

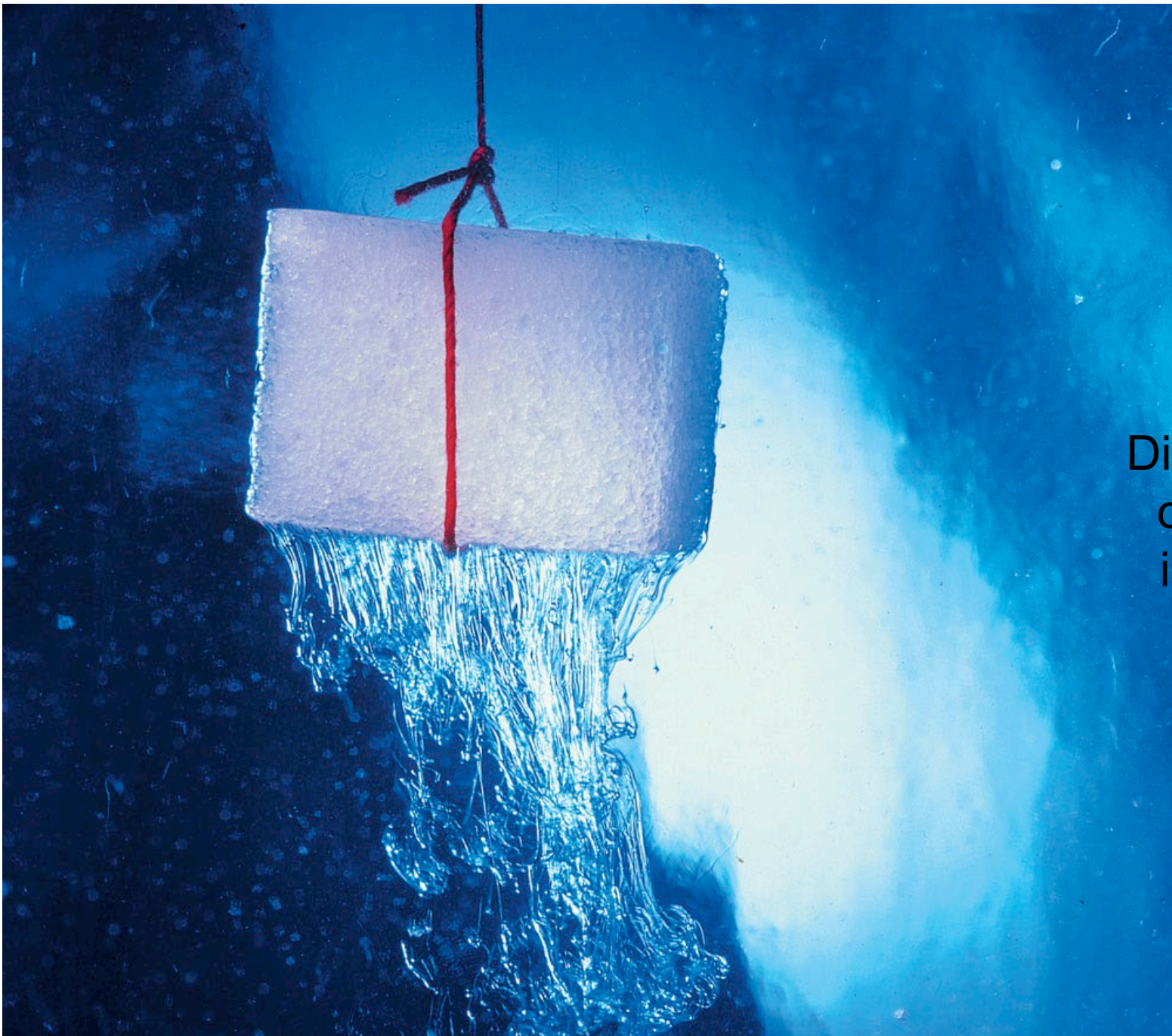
11

CHAPTER

SOLUTIONS

- Homogeneous systems that contain two or more substances are called solutions
- The major component is usually called the solvent, and minor components are called the solutes

- 11.1** Composition of Solutions
- 11.2** Nature of Dissolved Species
- 11.3** Reaction Stoichiometry in Solutions:
Acid-Base Titrations
- 11.4** Reaction Stoichiometry in Solutions:
Oxidation-Reduction Titrations
- 11.5** Phase Equilibrium in Solutions: Nonvolatile Solutes
- 11.6** Phase Equilibrium in Solutions: Volatile Solutes
- 11.7** Colloidal Suspensions



Dissolution
of sugar
in water

→ Several measures are used to specify the composition of a solution

11.1 COMPOSITION OF SOLUTIONS

➤ Percent composition

$$\text{Mass (or Weight) \%} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100$$

$$\text{Vol \%} = \frac{\text{vol of solute}}{\text{vol of solution}} \times 100$$

➤ Parts per million & parts per billion

$$\text{ppm} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 10^6 \approx \text{O}(\text{mg L}^{-1})$$

$$\text{ppb} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 10^9 \approx \text{O}(\mu\text{g L}^{-1})$$

➤ Mole Fraction

$$X_1 = \frac{n_1}{n_1 + n_2}, \quad X_2 = \frac{n_2}{n_1 + n_2} = 1 - X_1 \quad (\text{for a binary mixture})$$

➤ Molarity & Molality

$$\text{Molarity (M)} = \frac{\text{moles solute}}{\text{liters solution}} = \text{mol L}^{-1}$$

$$\text{Molality (m)} = \frac{\text{moles solute}}{\text{kilograms solvent}} = \text{mol kg}^{-1}$$

✓ Molality is independent of temperature!



(a)



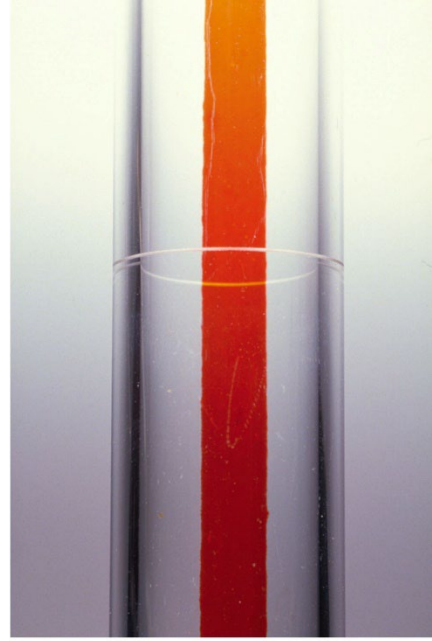
(b)



(c)



(d)



(e)

Preparing a solution of NiCl_2 using a volumetric flask

➤ Dilution of solution

Chemical amount conserved.

$$n = c_i V_i = c_f V_f \longrightarrow c_f = \frac{\text{moles solute}}{\text{final solution volume}} = \frac{c_i V_i}{V_f}$$

n : number of moles of solute

$c_{i(f)}$: initial (final) concentration in molarity

$V_{i(f)}$: initial (final) solution volume in liters

- (solvent-to-solvent and solute-to-solute attractions) are broken up and replaced, at least in part, by new solvent-to-solute attractions.
- liquid water is indisputably the best known and most important solvent.

11.2 NATURE OF DISSOLVED SPECIES

◆ Aqueous Solutions of Molecular Species

- Polar molecules dissolved by water ~ “Like dissolves like”
- Sugars: $C_m(H_2O)_n$
 - ~ Sucrose ($C_{12}H_{22}O_{11}$), Fructose ($C_6H_{12}O_6$), Ribose ($C_5H_{10}O_5$)
 - ~ Do not contain water molecules
 - ~ Include polar –OH groups
 - ~ Dipole-dipole interaction between –OH groups and water molecules → *hydrogen bonds*

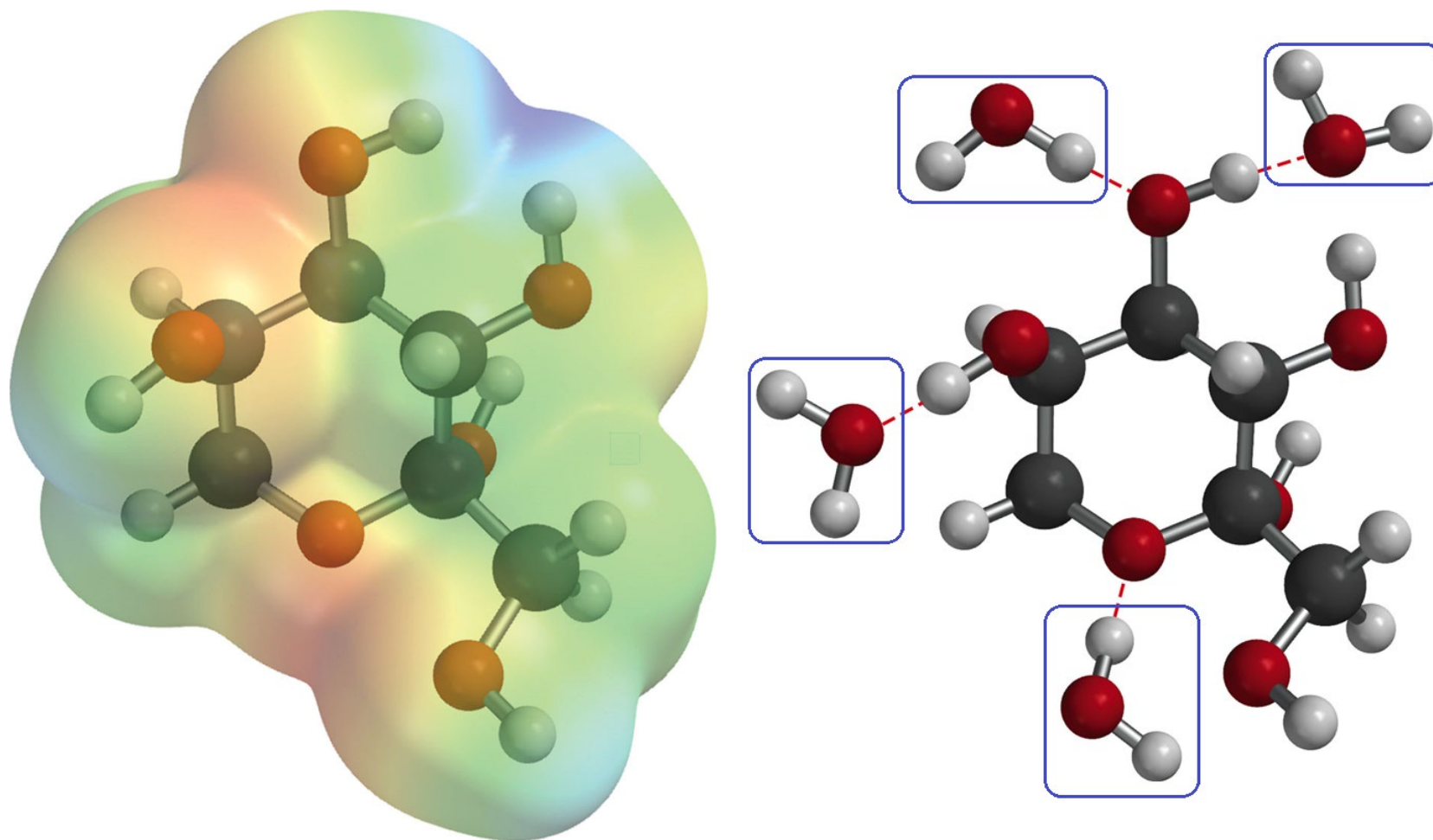
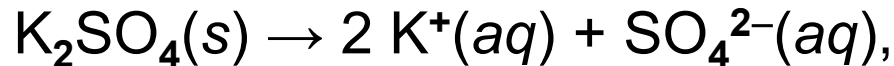


Fig. 11.2 Electrostatic potential energy surface of a glucose molecule and its hydrated form in aqueous solution. Four water molecules are bonded with hydrogen bondings.

◆ Aqueous Solutions of Ionic Species (Electrolytes)

➤ **Solubility:** Maximum mass dissolved in 1L at 25°C



Solubility of K_2SO_4 : 120 g L^{-1} at 25°C

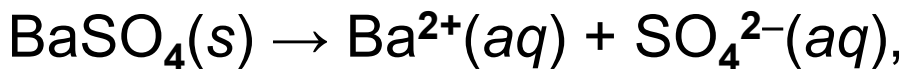
Dissolution of ionic species → Ion-dipole forces

Each ion is surrounded by an intact **solvation shell** of water molecules.

~ Good conductor, strong electrolyte

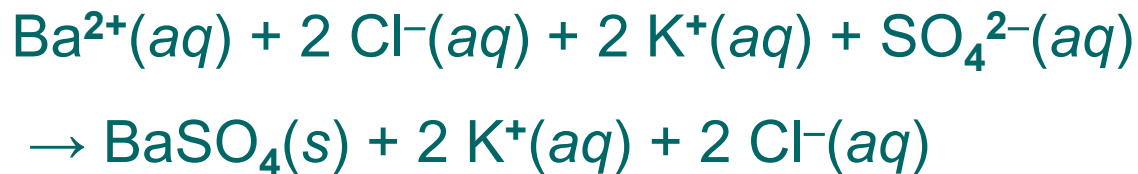
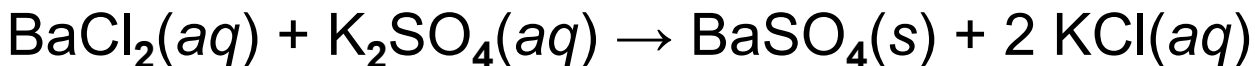
~ Electrophoresis under an electric field

❖ Insoluble salts

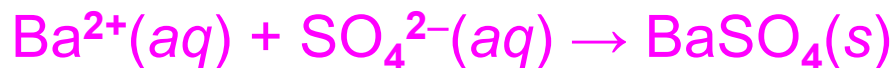


Solubility of BaSO_4 : 0.0025 g L^{-1} at 25°C

➤ Precipitation reaction



❖ Net ionic equation



Spectator ions: Cl^{-} and K^{+}

➤ Potassium sulfate (K_2SO_4)

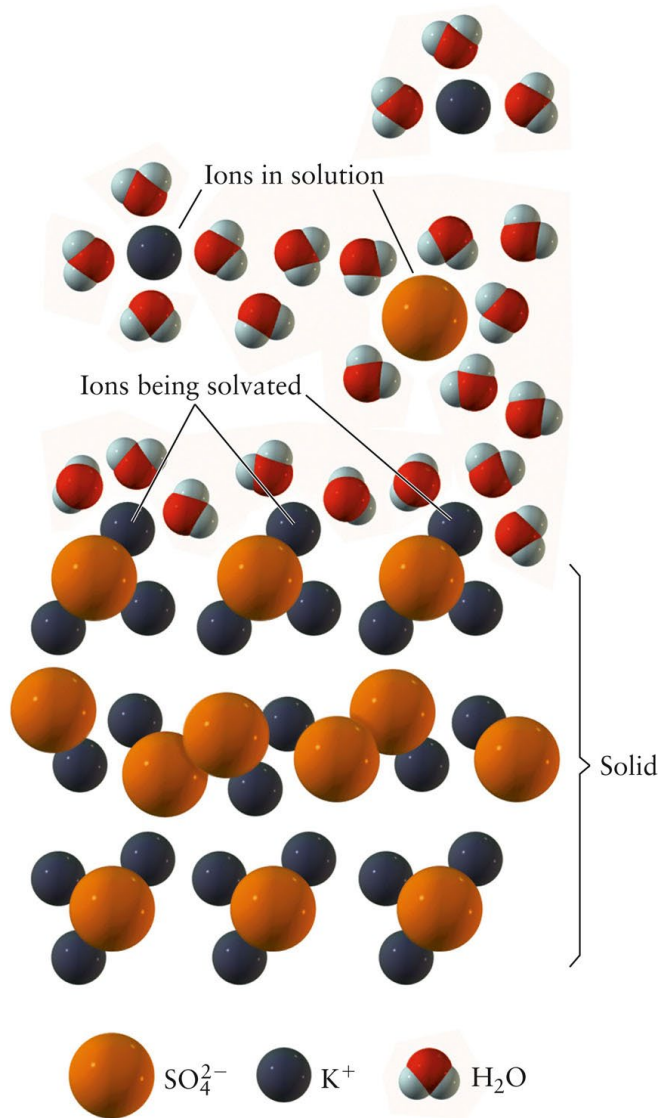
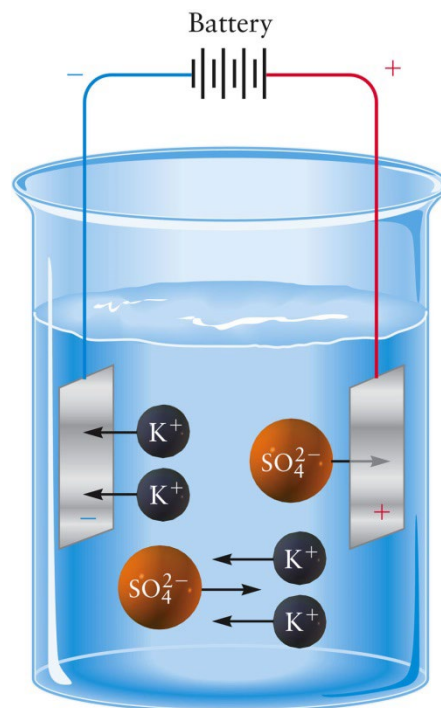


Fig. 11.3 Dissolves in water.
General Chemistry I



Conducts electricity.

Fig 11.4



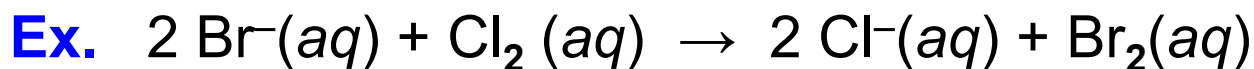
Reacts with $BaCl_2 \rightarrow BaSO_4 \downarrow$

Fig 11.5

→ Most chemical reactions that occur on the earth's surface, whether in living organisms or among inorganic substances, take place in aqueous solution.

11.3 REACTION STOICHIOMETRY IN SOLUTIONS: ACID-BASE TITRATIONS

➤ Reactions in Solution



We have 50.0 mL of 0.0600 M solution of NaBr.

Q. What is the volume of 0.0500 M Cl_2 to react completely with Br^- ?

$$n = (0.0500 \text{ L})(0.0600 \text{ mol/L}) = 3.00 \times 10^{-3} \text{ mol}$$

$$n = 3.00 \times 10^{-3} \text{ mol} \times (1/2) = 1.50 \times 10^{-3} \text{ mol}$$

$$V = (1.50 \times 10^{-3} \text{ mol}) / (0.0500 \text{ mol/L}) = 3.00 \times 10^{-2} \text{ L}$$

Q. What is the concentration of Cl^- ? $n_{\text{Cl}^-} = n_{\text{Br}^-}$

$$V_{\text{total}} = V_{\text{Br}^-(aq)} + V_{\text{Cl}_2(aq)} = 0.0500 \text{ L} + 0.0300 \text{ L} = 0.0800 \text{ L}$$

$$[\text{Cl}^-] = n_{\text{Cl}^-} / V_{\text{total}} = 3.00 \times 10^{-3} \text{ mol} / 0.0800 \text{ L} = 0.0375 \text{ M}$$

◆ Background on Acid-Base Reactions

T A B L E 11.1

Names of Common Acids

Binary Acids	Oxoacids	Organic Acids
HF, hydrofluoric acid	H ₂ CO ₃ , carbonic acid	HCOOH, formic acid
HCl, hydrochloric acid	H ₃ PO ₃ , phosphorus acid	CH ₃ COOH, acetic acid
HCN, hydrocyanic acid [†]	H ₃ PO ₄ , phosphoric acid	C ₆ H ₅ COOH, benzoic acid
H ₂ S, hydrosulfuric acid	HNO ₂ , nitrous acid	HOCCOOH, oxalic acid
	HNO ₃ , nitric acid	
	H ₂ SO ₃ , sulfurous acid	
	H ₂ SO ₄ , sulfuric acid	
	HClO, hypochlorous acid	
	HClO ₂ , chlorous acid	
	HClO ₃ , chloric acid	
	HClO ₄ , perchloric acid	

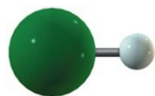
[†]Contains three elements but is named as a binary acid.

➤ Names of common acids

Binary acids

HF, HCl, H₂S

HCN

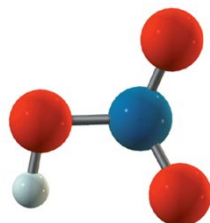


HCl

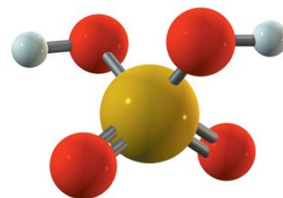
Oxoacids

H₂CO₃, HNO₃

H₂SO₄, H₃PO₄



HNO₃

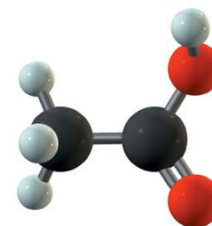


H₂SO₄

Organic acids

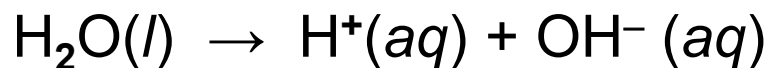
HCOOH, CH₃COOH (HAc)

C₆H₅COOH



HAc

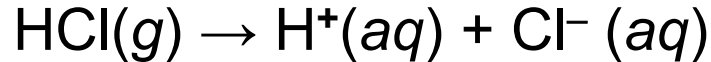
➤ Ionization of pure water



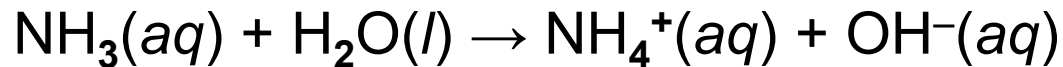
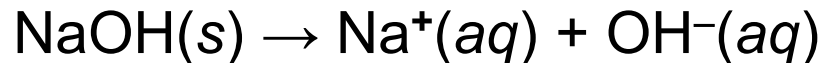
hydronium ion

➤ Arrhenius's definition of Acids and Bases

Acid ~ produces H^+ in aqueous solution ($> [H^+]_{\text{water}}$)



Base ~ produces OH^- in aqueous solution ($> [OH^-]_{\text{water}}$)



➤ Titration

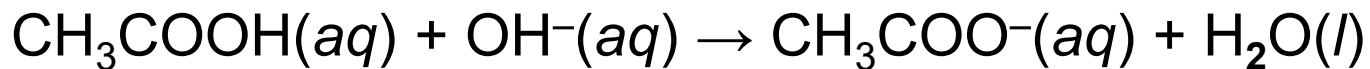
Determination of unknown amount of a sample

Titrant (*in buret, known concentration, volume to be measured*)

→ Titrate (*in flask, unknown concentration, known volume*)

End point, Indicator

➤ Acid-Base Titration



Indicator ~ Phenolphthalein

Ex. 31.66 mL of 1.306 M NaOH \rightarrow 50.00 mL of a vinegar sample
Calculate $[\text{CH}_3\text{COOH}(aq)]$ in the sample.

At the end point,

$$\begin{aligned}n(\text{NaOH}) &= n(\text{CH}_3\text{COOH}) = (1.306 \text{ mol/L})(0.03166 \text{ L}) \\ &= 4.135 \times 10^{-2} \text{ mol}\end{aligned}$$

$$[\text{CH}_3\text{COOH}] = (4.135 \times 10^{-2} \text{ mol}) / (0.0500 \text{ L}) = 0.827 \text{ M}$$

11.4 REACTION STOICHIOMETRY IN SOLUTIONS: OXIDATION-REDUCTION TITRATIONS

➤ Background on Oxidation-Reduction (Redox) Reactions

Oxidation ~ increase in the oxidation number, donate electrons

Reduction ~ decrease in the oxidation number, accept electrons

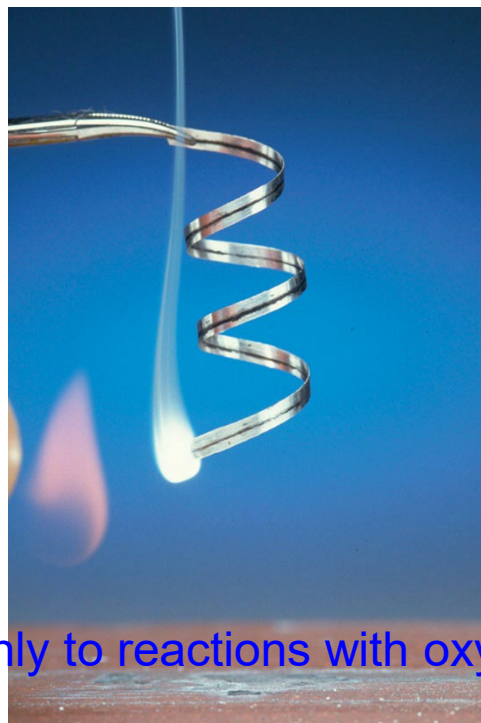
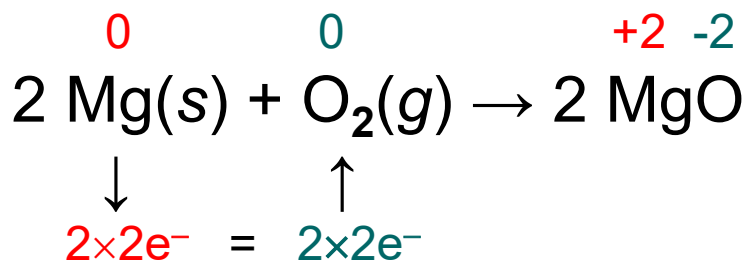
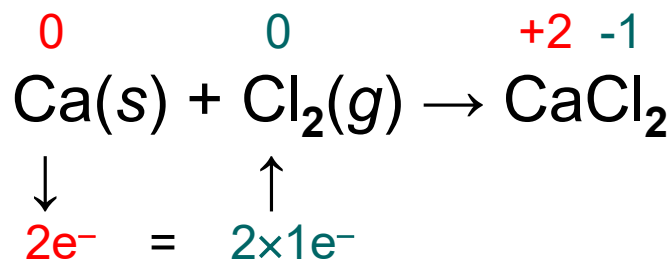
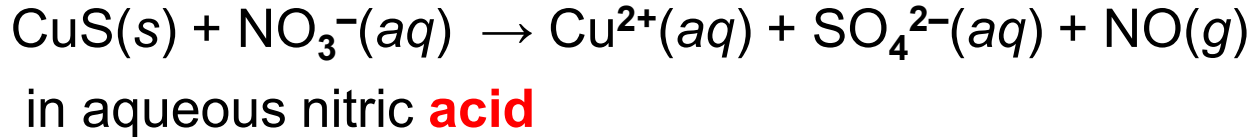


Fig. 11.6

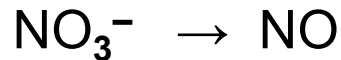
Mg burning in air.
Flash powder for
photograph
fireworks

→ Originally, the term oxidation referred only to reactions with oxygen
General Chemistry I

◆ Balancing Oxidation-Reduction Equations

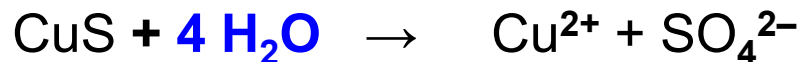


- Step 1. Divide into two unbalanced **half-reactions**.



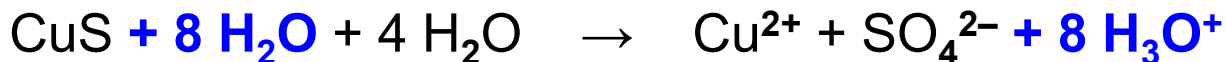
- Step 2. Balance **all elements** except oxygen and hydrogen.
Already done.

- Step 3. Balance **oxygen** by adding **H₂O**.

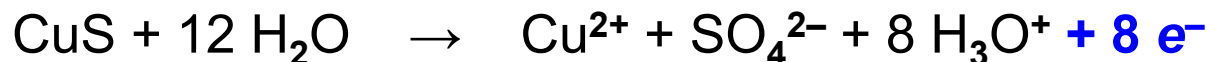


➤ Step 4. Balance **hydrogen**.

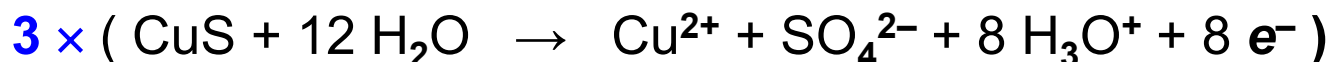
~ Add **H₃O⁺ / H₂O (acidic)** or **H₂O / OH⁻ (basic)**



➤ Step 5. Balance **charge** using **e⁻**.

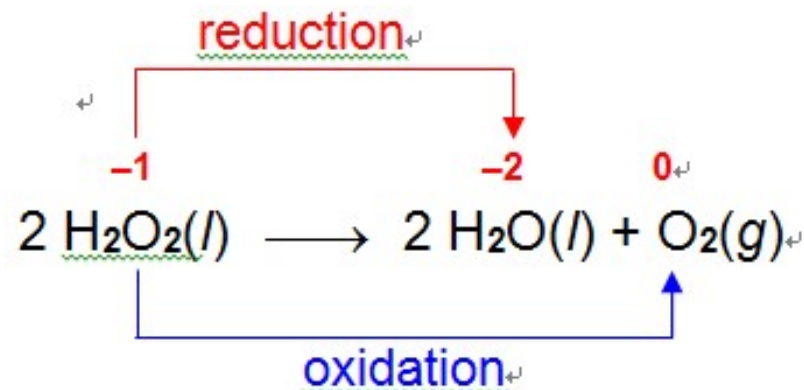


➤ Step 6. Combine the two half-reactions **canceling e⁻**.



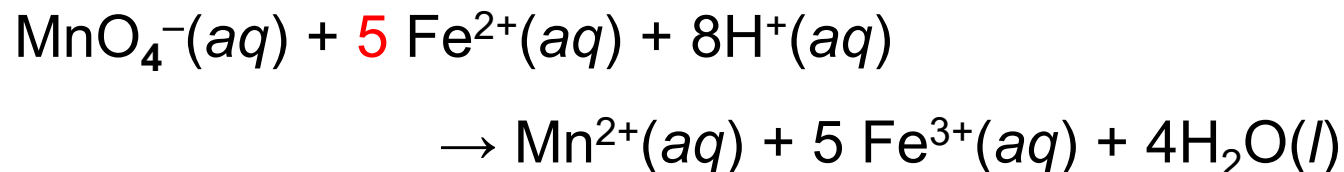
➤ Disproportionation

~ Redox reaction in which a single substance is both oxidized and reduced.



◆ Redox Titration

➤ Titration of Fe^{2+} in an iron ore with KMnO_4



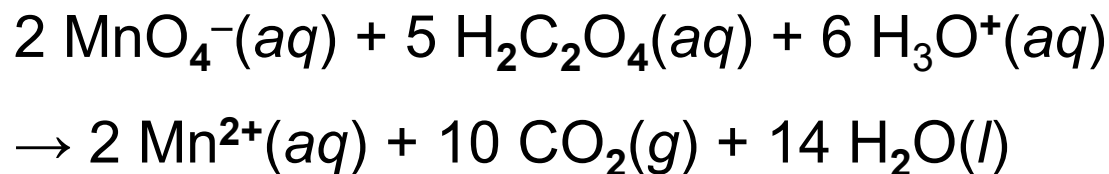
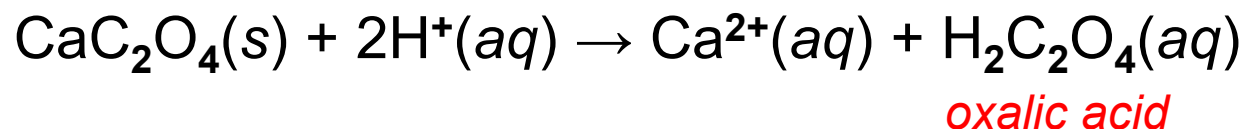
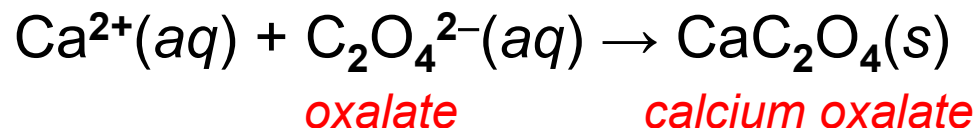
Volume of 0.09625 M KMnO_4 at the end point ~ 26.34 mL

$$n(\text{MnO}_4^-) = (0.02634 \text{ L})(0.09625 \text{ mol/L}) = 2.535 \times 10^{-3} \text{ mol}$$

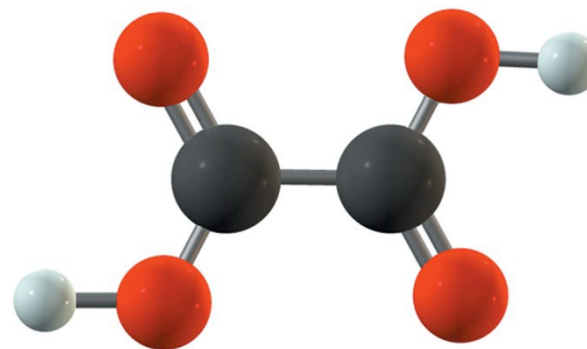
$$n(\text{Fe}^{2+}) = n(\text{MnO}_4^-) \times 5 = 1.268 \times 10^{-2} \text{ mol}$$

➤ **Titration of Ca^{2+} in an iron ore with KMnO_4**

~ *Indirect method*



Oxalic acid, $\text{H}_2\text{C}_2\text{O}_4$



→ “nonvolatile” we mean that the vapor pressure of the solute above the solution is negligible.

11.5 PHASE EQUILIBRIUM IN SOLUTIONS: NONVOLATILE SOLUTES

➤ Raoult's law

~ for Ideal solutions

Vapor pressure of solvent in solution

$P_1 \propto$ its mole fraction X_1

$$P_1 = X_1 P_1^\circ$$

P_1° : vapor press of pure solvent

Plot of P_1 vs. X_1 ~ a straight line

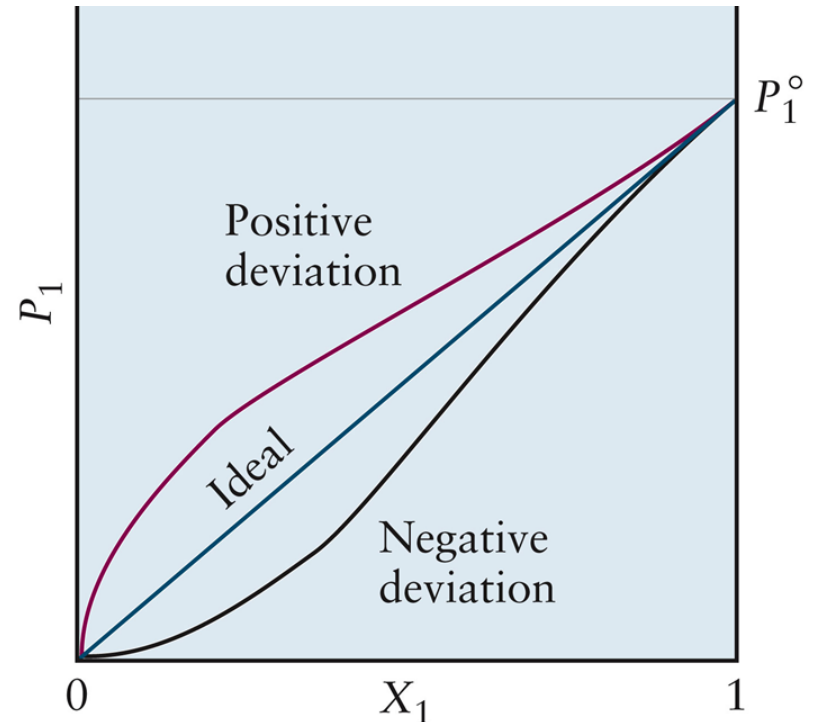


Fig. 11.10 Vapor pressure of solvent in ideal and nonideal solutions.

➤ Real solutions

~ *Positive or negative deviations* from the linear behavior of Raoult's law

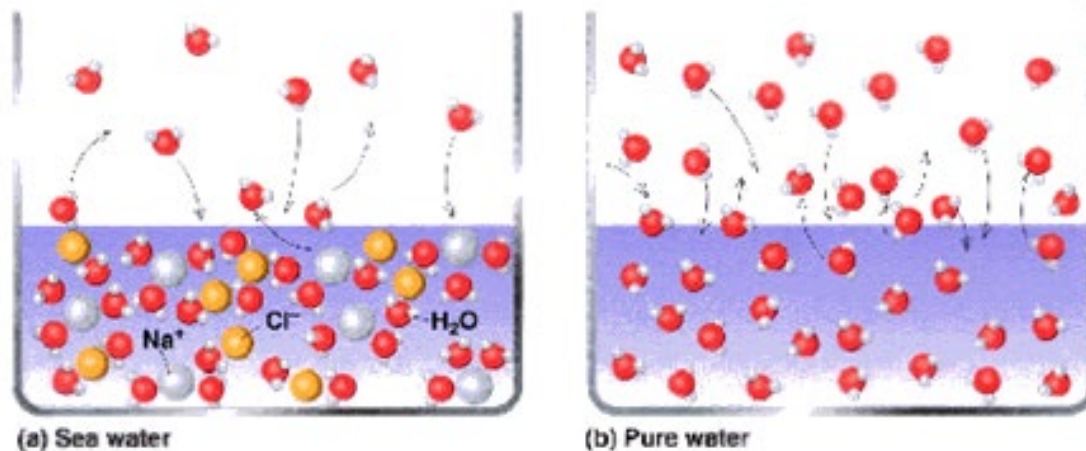
Real solutions → ideal solutions as $X_1 \rightarrow 1$ (dilute)

❖ *Negative deviations*

~ solute-solvent attractions > solvent-solvent attractions

❖ *Positive deviations*

~ solute-solvent attractions < solvent-solvent attractions



◆ Colligative properties

Collective properties depending on the *number* of dissolved particles rather than the *nature* of the particular particles involved

→ Determination of *Molar mass*

Let us consider

Nonvolatile solute, Nonelectrolyte, Binary solution

- ❖ Vapor pressure lowering
- ❖ Boiling-point elevation
- ❖ Freezing-point depression
- ❖ Osmosis

➤ Vapor-Pressure Lowering

$$\Delta P_1 = P_1 - P_1^\circ = X_1 P_1^\circ - P_1^\circ = -X_2 P_1^\circ$$

$$\Delta P_1 = -X_2 P_1^\circ$$

P_1 (above a dilute solution) < P_1° (above a pure solvent)

➤ Boiling-Point Elevation

Let $P_1^\circ = 1 \text{ atm}$ and $n_1 \gg n_2$ (dilute solution).

Slope of P_1 vs T curve: $S = -\Delta P_1 / \Delta T_b$

$$\Delta T_b = -\frac{\Delta P_1}{S} = \frac{X_2 P_1^\circ}{S} = \frac{1}{S} \left(\frac{n_2}{n_1 + n_2} \right) = \frac{1}{S} \frac{n_2}{n_1} = \frac{1}{S} \left(\frac{m_2/M_2}{m_1/M_1} \right)$$

❖ Boiling-point elevation constant
(or *Ebullioscopic constant*)

$$K_b = \frac{M_1}{(1000 \text{ g kg}^{-1}) S}$$

$$\Delta T_b = K_b \left(\frac{m_2 / M_2}{m_1 / (1000 \text{ g kg}^{-1})} \right)$$

$$\Delta T_b = K_b m$$

$$K_b = 0.512 \text{ K kg mol}^{-1} \text{ for water}$$

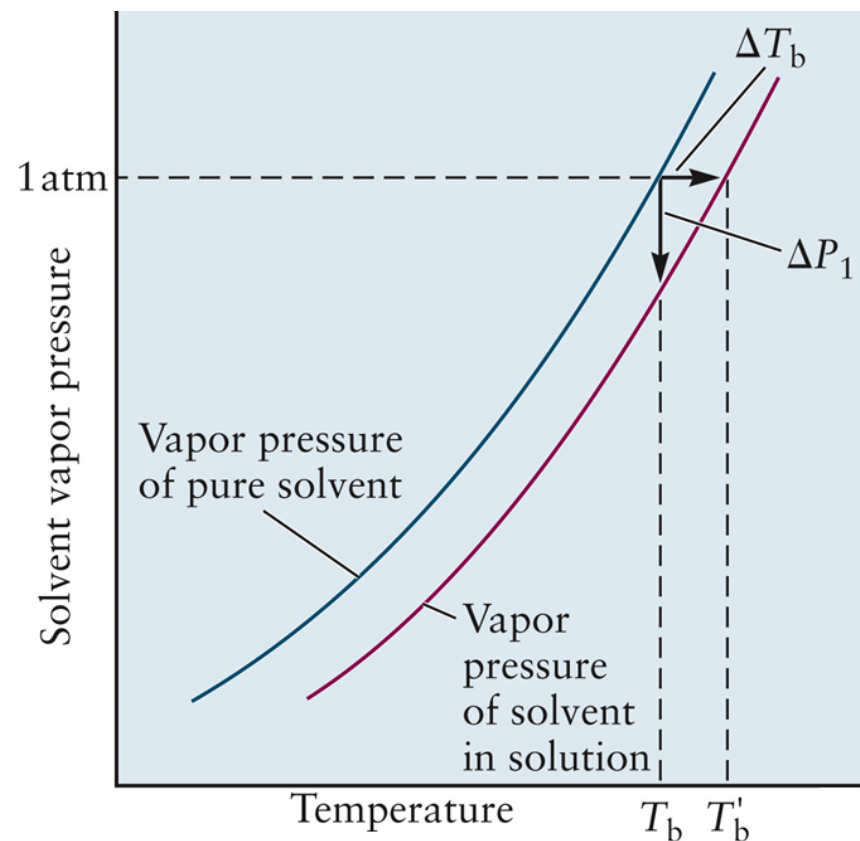


Fig. 11.11 Boiling point elevation.

T A B L E 11.2

Boiling-Point Elevation and Freezing-Point Depression Constants

Solvent	Formula	T_b (°C)	K_b (K kg mol ⁻¹)	T_f (°C)	K_f (K kg mol ⁻¹)
Acetic acid	CH ₃ COOH	118.1	3.07	17	3.9
Benzene	C ₆ H ₆	80.1	2.53	5.5	4.9
Carbon tetrachloride	CCl ₄	76.7	5.03	-22.9	32
Diethyl ether	C ₄ H ₁₀ O	34.7	2.02	-116.2	1.8
Ethanol	C ₂ H ₅ OH	78.4	1.22	-114.7	1.9
Naphthalene	C ₁₀ H ₈	—	—	80.5	6.8
Water	H ₂ O	100.0	0.512	0.0	1.86

EXAMPLE 11.12

When 6.30 g of an unknown hydrocarbon is dissolved in 150.0 g of Benzene, the boiling point of the solution increases by 0.597°C. What is the molar mass of the unknown substance?

$$m = \frac{\Delta T_b}{K_b} = \frac{0.597 \text{ K}}{2.53 \text{ K kg mol}^{-1}} = 0.236 \text{ mol kg}^{-1}$$

$$n = (0.236 \text{ mol kg}^{-1}) \times (0.1500 \text{ kg}) = 0.0354 \text{ mol}$$

$$\text{molar mass} = \frac{\text{mass}}{n} = \frac{6.30 \text{ g}}{0.0354 \text{ mol}} = 178 \text{ g mol}^{-1}$$

Hydrocarbon: anthracene (C₁₄H₁₀)

➤ Freezing-Point Depression

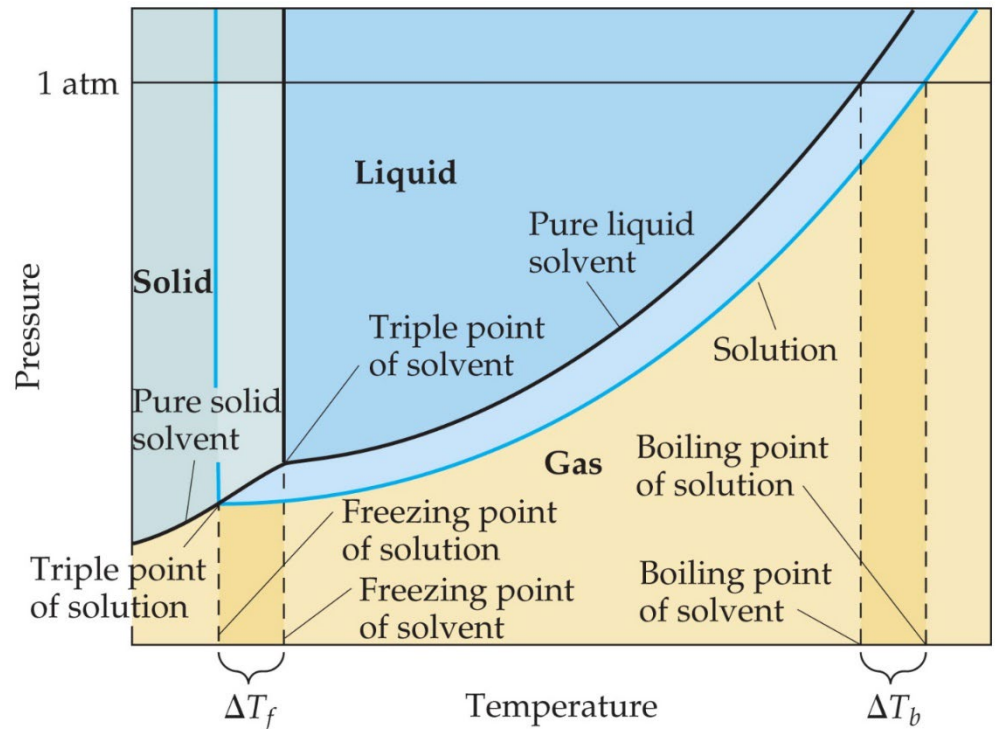
$$\Delta T_f = T'_f - T_f = -K_f m$$

K_f : cryoscopic constant

$K_f = 1.86 \text{ K kg mol}^{-1}$ for water

For dissociating solutes,
count total molalities.

$\text{Ca}(\text{NO}_3)_2$ total 3 moles
(Ca^{2+} , 2 NO_3^{-} 's)



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Fig. Freezing-point depression

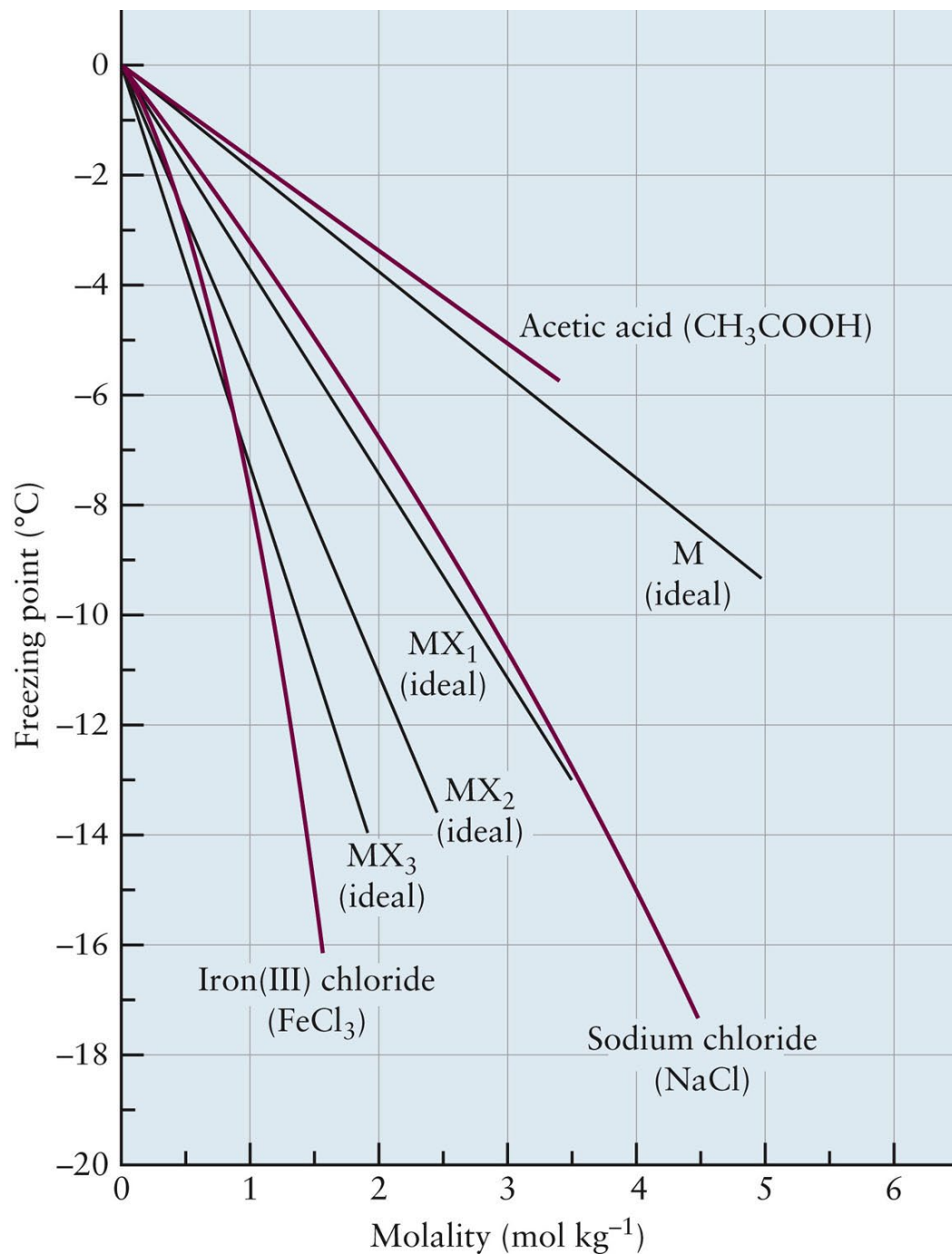


Fig. 11.13 Freezing-point depression of ionic substances.

HAc(M), NaCl(MX), FeCl₃(MX₃)

➤ Osmosis

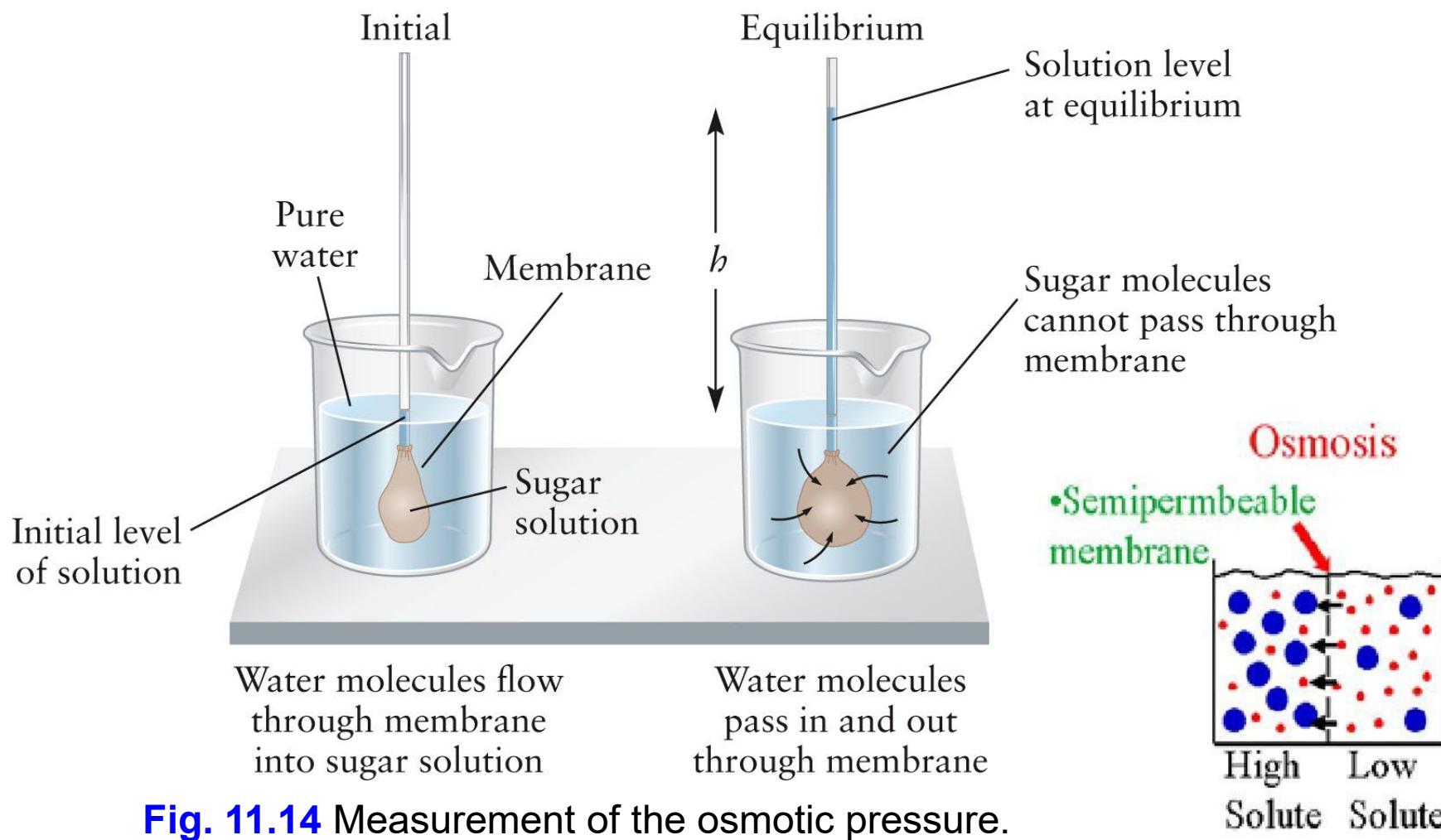


Fig. 11.14 Measurement of the osmotic pressure.

➤ Osmosis

Osmosis is the movement of **solvent** particles from a region of lower to a region of higher concentration through a semi-permeable membrane. (Larger solute molecules can not pass through the membrane.)

Osmotic pressure, π , is the pressure that must be applied to prevent the net flow of solvent.

$$\pi = cRT$$

van't Hoff equation

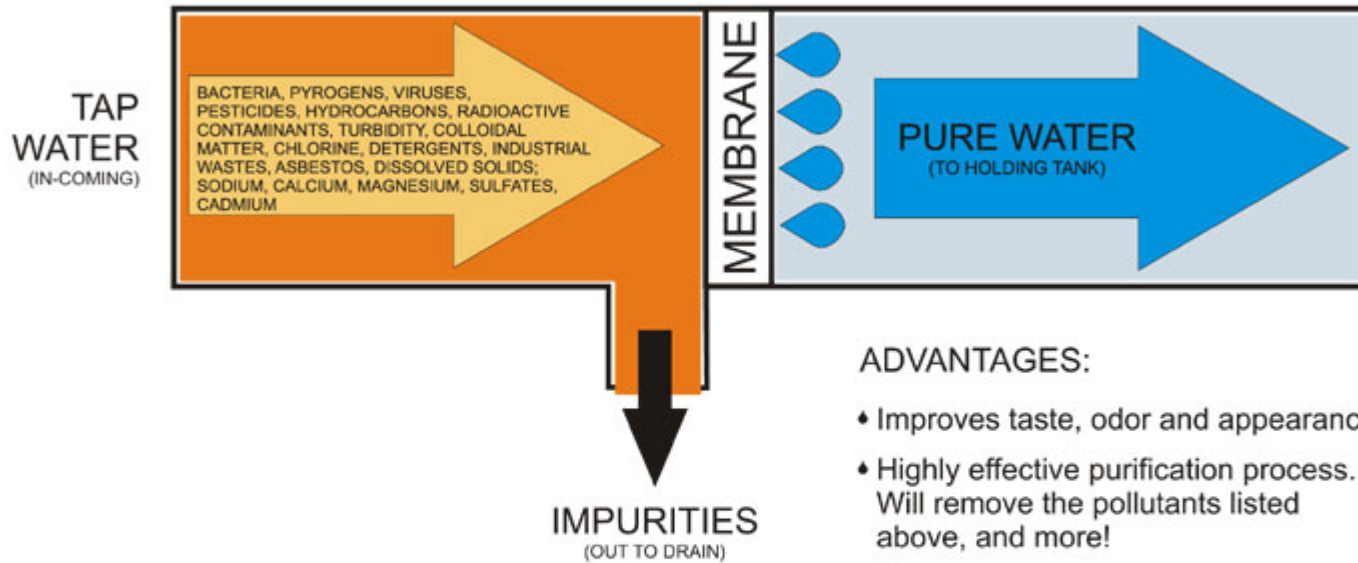
c = molarity

R = 0.0821 atm·L/mol·K

T = Kelvin temperature

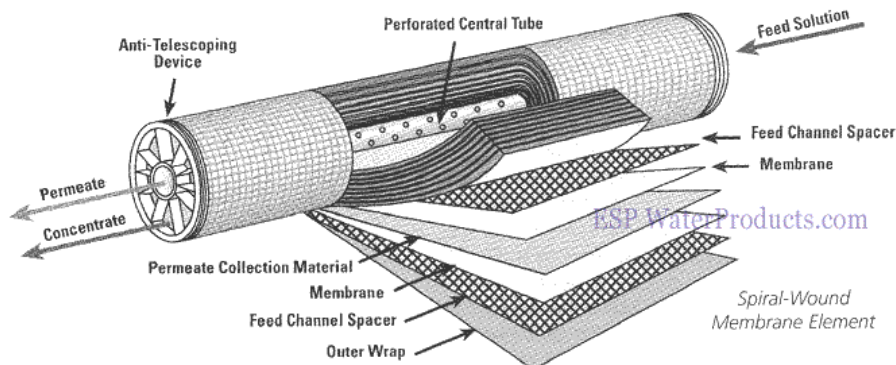
Reverse Osmosis

FROM TAP WATER TO PURE WATER



ADVANTAGES:

- ◆ Improves taste, odor and appearance
- ◆ Highly effective purification process. Will remove the pollutants listed above, and more!
- ◆ Consumes no energy
- ◆ Very convenient
- ◆ Flushes away pollutants, does not collect them
- ◆ Easy to keep clean
- ◆ Low production cost - gives you water of a guaranteed quality for pennies per gallon



EXAMPLE 11.16

A chemist dissolves 2.00 g of a protein in 0.100 L water. The osmotic pressure is 0.021 atm at 25°C. What is the approximate molar mass of the protein?

$$c = \frac{\pi}{RT} = \frac{0.021 \text{ atm}}{(0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1})(298 \text{ K})} = 8.6 \times 10^{-4} \text{ mol L}^{-1}$$

$$M = \frac{20.0 \text{ g}}{8.6 \times 10^{-4} \text{ mol}} = 23,000 \text{ g mol}^{-1}$$



Osmotic pressure is useful for large molecules with low solubilities.

Under the identical conditions,

Osmotic pressure with $h = 22 \text{ cm}$

Vapor-pressure lowering = $4.8 \times 10^{-7} \text{ atm}$

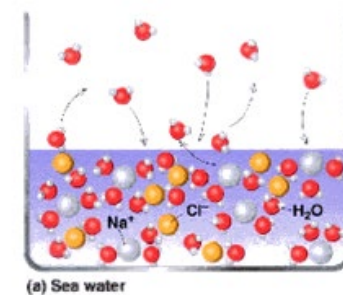
Boiling-point elevation = 0.00044 K

Freezing-point depression = 0.0016K

11.6 PHASE EQUILIBRIUM IN SOLUTIONS: VOLATILE SOLUTES

Ideal mixture of volatile substances

$$P_1 = X_1 P_1^\circ, \quad P_2 = X_2 P_2^\circ = (1 - X_1) P_2^\circ$$



➤ Henry's Law

For $X_2 \ll 1$,

$$P_2 = k_2 X_2$$

k_2 : Henry's law constant

For $X_1 \ll 1$, $P_1 = k_1 X_1$

- ~ Henry's law applies to a volatile *solute* in a dilute solution.
- ~ Carbonation of soft drinks
- ~ O_2 dissolved in blood

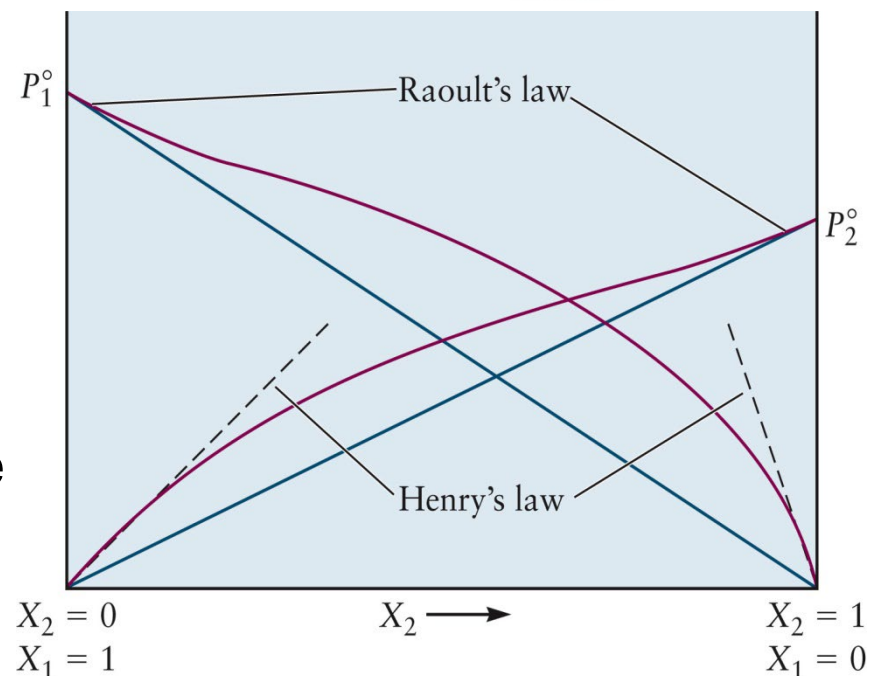


Fig. 11.15 Vapor pressures above a mixture of two volatile liquids.

➤ Distillation

$P_1^\circ = 0.198$ atm for hexane (C_6H_{14}) at $25^\circ C$.

$P_2^\circ = 0.0600$ atm for heptane (C_7H_{16}) at $25^\circ C$.

A solution of $n_1 = 4.00$ mol and $n_2 = 6.00$ mol.

❖ Mole fractions in the *solution*

$$X_1 = 0.400, X_2 = 0.600$$

$$P_1 = X_1 P_1^\circ = (0.400)(0.198 \text{ atm}) = 0.0792 \text{ atm}$$

$$P_2 = X_2 P_2^\circ = (0.600)(0.0600 \text{ atm}) = 0.0360 \text{ atm}$$

$$P_{\text{tot}} = P_1 + P_2 = 0.1152 \text{ atm}$$

❖ Mole fractions in the *vapor* (Dalton's law)

$$P_1 = Y_1 P_{\text{tot}}, P_2 = Y_2 P_{\text{tot}}$$

$$Y_1 = 0.0792 \text{ atm} / 0.1152 \text{ atm} = 0.688$$

$$Y_2 = 1 - Y_1 = 1 - 0.688 = 0.312$$

→ the vapor is enriched in the more volatile component

➤ Fractional Distillation

~ Separation of two or more components of a liquid solution by successive evaporation and condensation on the basis of their different boiling points

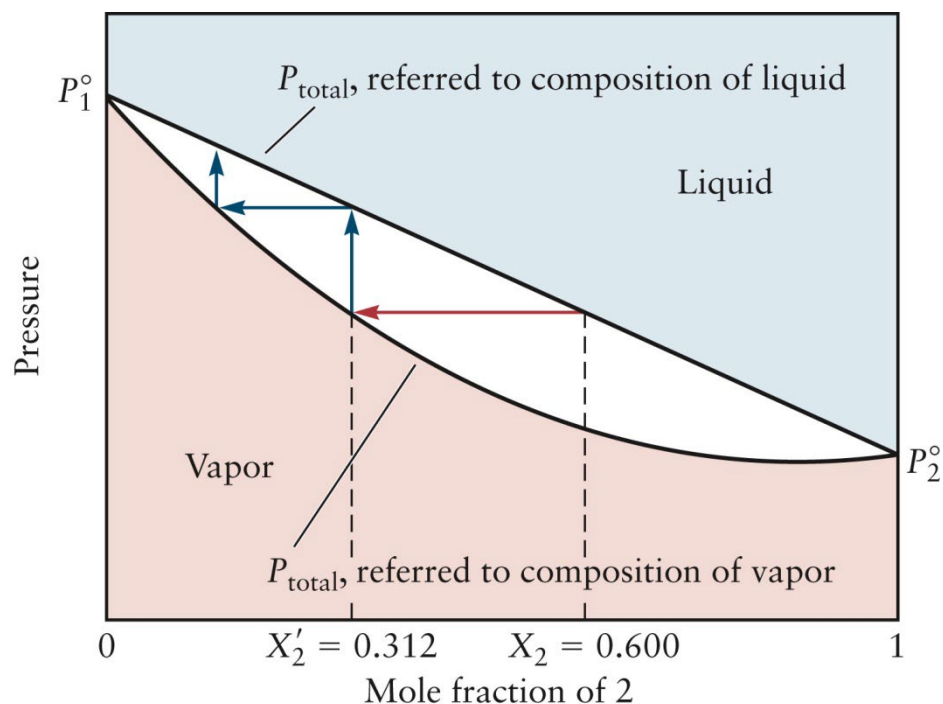


Fig. 11.16 Vapor pressure vs. X_2 .

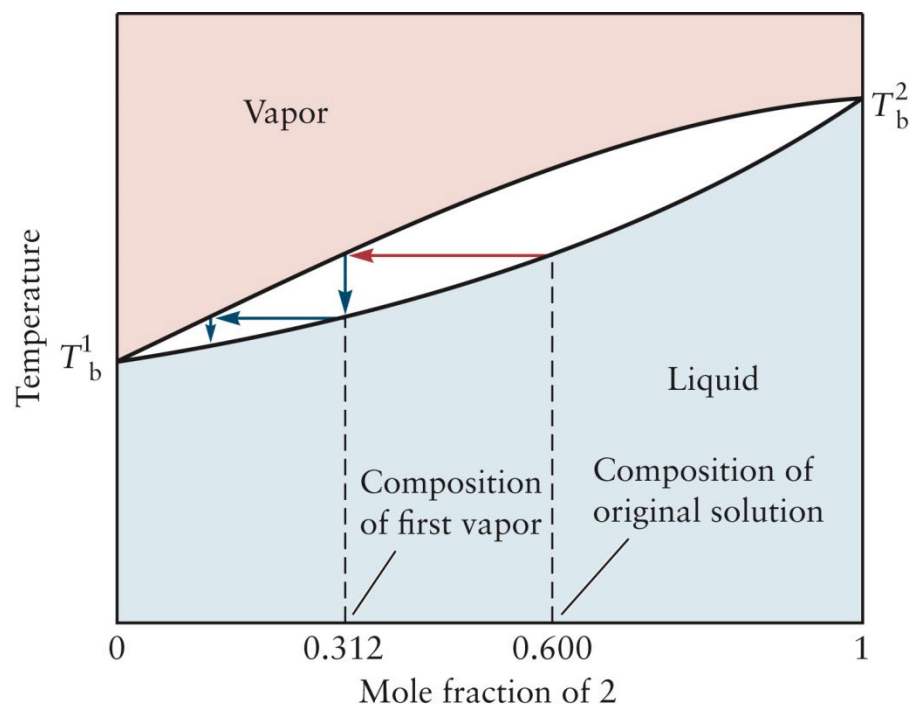


Fig. 11.17 Boiling temperature vs. X_2 .

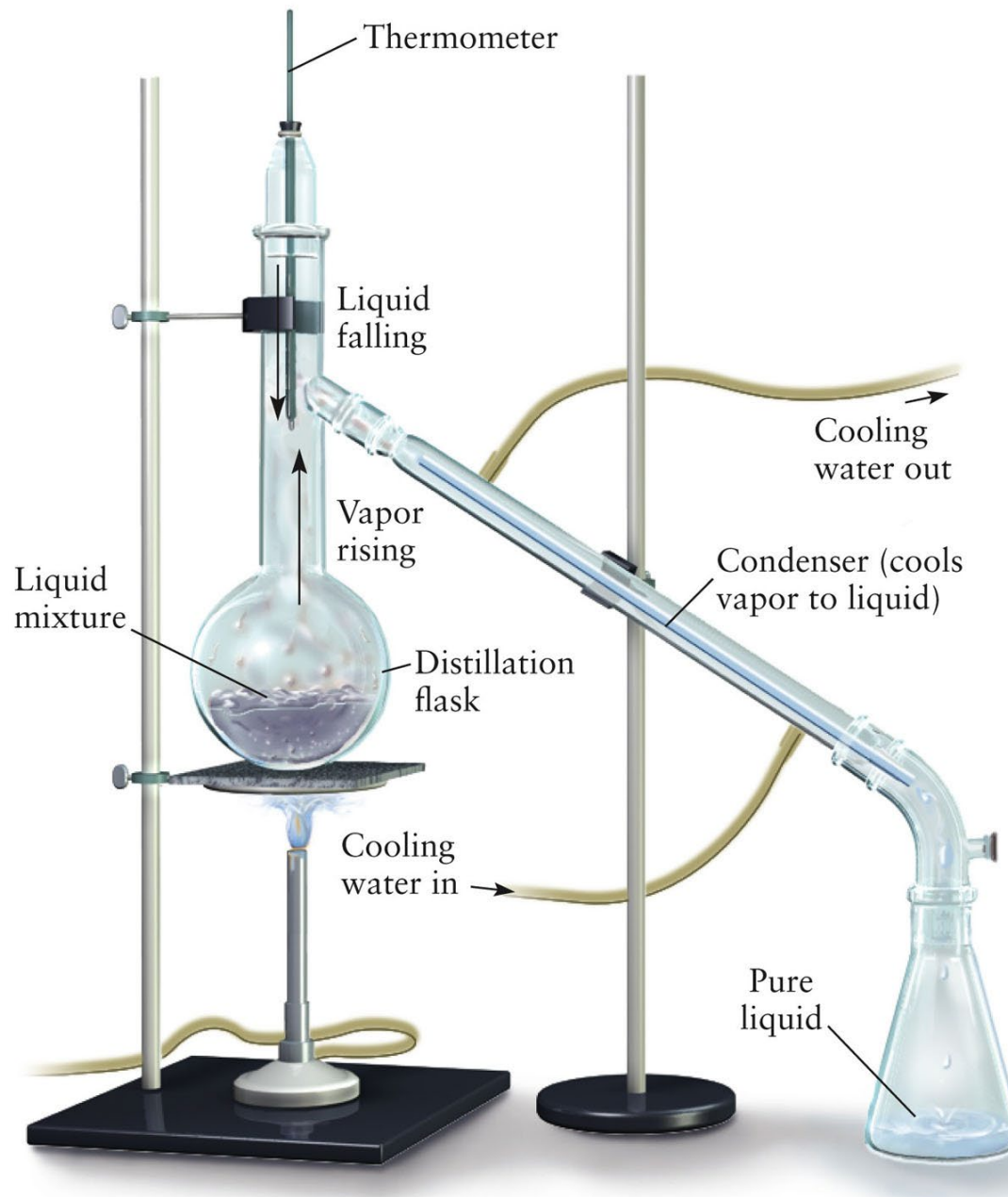


Fig. 11.18 An apparatus for fractional distillation.

◆ Azeotropes

➤ Maximum-boiling azeotrope **Fig 11.19a** HCl / H₂O

~ large negative deviation, strongly attractive

~ $T_b = 108.58\text{ °C}$ at $X_{\text{HCl}} = 0.202$

➤ Minimum-boiling azeotrope **Fig 11.19b** C₂H₅OH / H₂O

~ large positive deviation

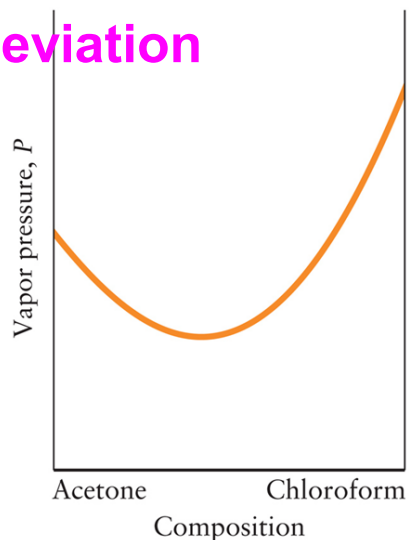
~ $T_b = 78.17\text{ °C}$ at $X_{\text{H}_2\text{O}} = 0.044$

~ the last 4% of water **can not be** removed by distillation

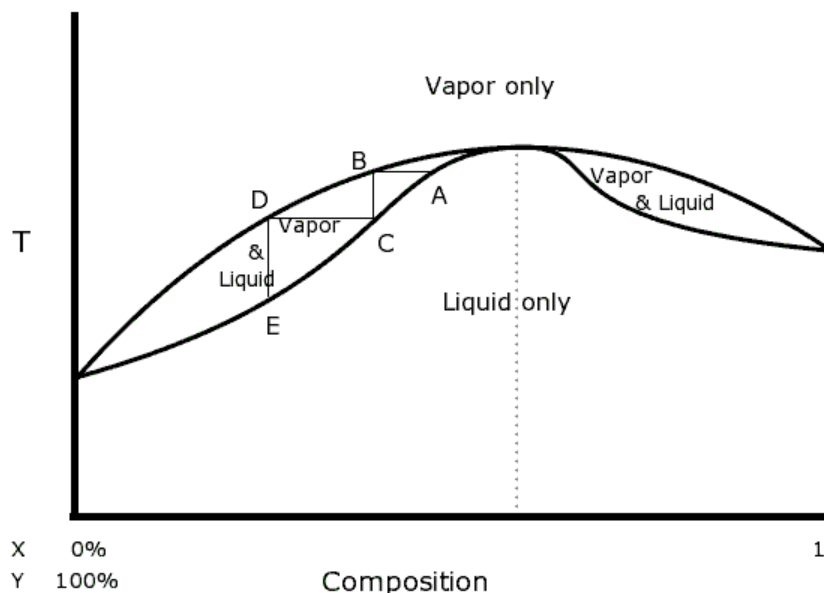
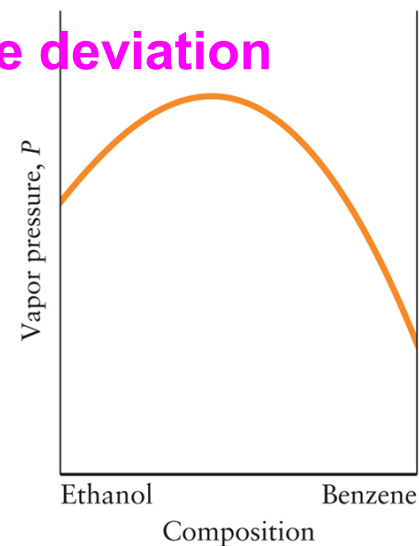
An azeotrope behaves like a single-component fluid.

Note that the numbers for X_{HCl} and $X_{\text{H}_2\text{O}}$ in Fig 11.19a & b are incorrect.

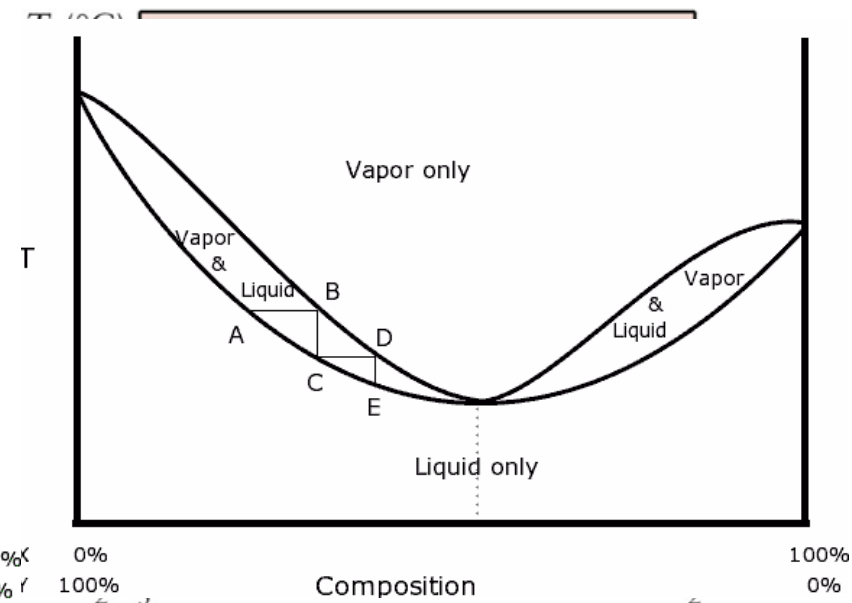
Negative deviation



Positive deviation



(a) Constant boiling maximum



(b) Constant boiling minimum

Fig. 11.19 (a) Maximum-boiling azeotrope. (b) Minimum-boiling azeotrope.



The Strongest Alcoholic Drink in the World

1



95 v%

2



80 v%

3



72 v%

4



76 v%

11.7 COLLOIDAL SUSPENSIONS

◆ Colloids

- A dispersion of large particles (1 nm ~ 1 μ m) in a solvent
- Intermediate between a solution and a heterogeneous mixture
- Homogenous appearance but scatters light

Dispersed phase	Dispersion medium	Technical name	Examples
solid	gas	aerosol	smoke
liquid	gas	aerosol	hairspray, mist, fog
solid	liquid	sol or gel	printing ink, paint
liquid	liquid	emulsion	milk, mayonnaise
gas	liquid	foam	fire-extinguisher foam
solid	solid	solid dispersion	ruby glass (Au in glass); some alloys
liquid	solid	solid emulsion	bituminous road paving; ice cream
gas	solid	solid foam	insulating foam

*Based on R. J. Hunter, *Foundations of Colloid Science*, Vol. 1 (Oxford: Oxford University Press, 1987).

➤ Flocculation

- ~ Acceleration of the settling out of a colloid through the addition of salts.
- ~ Salts **reduce** the electrostatic repulsions between suspended particles. (ex. river deltas, paints)

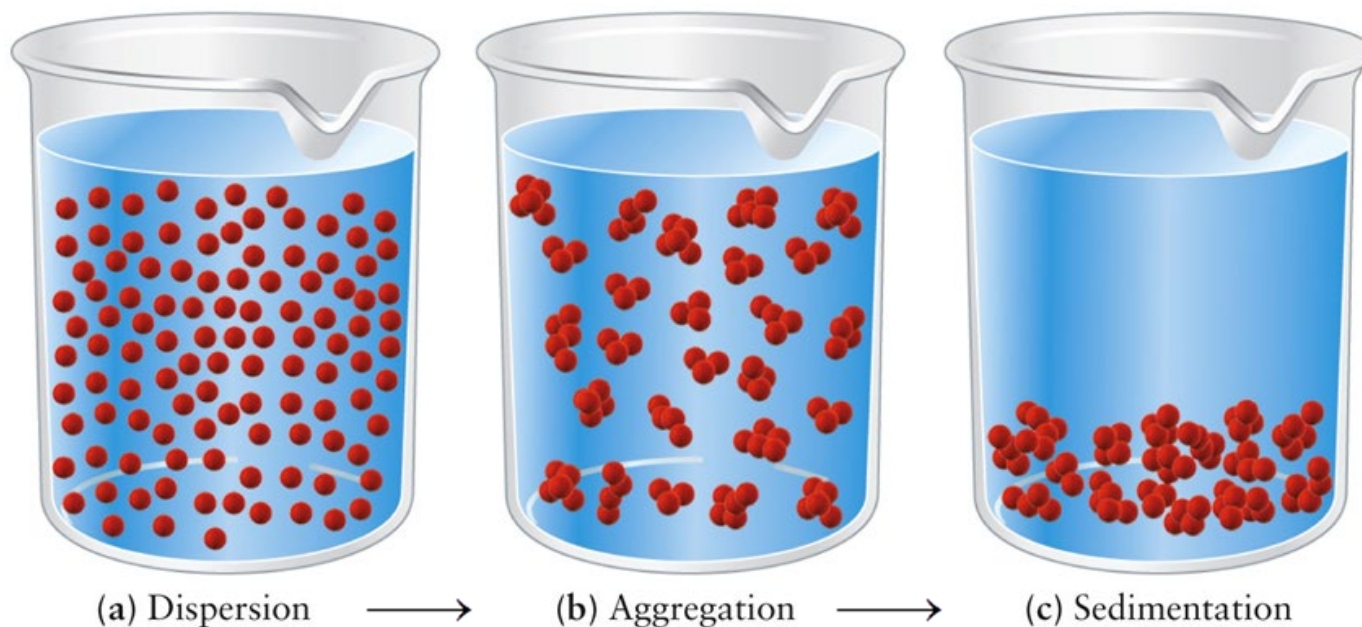


Fig. 11.21 Process of flocculation: Dispersion → Aggregation → Sedimentation



➤ Precipitation

~ flocculation, centrifugation, membrane filtration

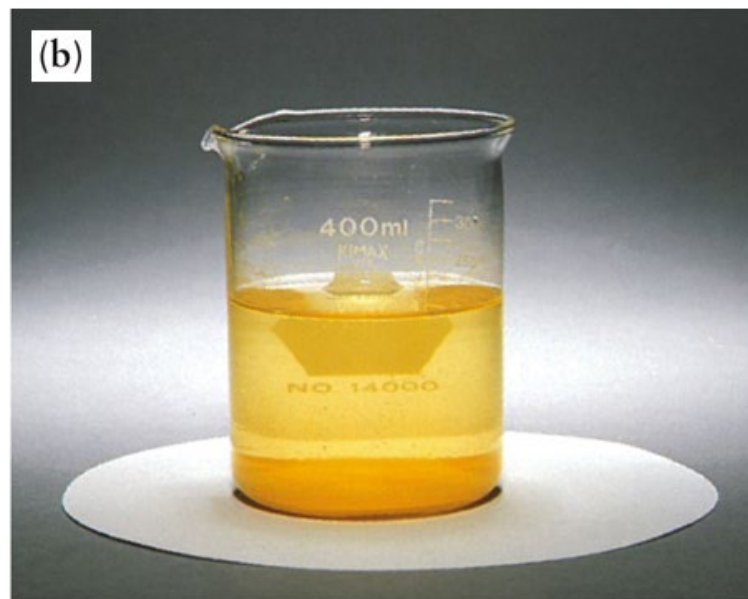
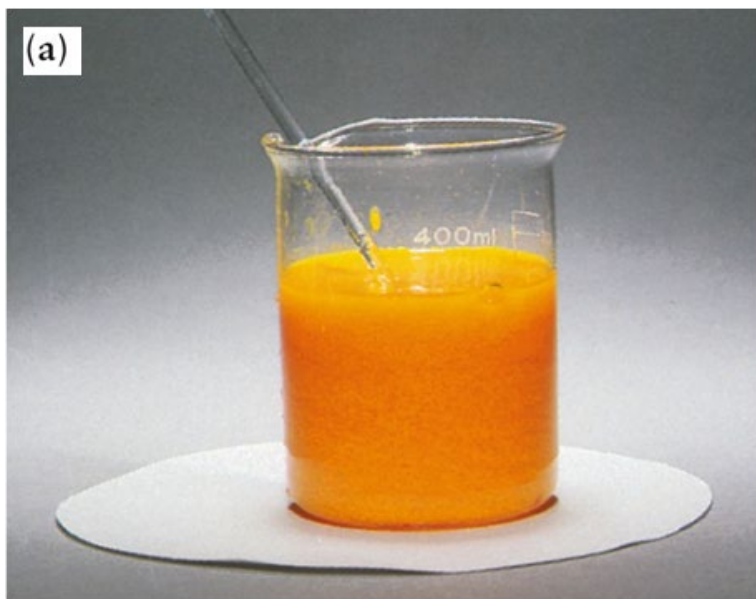


Fig. 11.22 (a) This colloidal suspension of PbCrO_4 appears cloudy. (b) After flocculation, the precipitate settles to the bottom.