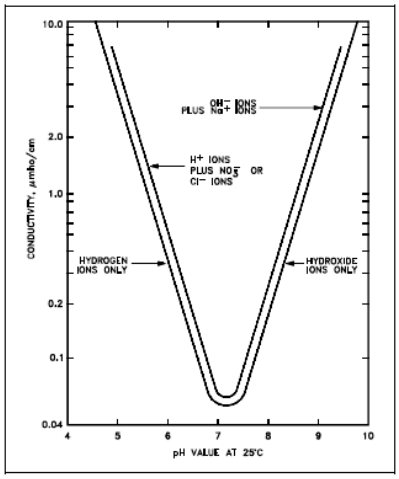


Figure 5 Theoretical Conductivity as a Function of pH

APPLICATION OF CONDUCTANCE MEASUREMENTS

SOLUBILITY DETERMINATION: (example AgCl)

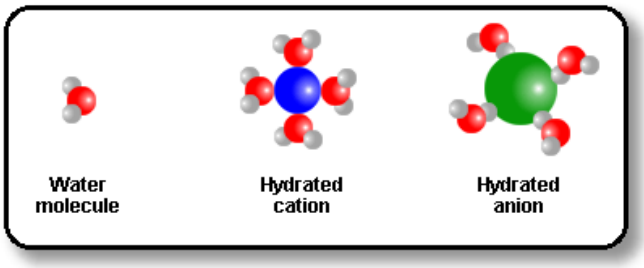
$$\Lambda = \frac{(1000 cm^3 L^{-1})\kappa}{c}$$

$$c = S = \frac{(1000 cm^3 L^{-1})\kappa}{\Lambda} = \frac{(1000 cm^3 L^{-1})\kappa}{\Lambda_o}$$

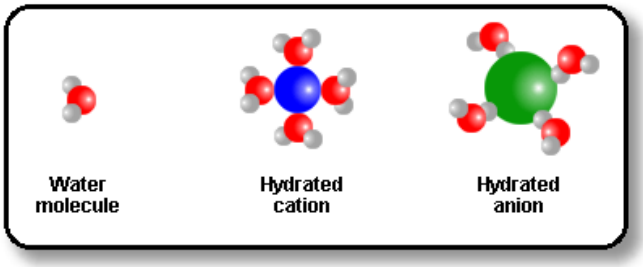
for AgCl specific conductance is $1.86 \times 10^{-6} \Omega^{-1} cm^{-1}$

subtract contribution from water (a weak electrolyte)

MOLECULAR VIEW OF THE SOLUTION PROCESS



MOLECULAR VIEW OF THE SOLUTION PROCESS



THERMODYNAMICS OF IONS IN SOLUTION

IONS CAN NOT BE STUDIED SEPARATELY.

ARBITRARILY ASSIGNED a ZERO VALUE TO H^+

For the following reaction:

$1/2H_2(g) + 1/2Cl_2(g) \longrightarrow H^+(aq) + Cl^-(aq)$

$\Delta_r H^o$ = = -167.2 kJ mol

SAMPLE PROBLEM:

Use the standard enthalpy of the reaction:

$Na(s) + 1/2Cl_2(g) \longrightarrow Na^+(aq) + Cl^-(aq)$

$\Delta_r H^o$ = -406.9 kJ/mol

To calculate the value of $\Delta_r H^o$ for $Na^+(aq)$.

IONIC ACTIVITY:

ELECTROLYTE SOLUTIONS DEVIATE FROM IDEAL BEHAVIOR MORE STRONGLY AND AT LOWER CONCENTRATIONS THAN A NONELECTROLYTE SOLUTIONS. WHY?

ACTIVITIES / ACTIVITY COEFFICIENTS ARE ESSENTIAL WHEN WORKING WITH ELECTROLYTES!

IONIC ACTIVITY

Consider the solution from the salt $M_{v+}X_{v-}$:

$$M_{v+}X_{v-}(s) \longrightarrow v+M^{z+} + v-X^{z-}$$

mean ionic molality is expressed as a geometric mean of the individual ionic molalities:

$$m_{\pm} = (m_{+}^{v+} m_{-}^{v-})^{1/v}$$

or

$$m = m\left[(v_{+}^{v+})(v_{-}^{v-})\right]^{1/v}$$

IONIC ACTIVITY: SAMPLE PROBLEM

Write the mean ionic molality expression for $Mg_3(PO_4)_2$

IONIC ACTIVITY:

mean ionic activity :

$$a_{\pm} = (a_{+}^{\nu+} a_{-}^{\nu-})^{1/\nu}$$

the mean ionic activity and the mean ionic molality are related by the mean ionic acitvity coefficient, $\gamma_{\pm}$

thus :

$$a_{\pm} = \gamma_{\pm} m_{\pm}$$

where : $\gamma_{\pm} = (\gamma_{+}^{\nu+} \gamma_{-}^{\nu-})^{1/\nu}$

$$a = a_{\pm}^{\nu}$$

IONIC ACTIVITY: SAMPLE PROBLEM

Write the expressions for the activities of a) KCl b) Na_2CrO_4 c) $Al_2(SO_4)_3$ in terms of their molalities and mean ionic activity coefficient.

COLLIGATIVE PROPERTIES OF ELECTROLYTE SOLUTIONS

0.1 *m* NaCl solution ⟶ 0.1 *m* Na^+ ions & 0.1 *m* Cl^- ions

Colligative properties are properties that depend only on the **number** of solute particles in solution and not on the **nature** of the solute particles.

0.1 *m* NaCl solution ⟶ 0.2 *m* ions in solution

$$\textbf{\textit{van't Hoff factor (i)}} = \frac{\text{actual number of particles in soln after dissociation}}{\text{number of formula units initially dissolved in soln}}$$

	i should be
nonelectrolytes	1
NaCl	2
$CaCl_2$	3

12.7

COLLIGATIVE PROPERTIES OF ELECTROLYTE SOLUTIONS

Boiling-Point Elevation $\Delta T_b = i\,K_b\,m$

Freezing-Point Depression $\Delta T_f = i\,K_f\,m$

Osmotic Pressure (π) $\pi = iMRT$

TABLE 12.3

The van't Hoff Factor of 0.0500 *M* Electrolyte Solutions at 25°C

Electrolyte	*i* (Measured)	*i* (Calculated)
Sucrose*	1.0	1.0
HCl	1.9	2.0
NaCl	1.9	2.0
$MgSO_4$	1.3	2.0
$MgCl_2$	2.7	3.0
$FeCl_3$	3.4	4.0

FREEZING POINT DEPRESSION

At what temperature will a 5.4 molal solution of NaCl freeze?

Solution

$\Delta T_{FP} = K_f \cdot m \cdot i$

$\Delta T_{FP} = (1.86\ ^oC/molal) \cdot 5.4\ m \cdot 2$

$\Delta T_{FP} = 20.1\ ^oC$

FP = 0 – 20.1 = -20.1 ^oC

COLLIGATIVE PROPERTIES OF ELECTROLYTE SOLUTIONS

Colligative properties of an electrolyte solution are influenced by the number of ions in solution.

For completely dissociated salts, like NaCl, the colligative properties are much like that of nonelectrolytes.

For incompletely dissociates salts: we define a factor, *i*

COLLIGATIVE PROPERTIES:

van't Hoff factor :

$$i = \frac{\text{actual no. of particles in solution}}{\text{no. of particles before dissolution}}$$

If a solution contains N units of an electrolyte, and α is the degress of dissociation, then

$$M_{v+}X_{v-} \Leftrightarrow v + M^{z+} + v - X^{z-}$$

$$N(1-\alpha) \qquad Nv + \alpha \qquad Nv - \alpha$$

$N(1-\alpha)$; *undissociated units*

$Nv\alpha$; *ions in solution at equilibrium*

THERMODYNAMICS OF IONS IN SOLUTION

van't Hoff's factor :

$$i = \frac{N(1-\alpha) + Nv\alpha}{N} = 1 - \alpha + v\alpha$$

and

$$\alpha = \frac{i-1}{v-1}$$

SAMPLE PROBLEM:

Calculate the freezing point of a solution made by dissolving 3.50 g of potassium chloride (molar mass = 74.55 g/mol) in 100.0 g of water. Assume ideal behavior for the solution; K_f = 1.86°C/*m*.

SAMPLE PROBLEM:

A 0.100 *m* K_2SO_4 solution has a freezing point of -0.43°C. What is the van't Hoff factor for this solution? K_f = 1.86°C/*m*

The osmotic pressures of a 0.01m solution of $CaCl_2$ and 0.01m sucrose solution at 298K are 0.605 atm and 0.224 atm, respectively, Calculate the van' t Hoff' s factor and the degree of dissociation for $CaCl_2$. Assume ideal behavior

SAMPLE PROBLEM:

SAMPLE PROBLEM:

The freezing point depression of a 0.01m acetic acid is 0.0193K. Calculate the degree of dissociation for acetic acid at this concentration. K_f = 1.86 $^oC/m$

DEBYE HUCKEL THEORY OF ELECTROLYTES

ASSUMPTIONS:

- electrolytes are completely dissociated into ions
- the solutions are dilute (<0.01 m)
- presence of an ionic atmosphere, each ion is surrounded by ions of opposite charge.

In Debye Huckel calculation the Gibbs energy is related to the activity coefficient of the individual ions.

$$\log \gamma_{\pm} = -\frac{1.824 \times 10^6}{(\varepsilon T)^{3/2}} |z_+ z_-| \sqrt{I}$$

DEBYE HUCKEL THEORY:

$$\log \gamma_{\pm} = -\frac{1.824 \times 10^{6}}{(\varepsilon T)^{3/2}}$$

I is the ionic strength defined as :

$$I = \frac{1}{2}\sum_{i} m_i z_i^2$$

where m_i and z_i are the molality and charge of ith ion in the electrolyte.

DEBYE HUCKEL THEORY:

at standard conditions (T = 298K), and solutions in water (ε = 78.54) the Debye Huckel equation become :

$$\log \gamma_{\pm} = -0.509 |z_+ z_-| \sqrt{I}$$

Debye - Huckel limiting law

SAMPLE PROBLEM:

Calculate the mean activity coefficient ($\gamma_{\pm}$) of a 0.01m aqueous solution of $CuSO_4$ at 298 K.

END OF CHAPTER 8