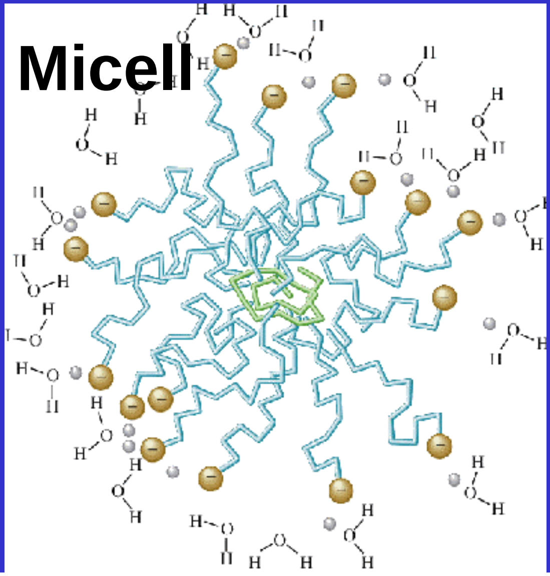
Solutions

Homogeneous mixture of molecules in gas, liquid or solid phase

- **True** solutions
- **Micellar and colloidal** solutions (suspensions): particles 1 nm – 10 mm

Tyndall effect – light dispersion



Types of Solutions

Comp 1	Comp 2	State	Example
G	G	G	Air
G	L	L	Carbonated water (CO_2)
G	S	S	H_2(850 cm^3) in Pd(1 cm^3)
L	L	L	Ethanol in water
S	L	L	NaCl in water
S	S	S	Brass (Cu/Zn) Solder (Sn/Pb)

Composition of Solutions

1 = solvent
2 = solute

Mass fraction
and percent
w/w

$$w\% = \frac{m_2}{m_{solution}}100$$

Volume fraction
and percent v/v

$$v\% = \frac{V_2}{\Sigma V_i}100$$

Before mixing

Mass concentration
w/v
g cm^{-3}

$$c = \frac{m_2}{V_{solution}} = \frac{m_2 \rho_{solution}}{m_{solution}}$$

Composition of Solutions

Molar concentration [mol l^{-1}]

$$c_M = \frac{n_2}{V_{solution}}$$

Molal concentration [mol kg^{-1}]
Does not depend on T

$$c_m = \frac{n_2}{m_1}$$

1 = solvent
2 = solute

Molar fraction

$$x_i = \frac{n_i}{n_1 + n_2 + \ldots + n_i + \ldots}$$

Composition of Solutions

ppm	1 part in 10^6 parts
ppb	1 part in 10^9 parts
ppt	1 part in 10^{12} parts

Solubility

Complicated process – no simple theory of solubility

Empirical rule : Like dissolves like

Good solubility :

Polar compounds in polar solvents (water, acetone, alcohols, CH_3CN, DMF, DMSO,....)

Nonpolar compounds in nonpolar solvents (CCl_4, alkanes, benzene,...)

Factors Influencing Solubility

1. Solute type
2. Solvent type
3. Temperature
4. Pressure (gases – Henry’s Law)
5. Other dissolved compounds – salting out

Like dissolves Like !

Solubility in Water and Hexane

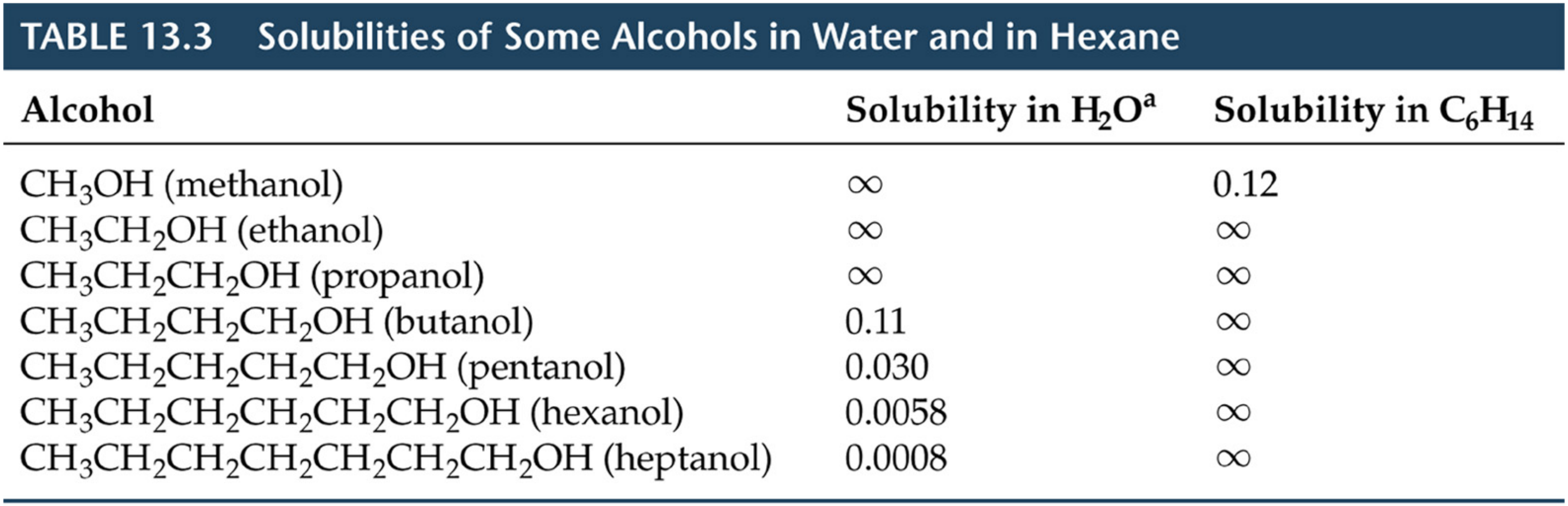


TABLE 13.3 Solubilities of Some Alcohols in Water and in Hexane

Alcohol	Solubility in H_2O^a	Solubility in C_6H_{14}
CH_3OH (methanol)	∞	0.12
CH_3CH_2OH (ethanol)	∞	∞
$CH_3CH_2CH_2OH$ (propanol)	∞	∞
$CH_3CH_2CH_2CH_2OH$ (butanol)	0.11	∞
$CH_3CH_2CH_2CH_2CH_2OH$ (pentanol)	0.030	∞
$CH_3CH_2CH_2CH_2CH_2CH_2OH$ (hexanol)	0.0058	∞
$CH_3CH_2CH_2CH_2CH_2CH_2CH_2OH$ (heptanol)	0.0008	∞

Solvent – Solute Interactions

Dissolution in 3 steps

1. **Separation of solute molecules**

   Usually endothermic (+ΔH_{AA}) process except dissolution of gases. Lattice energy for ionic compounds. Increase of entropy (+ΔS)

2. **Formation of voids in solvent**

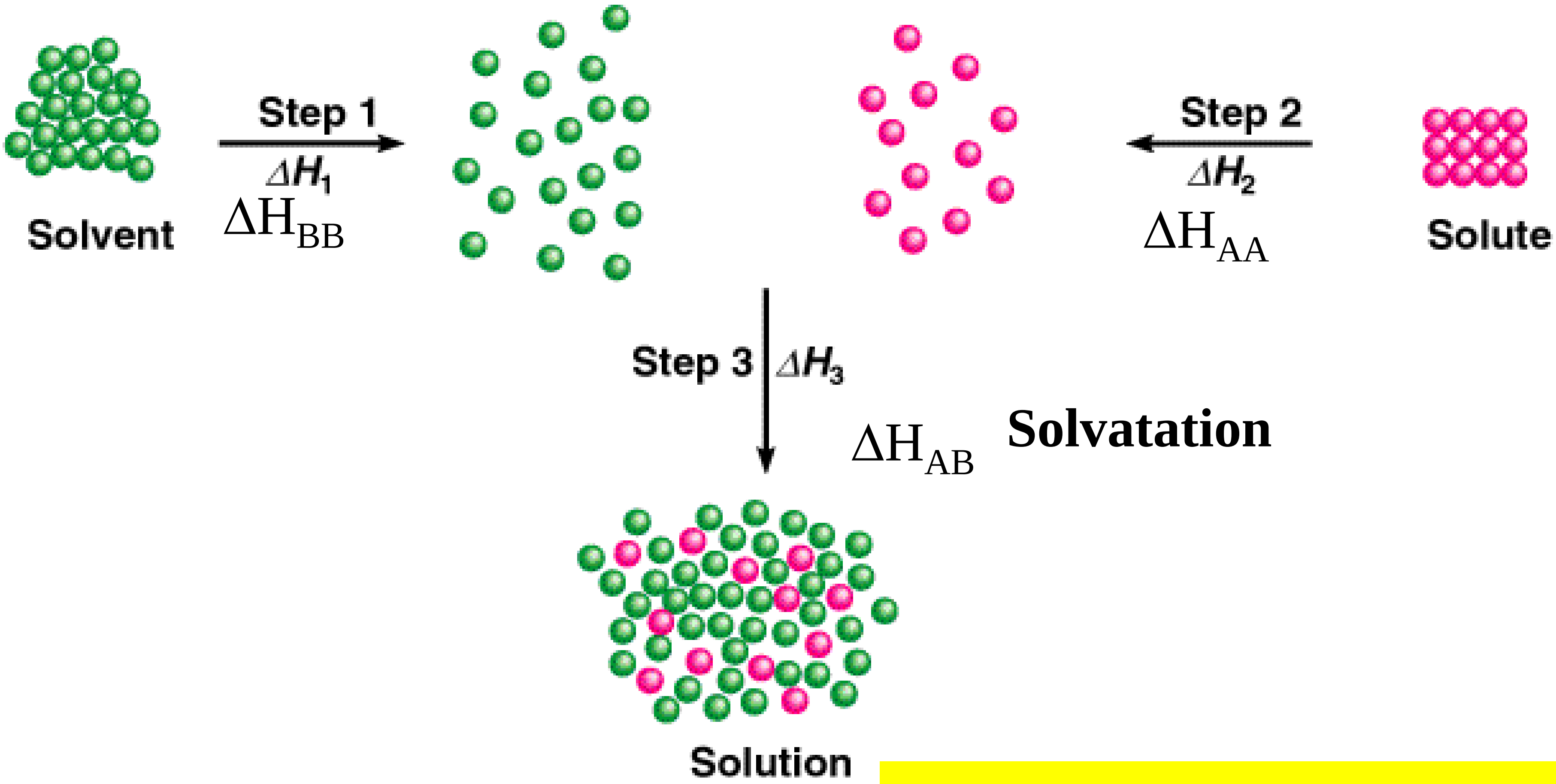
   Usually endothermic (+ΔH_{BB}) process except dissolution in gases.

3. **Solvatation of solute molecules by solvent**

   Usually exothermic (– ΔH_{AB}) process except dissolution of gases in gases. (+ΔS)

$$\Delta H_{diss} = \Delta H_{AA} + \Delta H_{BB} + \Delta H_{AB}$$

Dissolution in 3 Steps



ΔH_{BB}

ΔH_{AA}

ΔH_{AB} **Solvatation**

$$\Delta H_{diss} = \Delta H_{AA} + \Delta H_{BB} + \Delta H_{AB}$$

Solvent – Solute Interactions

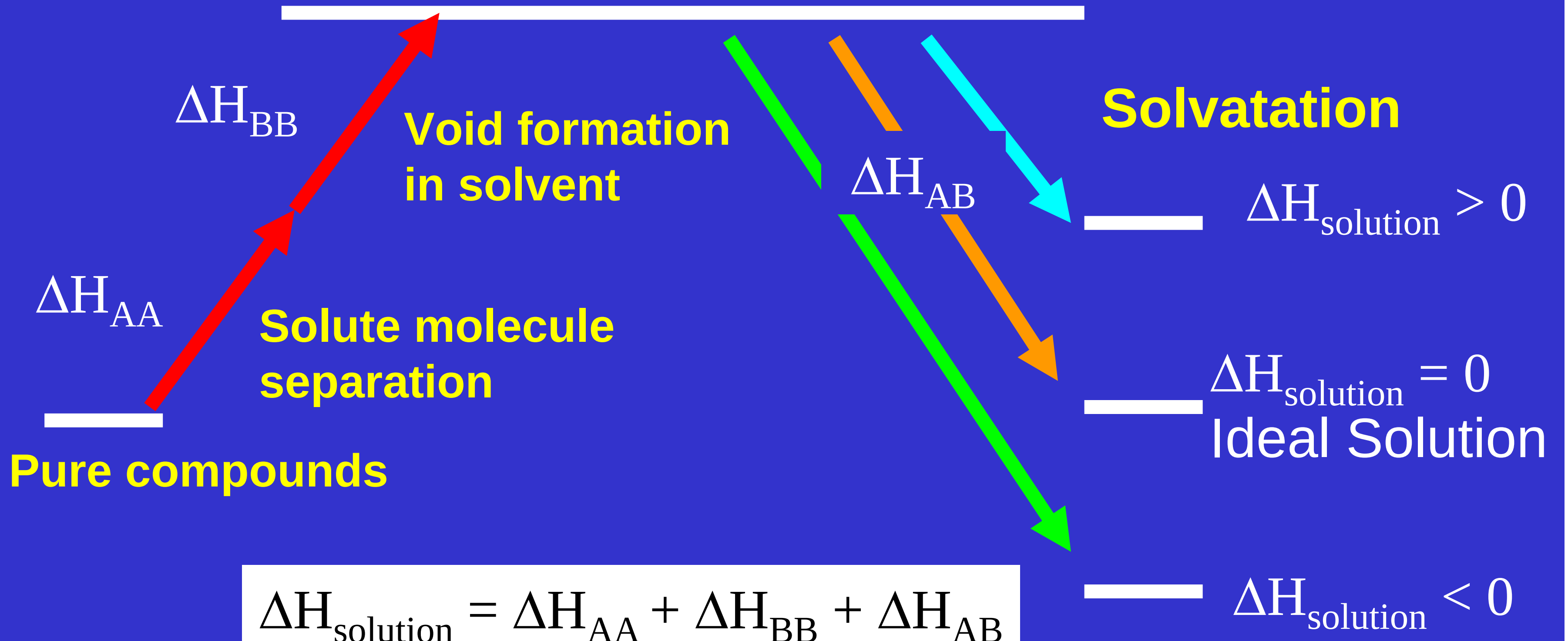
In case that dissolution is energetically neutral or slightly endothermic (+ΔH), it can still proceed because of the entropic driving force (+ΔS) !

Entropy of mixing is always positive. A mixture has higher entropy than pure components.

$$\Delta G^0 = \Delta H^0 - T\,\Delta S^0$$

$$\Delta G^0 < 0$$

Ideal and Nonideal Solutions



ΔH_{BB}

Void formation in solvent

ΔH_{AA}

Solute molecule separation

Pure compounds

ΔH_{AB}

Solvatation

$\Delta H_{solution} > 0$

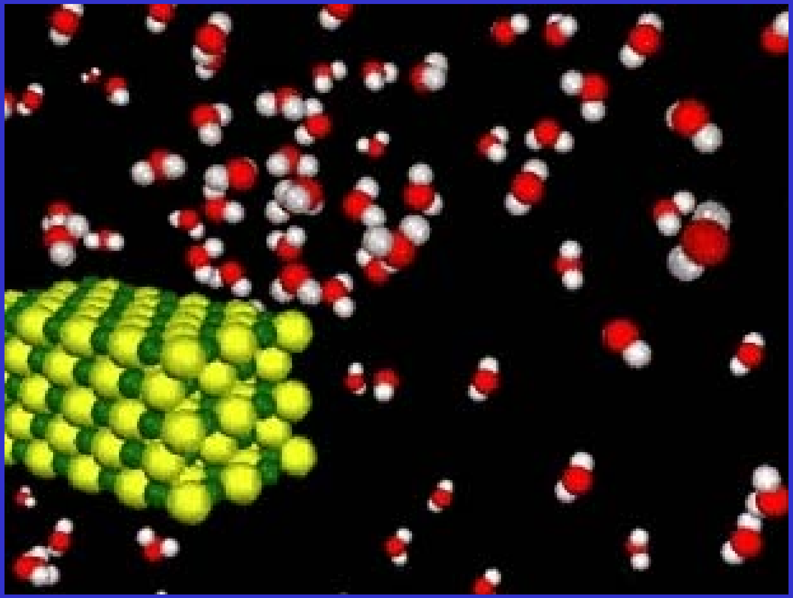
$\Delta H_{solution} = 0$

Ideal Solution

$\Delta H_{solution} < 0$

$$\boxed{\Delta H_{solution} = \Delta H_{AA} + \Delta H_{BB} + \Delta H_{AB}}$$

Solution Enthalpy



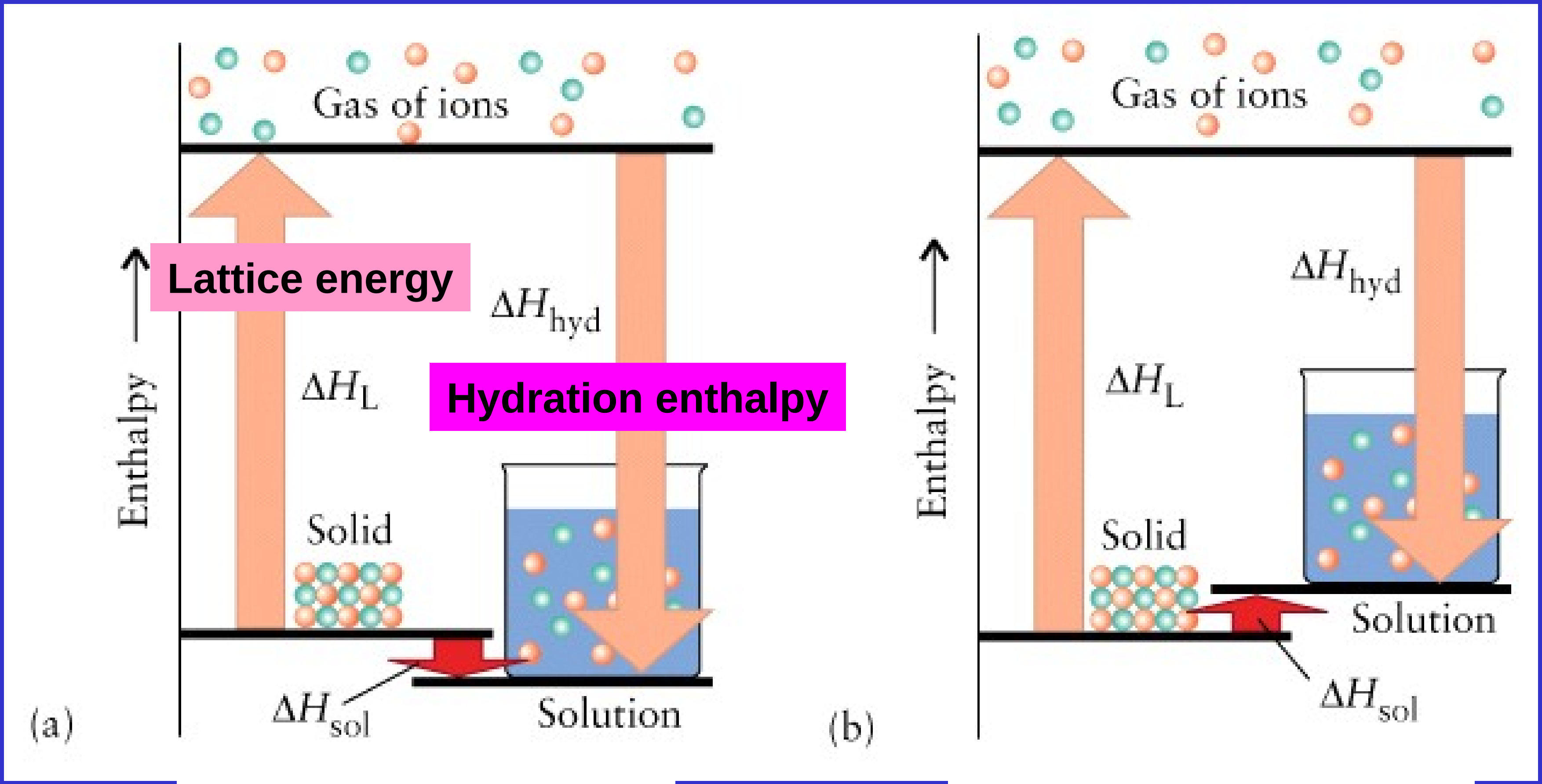
NaOH in water $\Delta H_{soln} = – 44.48\ kJ\ mol^{–1}$

NH_4NO_3 in water $\Delta H_{soln} = + 26.4\ kJ\ mol^{–1}$

Solvent – Solute Interactions

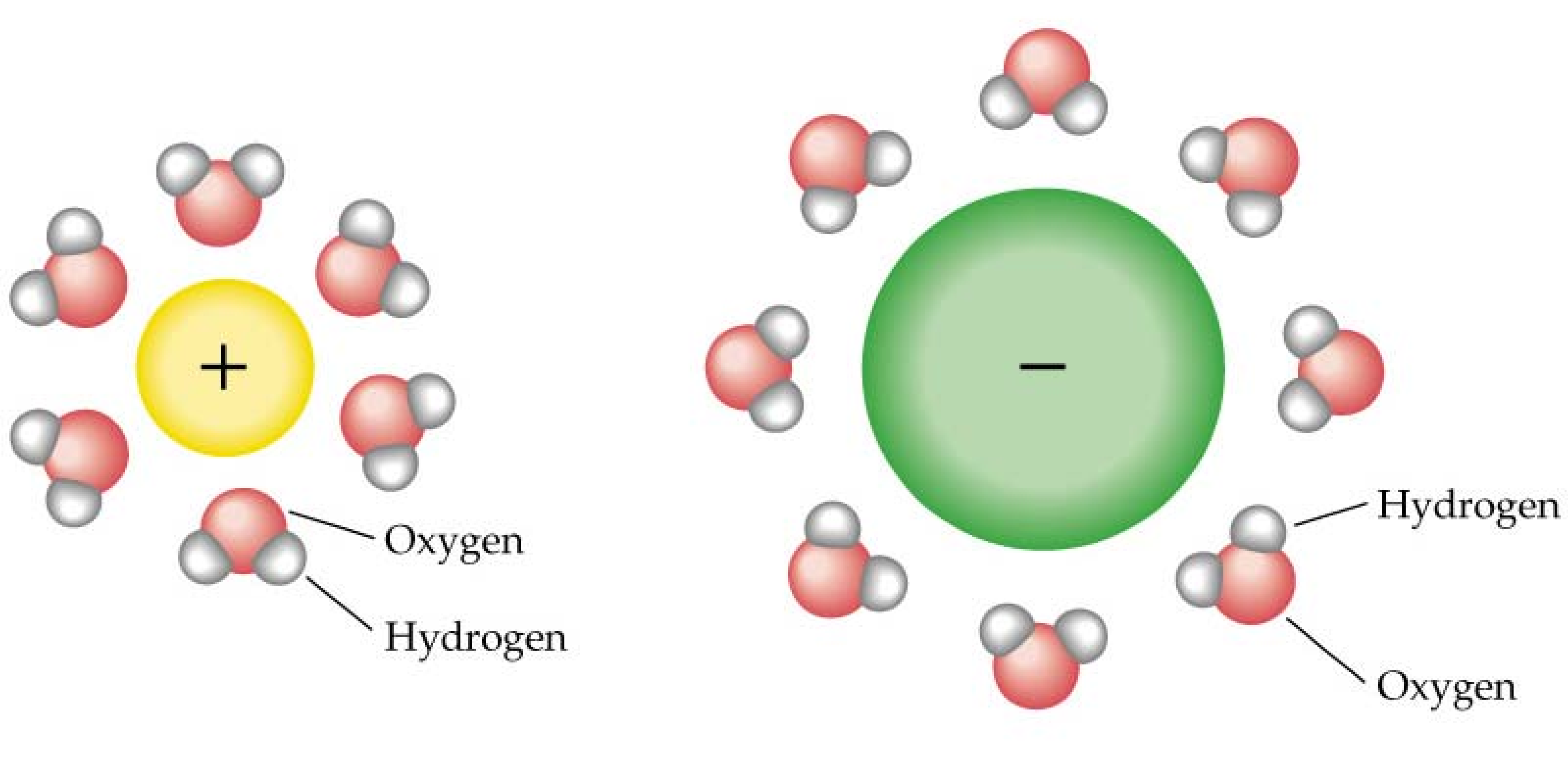
Solubility depends on enthalpy ΔH and entropy ΔS of solution

$$\Delta G^0 = \Delta H^0 - T\,\Delta S^0$$

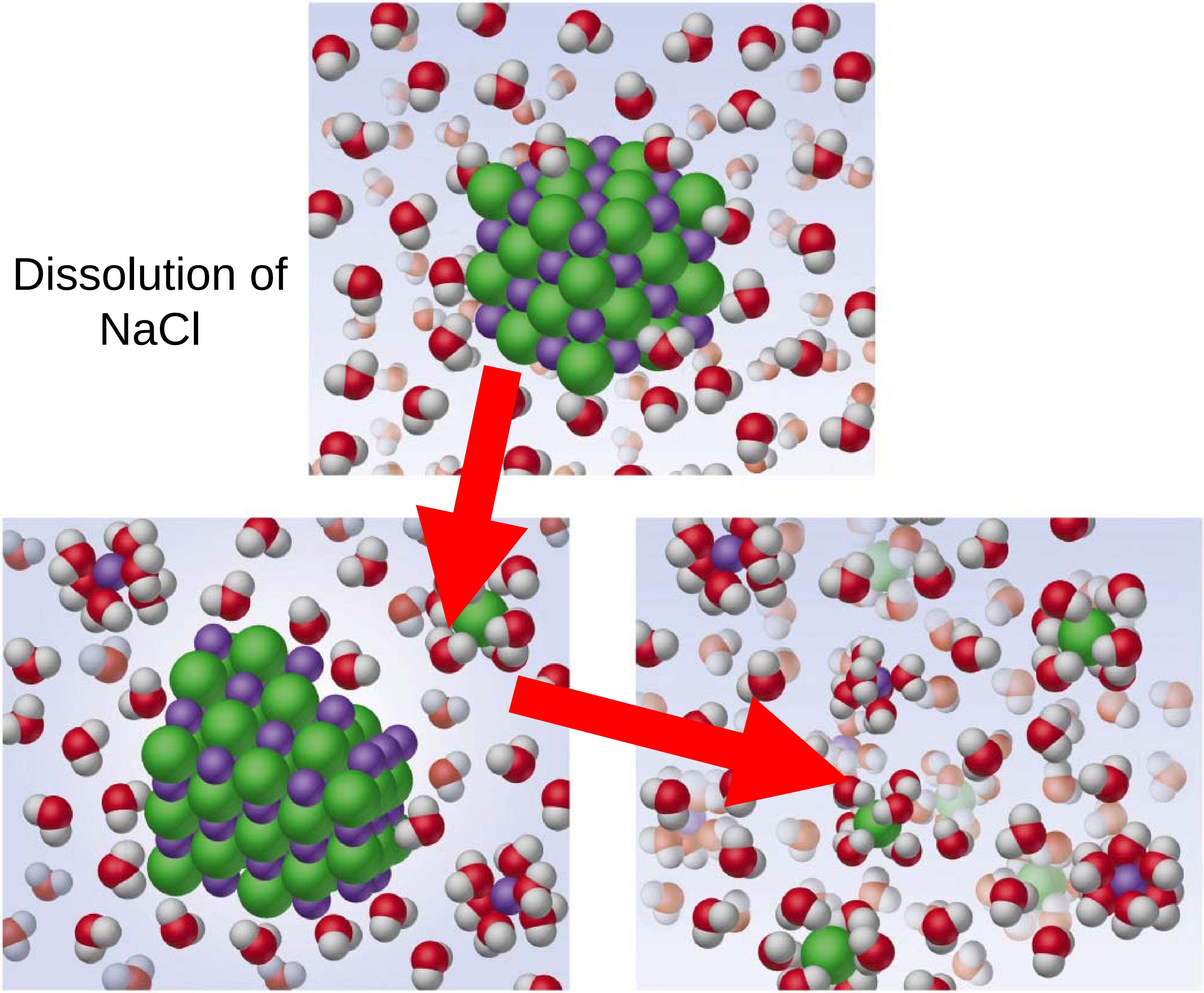


Solution enthalpy - exo **Solution enthalpy - endo**

Hydration - Solvation



Dissolution of NaCl



Solution Enthalpies

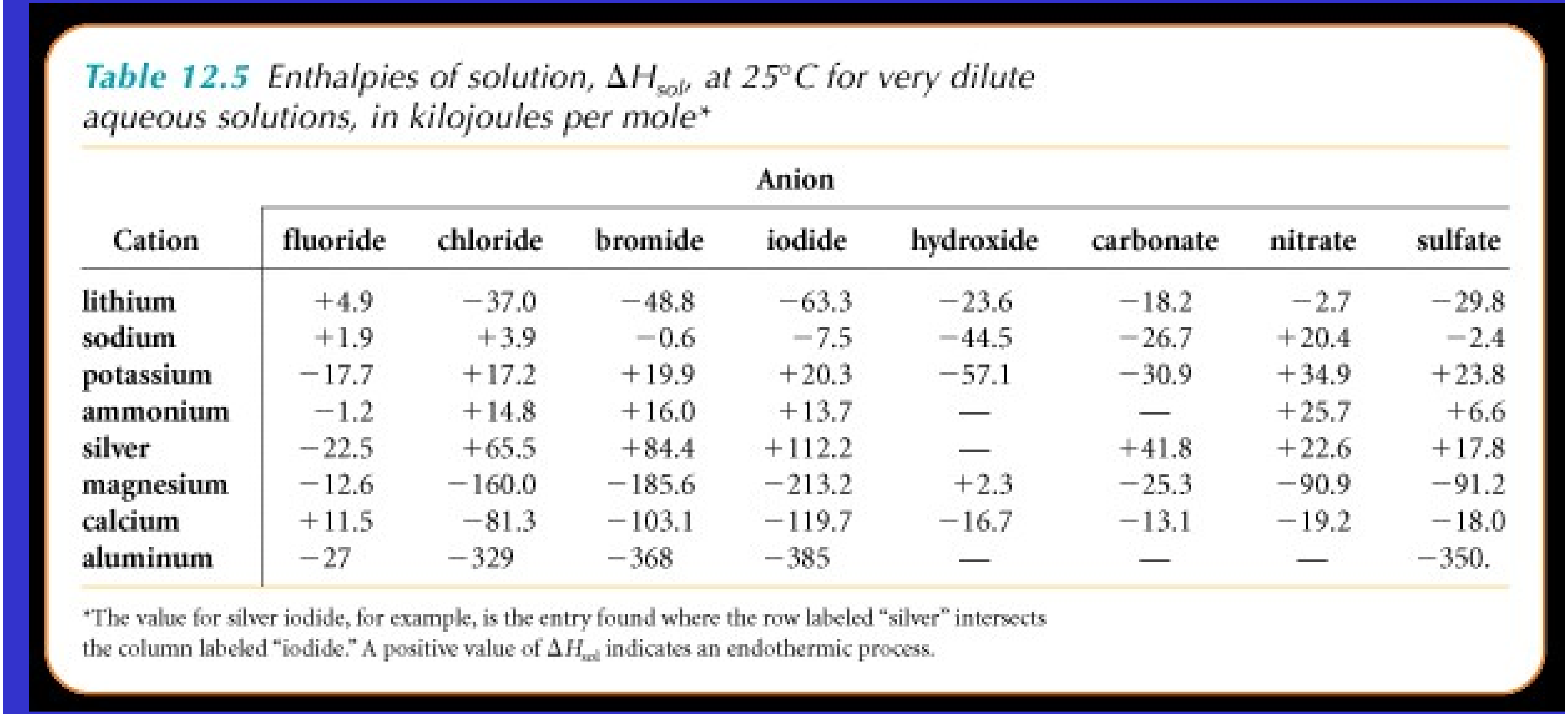


Table 12.5 *Enthalpies of solution, ΔH_{sol}, at 25°C for very dilute aqueous solutions, in kilojoules per mole**

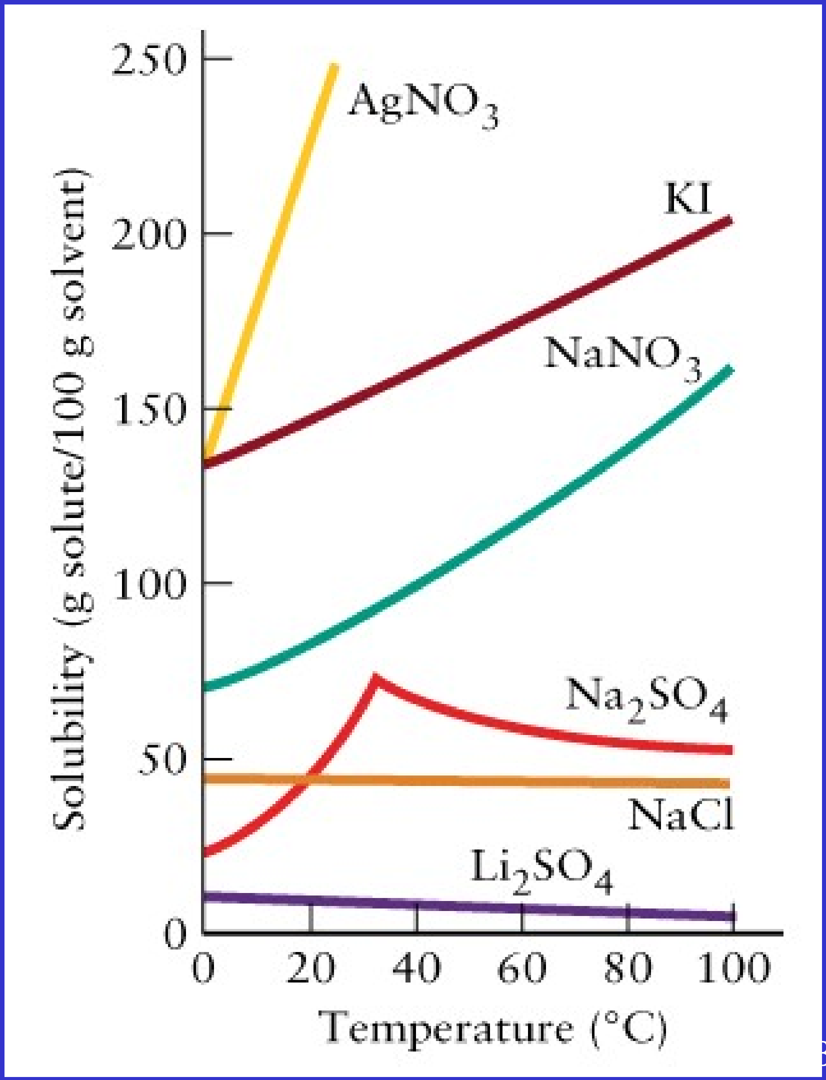
	Anion							
Cation	**fluoride**	**chloride**	**bromide**	**iodide**	**hydroxide**	**carbonate**	**nitrate**	**sulfate**
lithium	+4.9	−37.0	−48.8	−63.3	−23.6	−18.2	−2.7	−29.8
sodium	+1.9	+3.9	−0.6	−7.5	−44.5	−26.7	+20.4	−2.4
potassium	−17.7	+17.2	+19.9	+20.3	−57.1	−30.9	+34.9	+23.8
ammonium	−1.2	+14.8	+16.0	+13.7	—	—	+25.7	+6.6
silver	−22.5	+65.5	+84.4	+112.2	—	+41.8	+22.6	+17.8
magnesium	−12.6	−160.0	−185.6	−213.2	+2.3	−25.3	−90.9	−91.2
calcium	+11.5	−81.3	−103.1	−119.7	−16.7	−13.1	−19.2	−18.0
aluminum	−27	−329	−368	−385	—	—	—	−350.

*The value for silver iodide, for example, is the entry found where the row labeled "silver" intersects the column labeled "iodide." A positive value of ΔH_{sol} indicates an endothermic process.

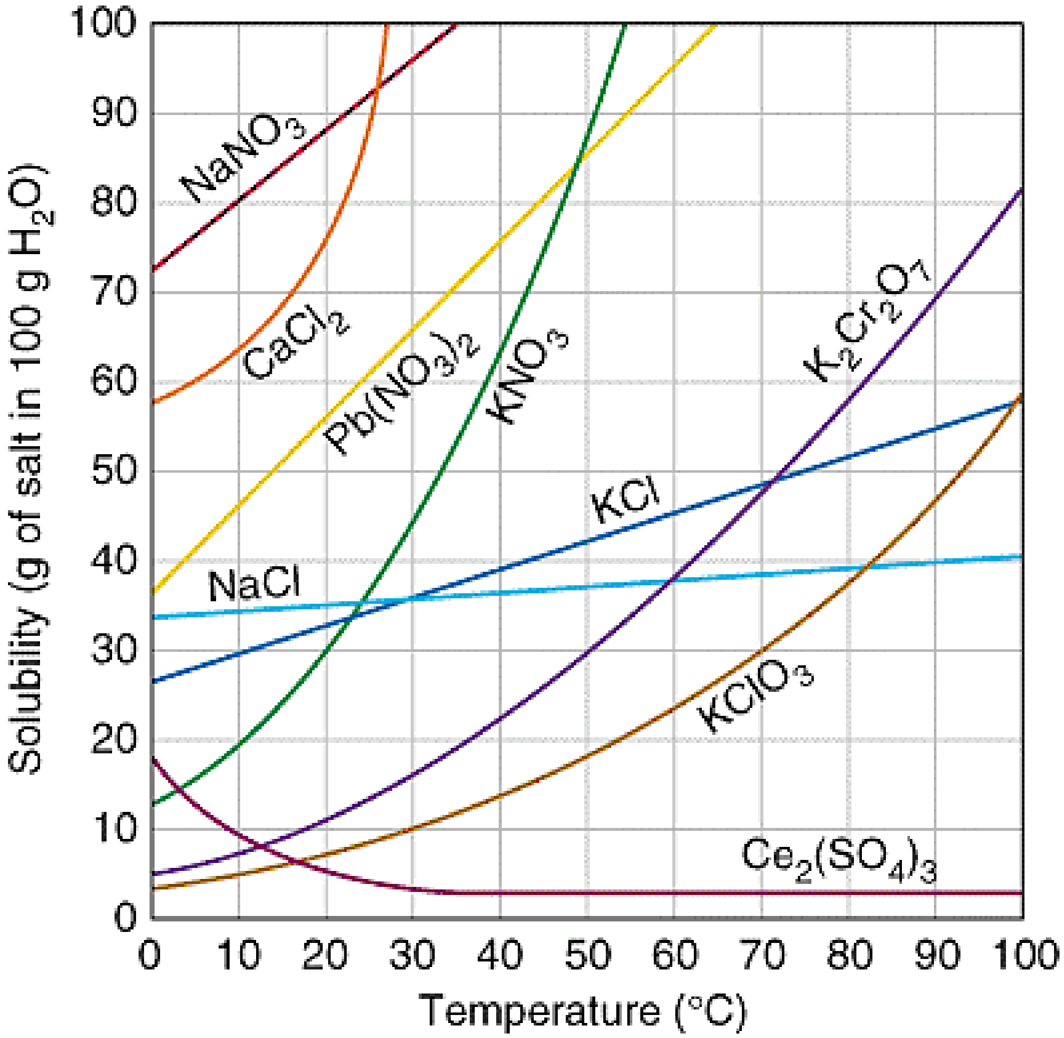
Solubility and Temperature

Solubility with increasing temperature

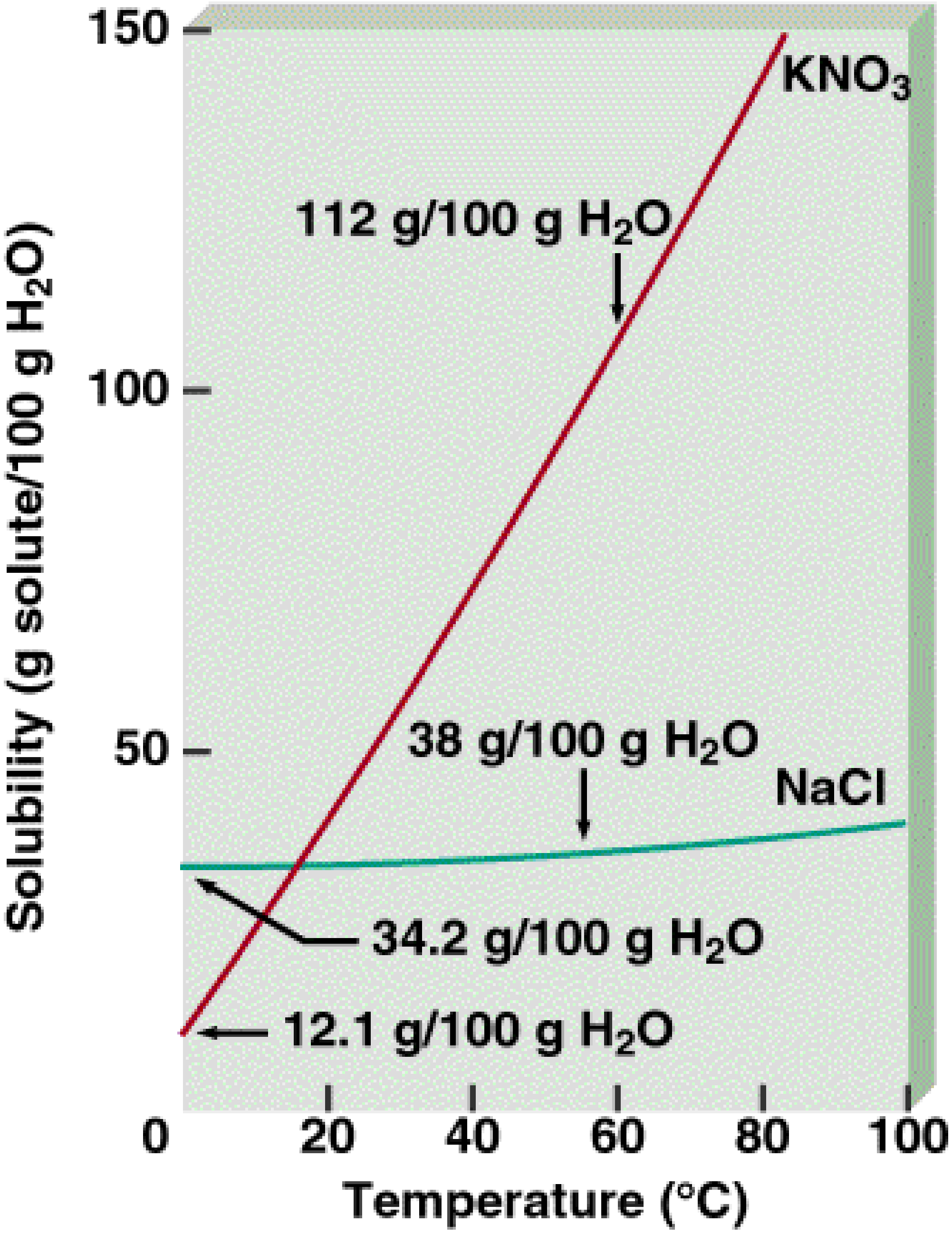
- Increases (majority, 95%)
- Consatnt (NaCl)
- Decreases (ususally sulfates)



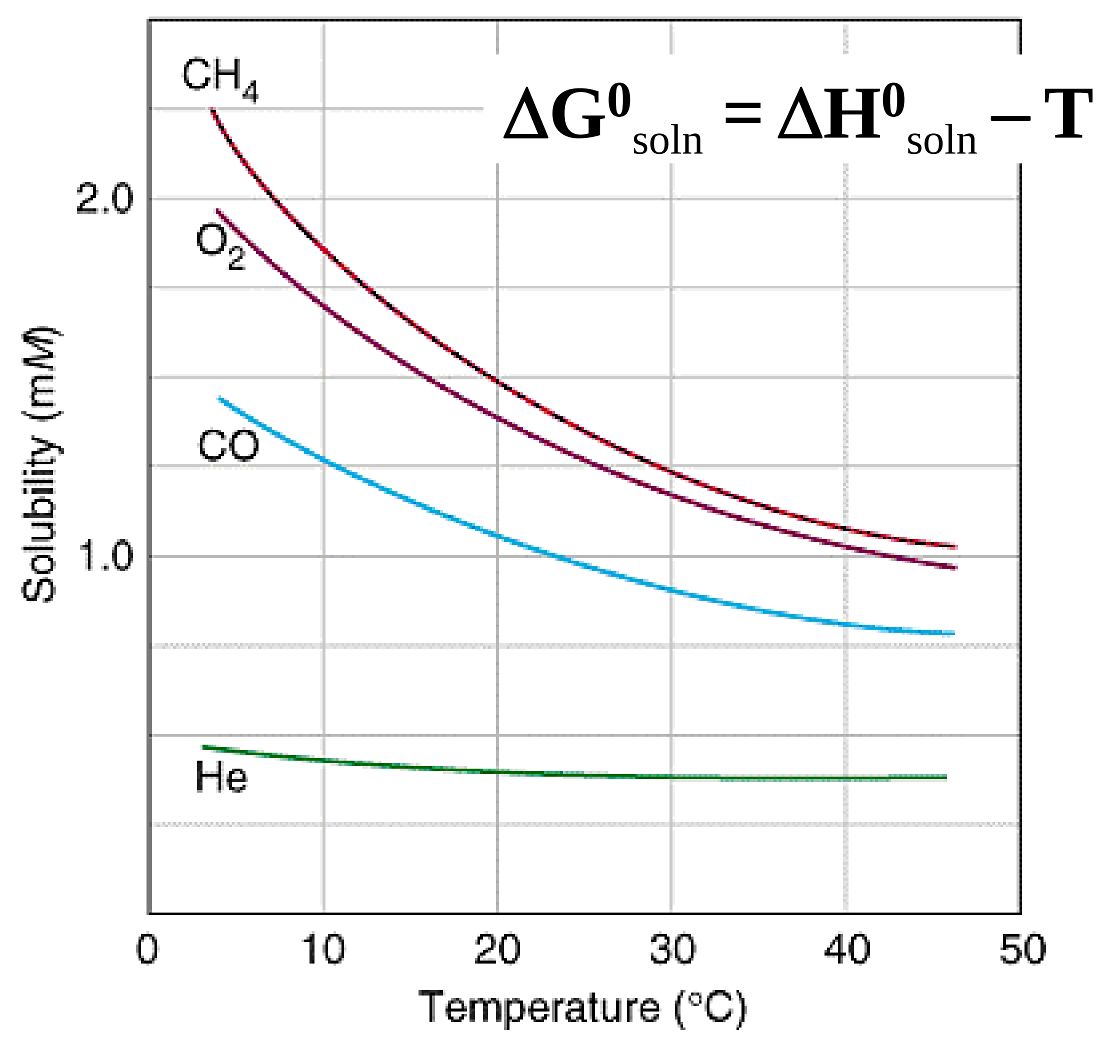
Solubility and Temperature



Fractional crystallization



Solubility of gases and Temperature



$$\Delta G^0_{soln} = \Delta H^0_{soln} - T\,\Delta S^0_{soln}$$

$\Delta H_{soln} < 0$

$\Delta S^0_{soln} < 0$

Henry’s Law

Molar solubility increases with partial pressure of the component

S [mol l^{-1}] = const × partial pressure (at const. T)

$$S_2 = k_H \times P_2$$

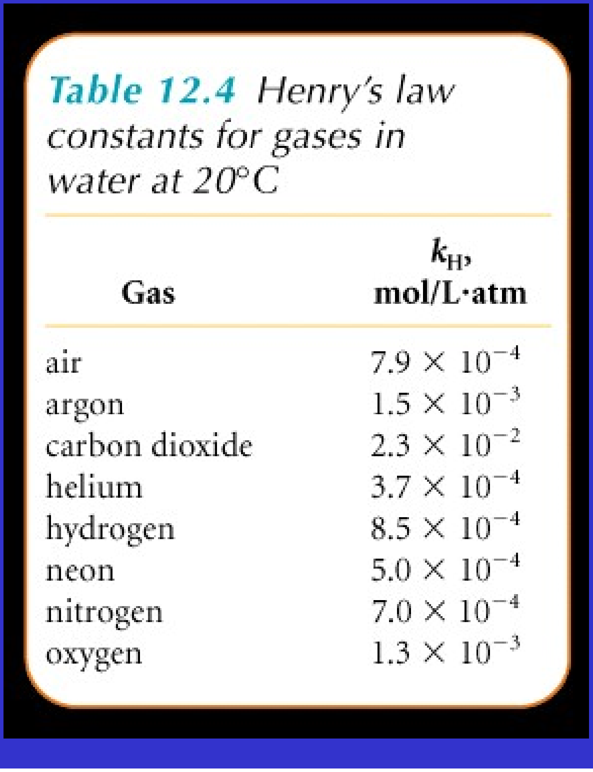
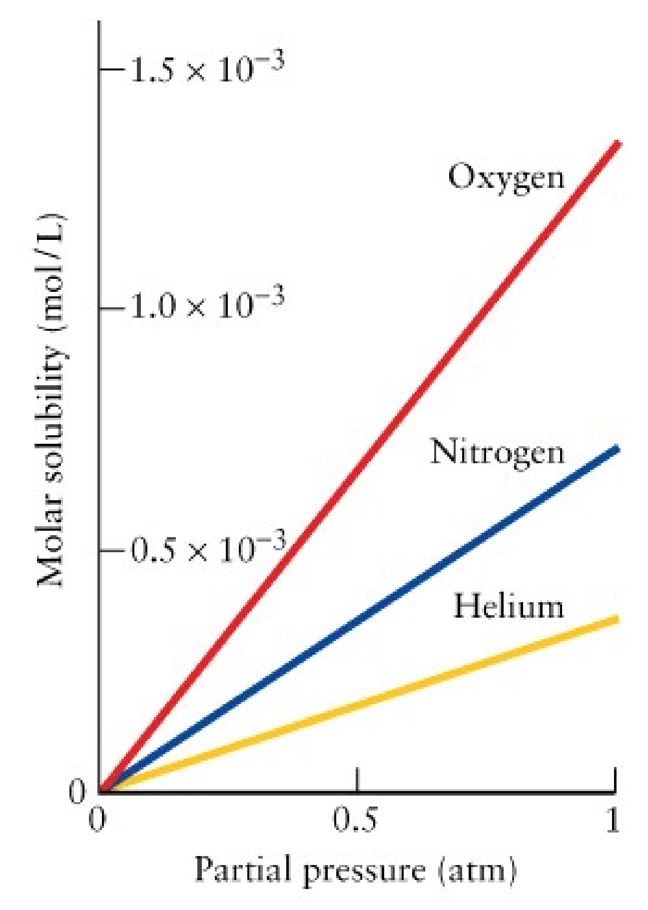


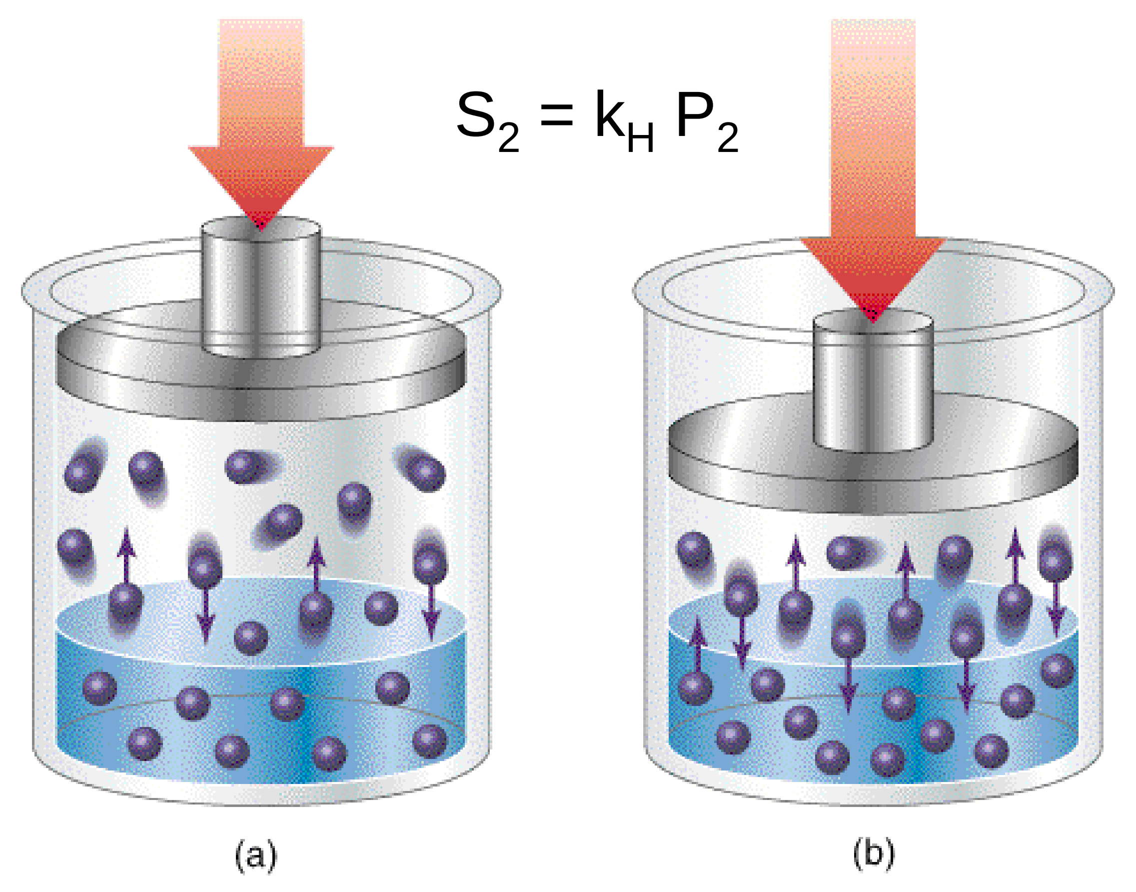
Table 12.4 Henry’s law constants for gases in water at 20°C

Gas	**k_H, mol/L·atm**
air	7.9×10^{-4}
argon	1.5×10^{-3}
carbon dioxide	2.3×10^{-2}
helium	3.7×10^{-4}
hydrogen	8.5×10^{-4}
neon	5.0×10^{-4}
nitrogen	7.0×10^{-4}
oxygen	1.3×10^{-3}



Henry’s Law

Molar solubility increases with partial pressure of the component



$$S_2 = k_H P_2$$

Electrolytic Dissociation

In water

$NaCl \rightarrow Na^+ + Cl^-$ strong electrolytes

$HCN \leftrightarrows H^+ + CN^-$ weak electrolytes

Svante Arrhenius
(1859-1927)
NP in Chemistry1903

Dissociation degree

$\alpha = n_{disoc} / n_0$

Dissociation constant

$$\boxed{K_d = \frac{[H^+].[CN^-]}{[HCN]}}$$

$[H^+] = [CN^-] = \alpha\ [HCN]_0$

$[HCN] = (1 - \alpha)\ [HCN]_0 \qquad \alpha \ll 1$

$K_d = (\alpha\ [HCN]_0)^2 / (1 - \alpha)\ [HCN]_0 = \alpha^2\ [HCN]_0$

Ostwald Dilution Law

$K_d = (\alpha\ [HCN]_0)^2 / (1 - \alpha)\ [HCN]_0 = \alpha^2\ [HCN]_0$

$$\alpha^2 = \frac{K_d}{[HCN]_0}$$

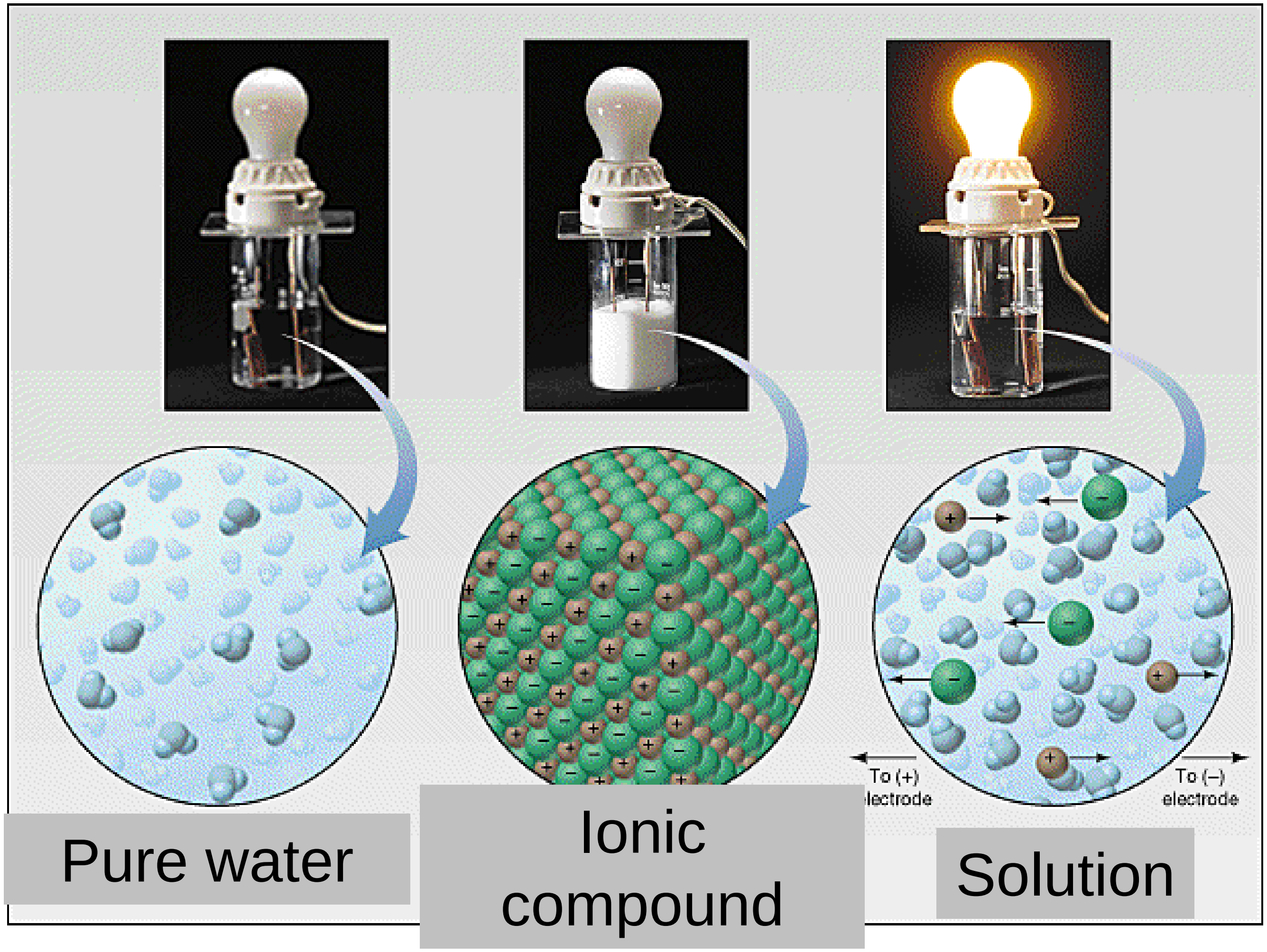
With increasing **concentration of** electrolyte **dissociation degree decreases**

Dilution increases **dissociation degree**

$F = const\ q_1\ q_2 / r^2$

Dilution increases interionic distances, r, attractive force decreases

Electrolytic Conductivity



Pure water

Ionic compound

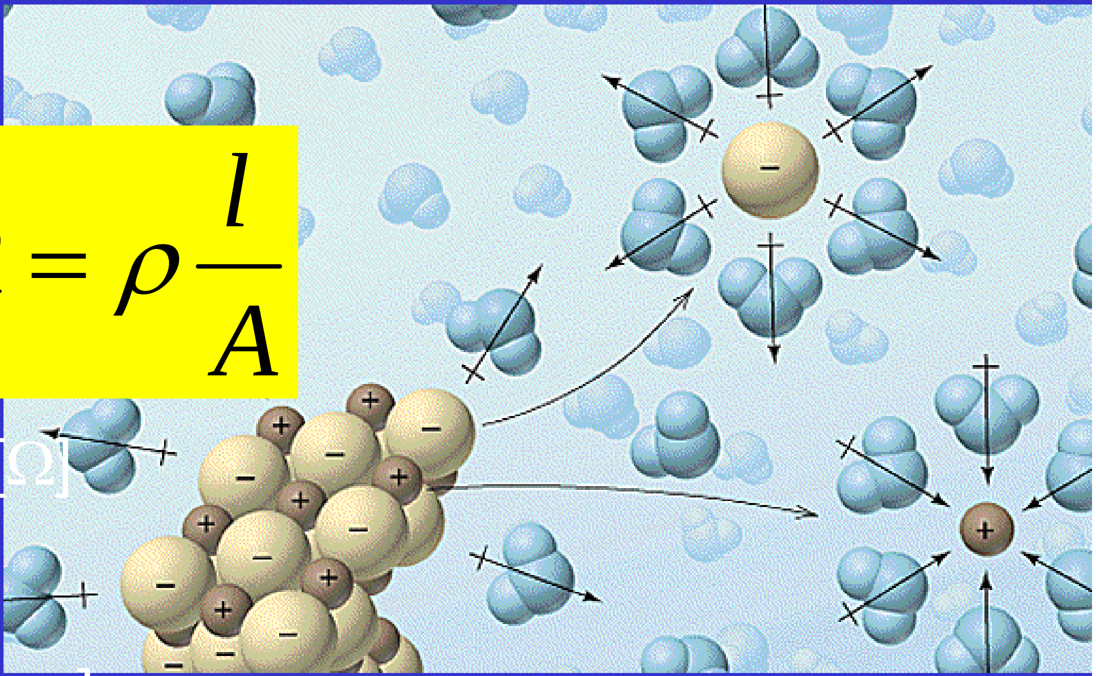
Solution

Electrolytic Conductivity

Ionic compound solutions

Free moving of ions
Charge cerriers

$$R = \rho \frac{l}{A}$$



Electrical resistance, R [Ω]
l = length
A = area
ρ = specific resistivity [Ω m]

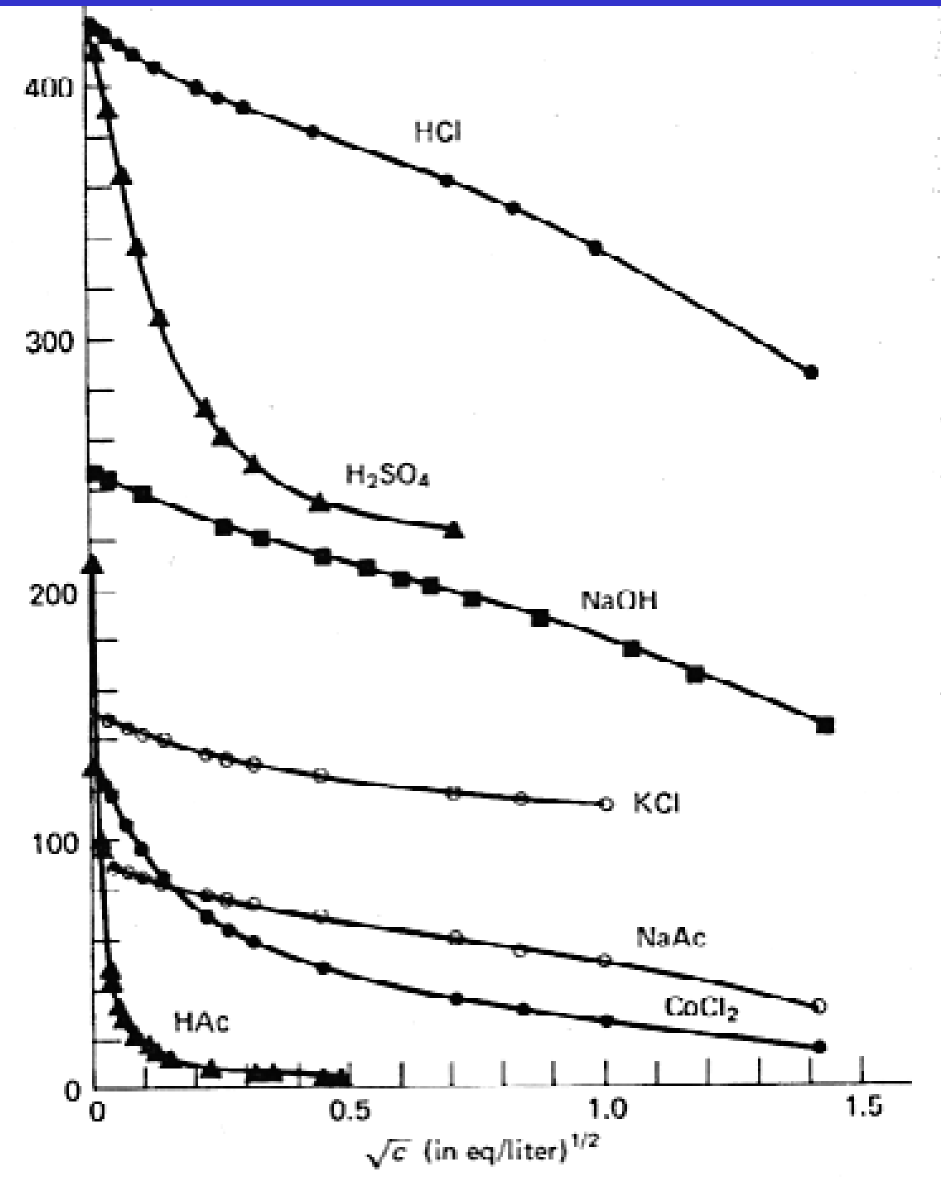
σ = 1 / ρ = specific conductivity

Molar conductivity, Λ
Λ = σ / c   Λ decreases with incr concentration

Molar conductivity, Λ

$\Lambda = \sigma / c$

Λ decreases with incr concentrationc



Electrolyte Activity

Asociation of ions at increasing concentration, ion pairs
Number of particles decrease
Conductivity decreasses – ion pairs do not carry electric current. Only free ions remain active – correction of concentration for **association**

Activity, a

$$a = \gamma_{\pm}\, c$$

Mean activity coefficient, $g_{\pm}$ (values 0 – 1)

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

Ionic strength of solution, $I = \frac{1}{2} \Sigma\, c_i\, z_i^{2}$ c_i molality [mol kg^{-1}]

Mean Activity Coefficient, $\gamma_\pm$

Molality [mol kg^{-1}]

Comp.	0.001	0.01	0.1
HCl	0.966	0.904	0.796
NaCl	0.966	0.904	0.780
$BaCl_2$	0.880	0.729	0.512
$ZnSO_4$	0.700	0.387	0.150

at 25 °C

$$I = \tfrac{1}{2} \Sigma c_i z_i^2$$

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

Solubility Product

$$\boxed{A_xB_y\ (s)} \xrightleftharpoons{H_2O} x\ [A(H_2O)_n]^{y+} + y\ B(H_2O)_n]^{x-}$$

hydratované (solvatované) ionty

tuhá látka, krystal

Solubility product: $K_s = [A]^x\ [B]^y$

Conditions:

- Strong electrolyte, 100% dissociation
- Ionic strength $I = ½\ \Sigma\ c_i\,z_i^2 = 0$
- Activity coefficients $\gamma = 1$
- No extra ions or side reactions

Fulfilled only rarely!

Solubility Product

Solid phase activity = 1

$$AgCl_s \rightleftarrows Ag^+_{aq} + Cl^-_{aq}$$

$$K = \frac{[Ag^+_{aq}][Cl^-_{aq}]}{[AgCl_s]} = \frac{[Ag^+_{aq}][Cl^-_{aq}]}{1}$$

$$K_L = [Ag^+_{aq}][Cl^-_{aq}]$$

$$A_2B_{3,s} \rightleftarrows 2A^{2+}_{aq} + 3B^{2-}_{aq}$$

$$K_L = [A^{2+}_{aq}]^2\,[B^{2-}_{aq}]^3$$

Solubility Product

$$\boxed{A_xB_y\ (s)} \xrightleftharpoons{H_2O} x\,[A(H_2O)_n]^{y+} + y\ B(H_2O)_n]^{x-}$$

tuhá látka, krystal

hydratované (solvatované) ionty

$$K_s = [A]^x\,[B]^y = (x\ R)^x\,(y\ R)^y$$

R = Solubility

$$R = \left(\frac{K_s}{x^x y^y}\right)^{\frac{1}{x+y}}$$

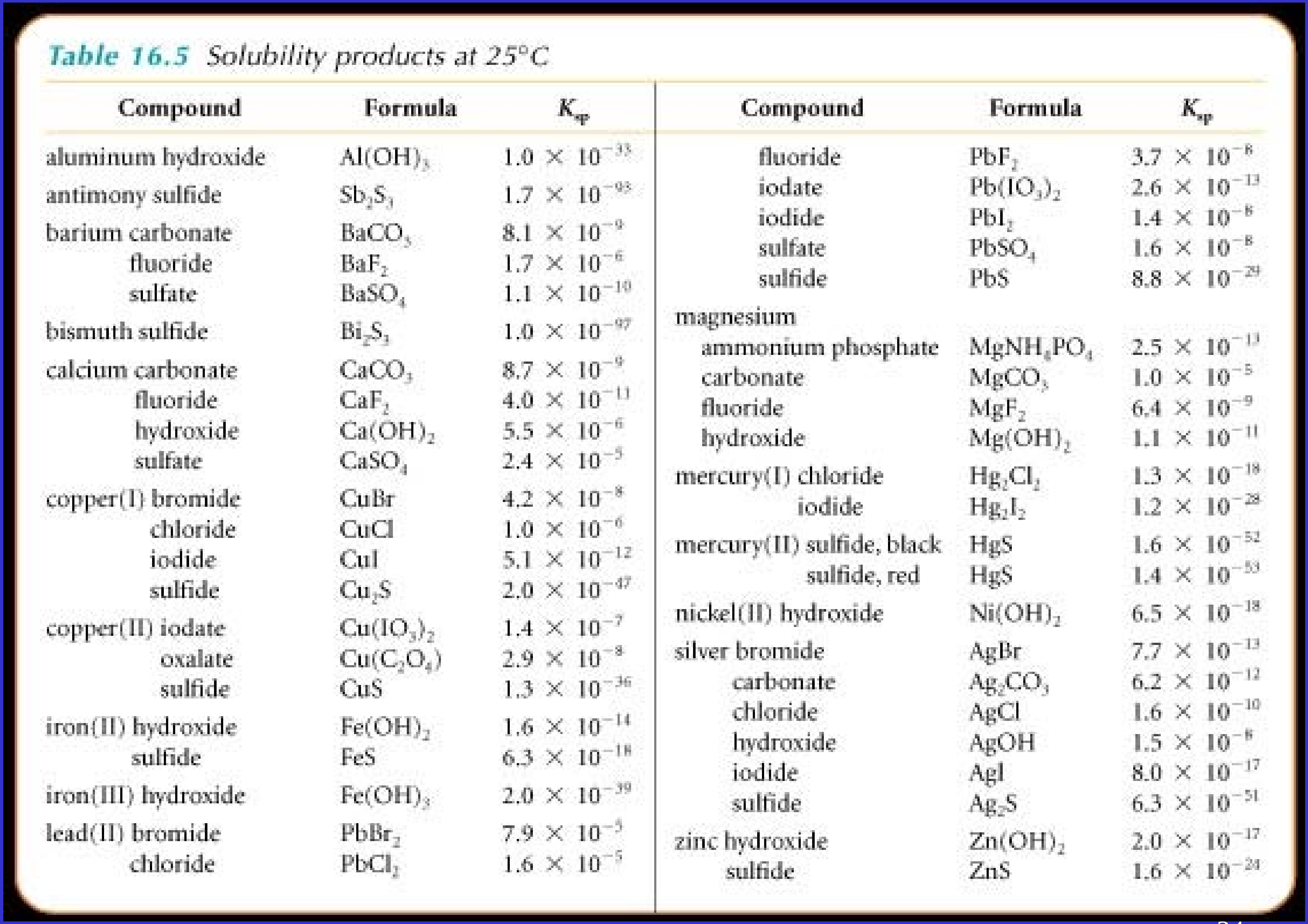


Table 16.5 *Solubility products at 25°C*

Compound	Formula	K_{sp}
aluminum hydroxide	$Al(OH)_3$	1.0×10^{-33}
antimony sulfide	Sb_2S_3	1.7×10^{-93}
barium carbonate	$BaCO_3$	8.1×10^{-9}
fluoride	BaF_2	1.7×10^{-6}
sulfate	$BaSO_4$	1.1×10^{-10}
bismuth sulfide	Bi_2S_3	1.0×10^{-97}
calcium carbonate	$CaCO_3$	8.7×10^{-9}
fluoride	CaF_2	4.0×10^{-11}
hydroxide	$Ca(OH)_2$	5.5×10^{-6}
sulfate	$CaSO_4$	2.4×10^{-5}
copper(I) bromide	$CuBr$	4.2×10^{-8}
chloride	$CuCl$	1.0×10^{-6}
iodide	CuI	5.1×10^{-12}
sulfide	Cu_2S	2.0×10^{-47}
copper(II) iodate	$Cu(IO_3)_2$	1.4×10^{-7}
oxalate	$Cu(C_2O_4)$	2.9×10^{-8}
sulfide	CuS	1.3×10^{-36}
iron(II) hydroxide	$Fe(OH)_2$	1.6×10^{-14}
sulfide	FeS	6.3×10^{-18}
iron(III) hydroxide	$Fe(OH)_3$	2.0×10^{-39}
lead(II) bromide	$PbBr_2$	7.9×10^{-5}
chloride	$PbCl_2$	1.6×10^{-5}
fluoride	PbF_2	3.7×10^{-8}
iodate	$Pb(IO_3)_2$	2.6×10^{-13}
iodide	PbI_2	1.4×10^{-8}
sulfate	$PbSO_4$	1.6×10^{-8}
sulfide	PbS	8.8×10^{-29}
magnesium		
ammonium phosphate	$MgNH_4PO_4$	2.5×10^{-13}
carbonate	$MgCO_3$	1.0×10^{-5}
fluoride	MgF_2	6.4×10^{-9}
hydroxide	$Mg(OH)_2$	1.1×10^{-11}
mercury(I) chloride	Hg_2Cl_2	1.3×10^{-18}
iodide	Hg_2I_2	1.2×10^{-28}
mercury(II) sulfide, black	HgS	1.6×10^{-52}
sulfide, red	HgS	1.4×10^{-53}
nickel(II) hydroxide	$Ni(OH)_2$	6.5×10^{-18}
silver bromide	$AgBr$	7.7×10^{-13}
carbonate	Ag_2CO_3	6.2×10^{-12}
chloride	$AgCl$	1.6×10^{-10}
hydroxide	$AgOH$	1.5×10^{-8}
iodide	AgI	8.0×10^{-17}
sulfide	Ag_2S	6.3×10^{-51}
zinc hydroxide	$Zn(OH)_2$	2.0×10^{-17}
sulfide	ZnS	1.6×10^{-24}

Colligative Properties

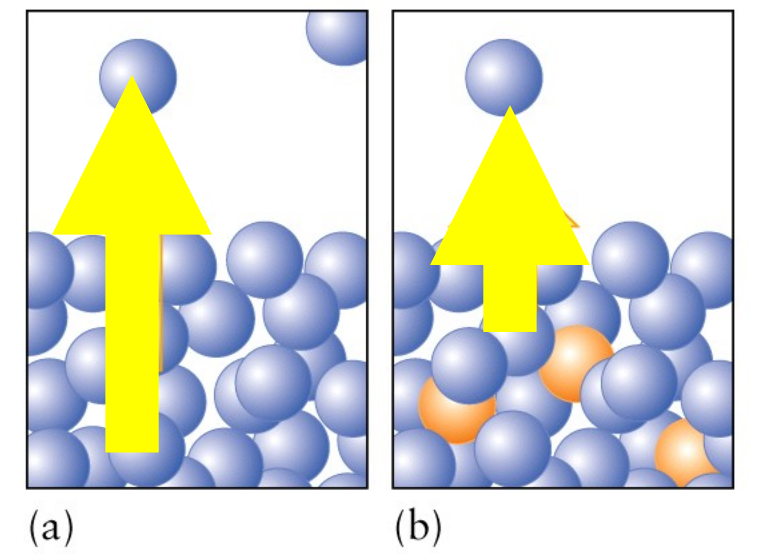
Properties of solutions that do not depend on the kind of solute but only on its amount number of molecules.

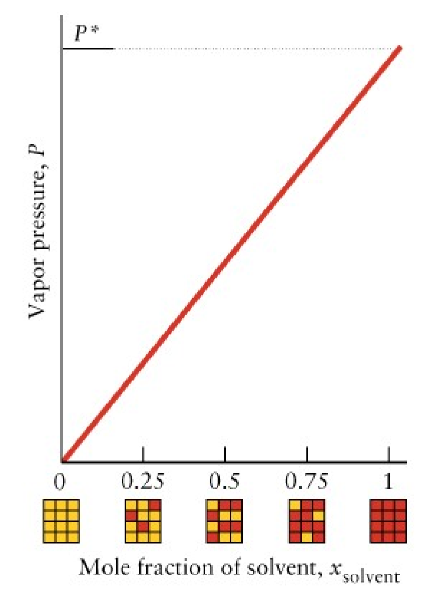
- Vapor pressure
  - – Lowering the vapor pressure by dissolved solute
- Boiling point
  - – Boiling point elevation by dissolved solute = ebulioscopic effect
- Melting point
  - – Melting point depression by dissolved solute = cryoscopic effect
- Osmosis
  - – Osmotic pressure = difference of concentrations of dissolved compounds

Lowering the Vapor Pressure

Addition of solute to the solvent lowers the vapor pressure by two mechanisms:

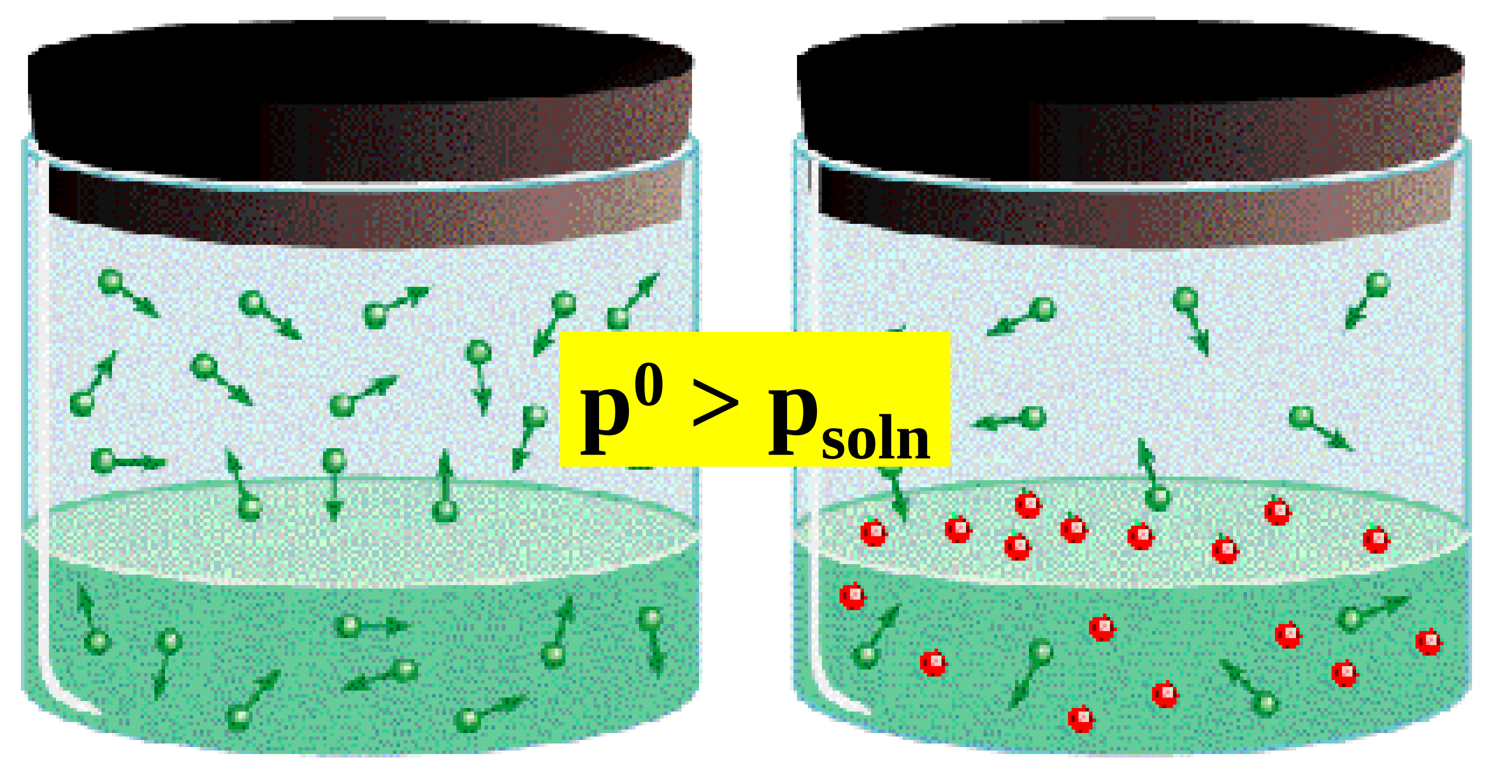
1. Increased entropy decreases driving force to evaporation
2. Dilution of solvent decreases number of molecules capable of leaving the surface of solution





Lowering the Vapor Pressure of a Solution

Dilution of solvent decreases number of molecules capable of leaving the surface of solution



$p^0 > p_{soln}$

Raoult’s Law

Vapor pressure of solvent above a solution

$$p_{solvent} = x_{solvent} P^0_{solvent}$$

$$p_{tot} = p_{solvent} + p_{solute}$$

$= 0$ for nonvolatile compounds

$$p_{tot} = x_{solvent} P^0_{solvent}$$

Raoult’s Law

$P_1 = x_1 P_1°$ (x$_1$ = solvent)

$x_1 = 1 - x_2$ (x_2 = solute)

$P_1 = (1- x_2) P_1°$

$P_1 = P_1° - x_2 P_1°$

$P_1° - P_1 = \Delta P_1 = x_2 P_1°$ Lowering of vapor pressure

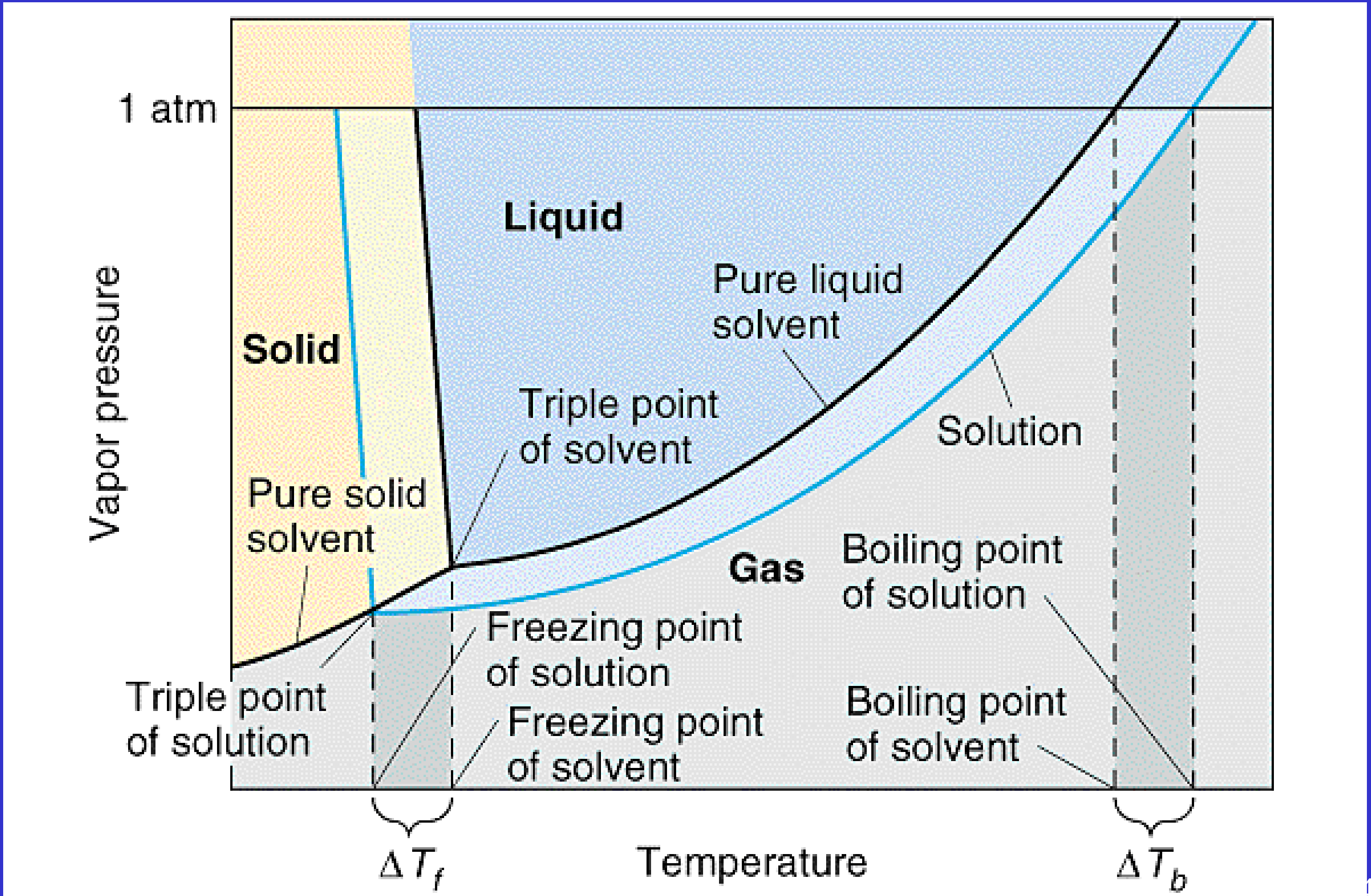
Two volatile compounds, A and B

$P_A = x_A P_A°$

$P_B = x_B P_B°$

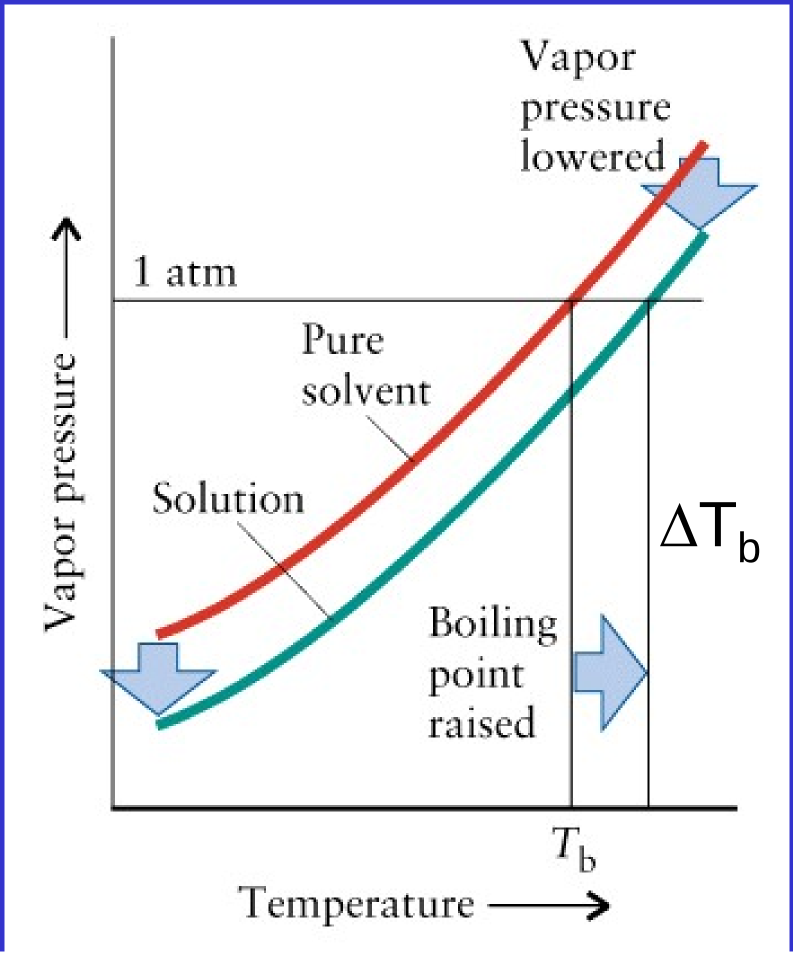
$P_{tot} = P_A + P_B = x_A P_A° + x_B P_B°$

Boiling Point Elevation
and Melting Point Depression



Boiling Point Elevation

Boiling Point = temperature at which the vapor pressure equals the ambient pressure



Boiling Point Elevation

$\Delta T_b = i\, k_b\, c_m$

i = van’t Hoff factor, number of particles

k_b = ebullioscopic constant

c_m = molality [mol kg^{-1}]

Melting Point Depression

$\Delta T_f = i\, k_f\, c_m$

i = van’t Hoff factor, number of particles
k_f = cryoscopic constant
c_m = molality [mol kg^{-1}]

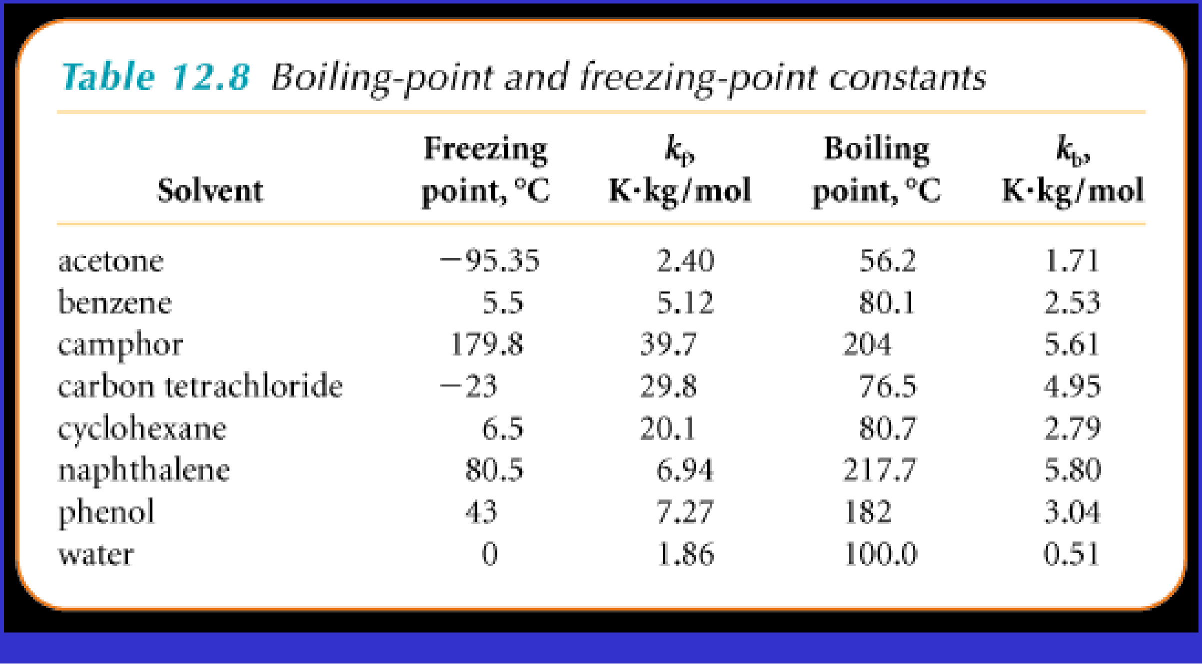
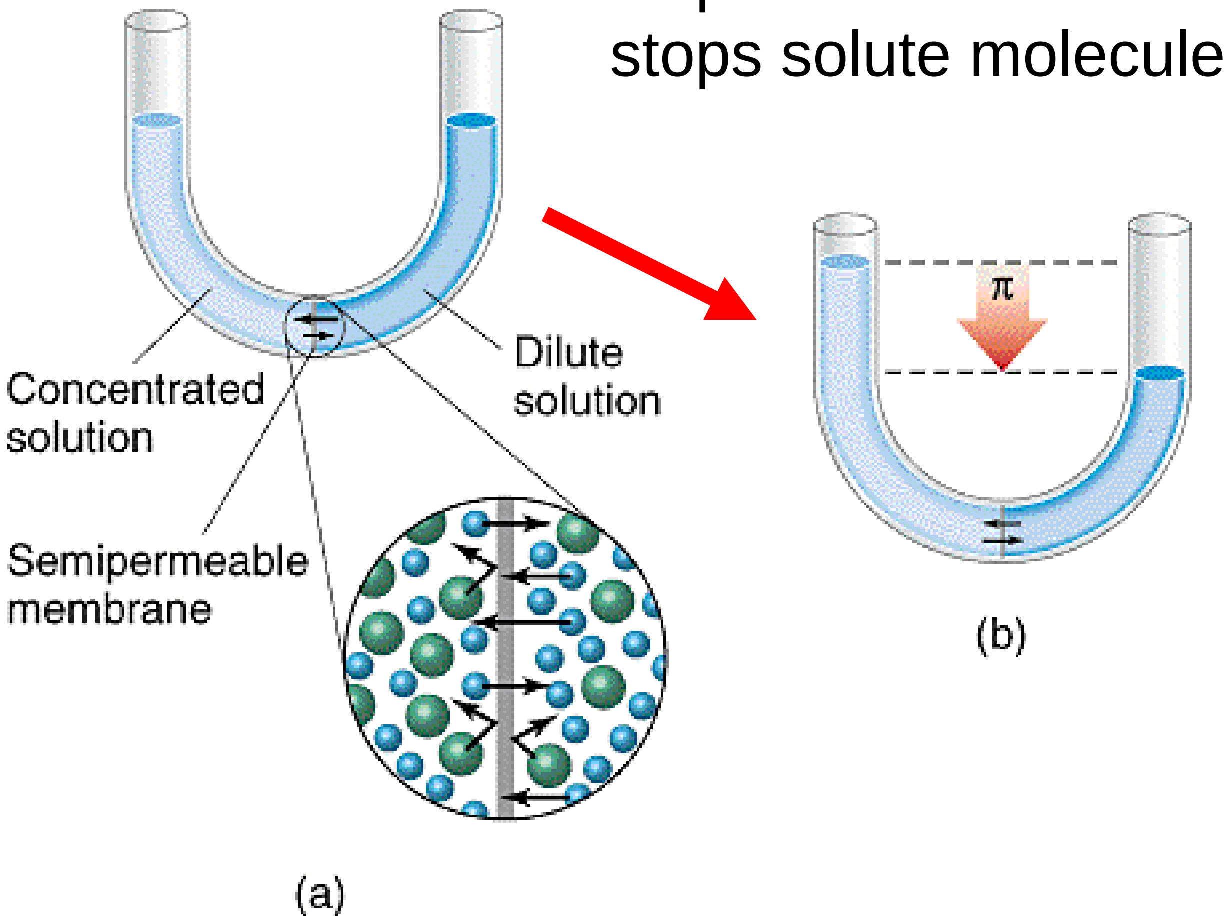


Table 12.8 *Boiling-point and freezing-point constants*

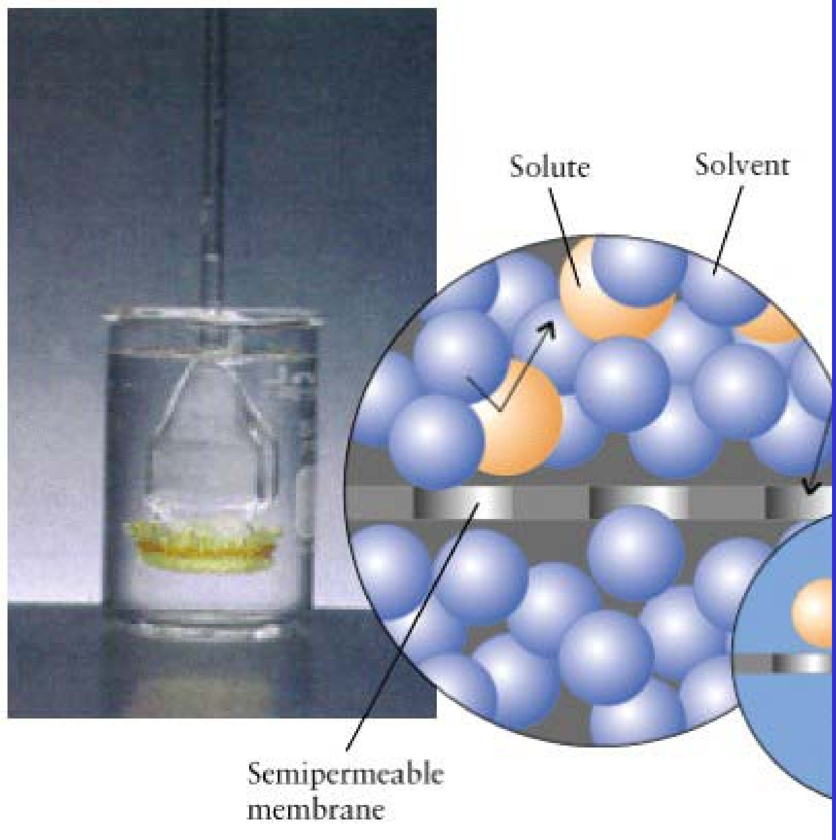
Solvent	Freezing point, °C	k_f, K·kg/mol	Boiling point, °C	k_b, K·kg/mol
acetone	−95.35	2.40	56.2	1.71
benzene	5.5	5.12	80.1	2.53
camphor	179.8	39.7	204	5.61
carbon tetrachloride	−23	29.8	76.5	4.95
cyclohexane	6.5	20.1	80.7	2.79
naphthalene	80.5	6.94	217.7	5.80
phenol	43	7.27	182	3.04
water	0	1.86	100.0	0.51

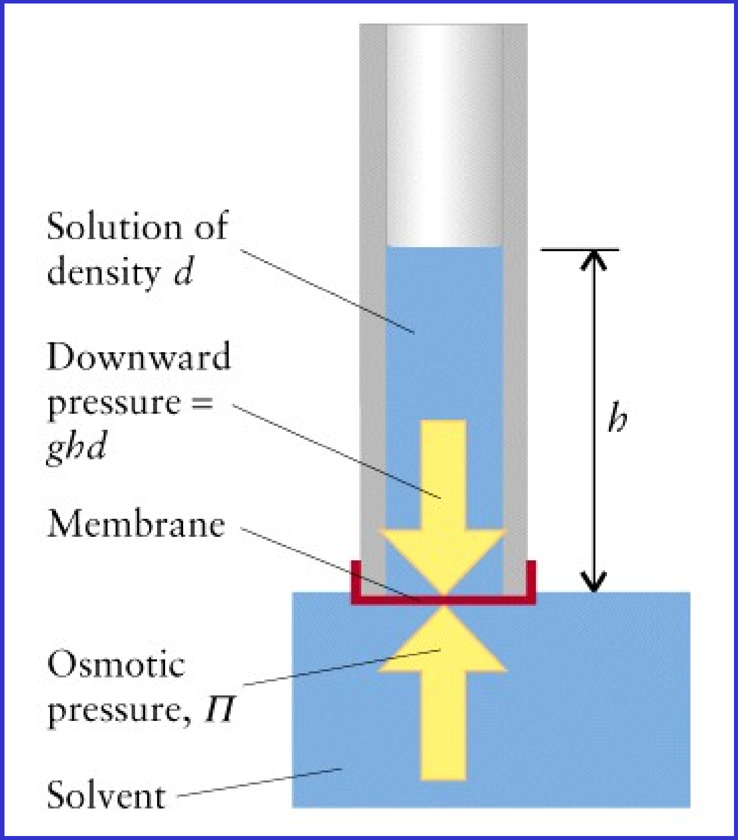
Osmosis

Semipermeable membrane
let pass solvent molecules and
stops solute molecules



Osmosis


Solute
Solvent
Semipermeable membrane


Solution of density *d*
Downward pressure = *ghd*
Membrane
Osmotic pressure, *Π*
Solvent
h

Osmotic Pressure

$\Pi = c_M\ R\ T$

for ionic solutions

$\Pi = i\ c_M\ R\ T$

c_M = molar concentration
R = gas constant
P = osmotic pressure
T = temperature, K
i = van’t Hoff factor

Similar to ideal gas equation.
Similar effect = molecular collisions create pressure

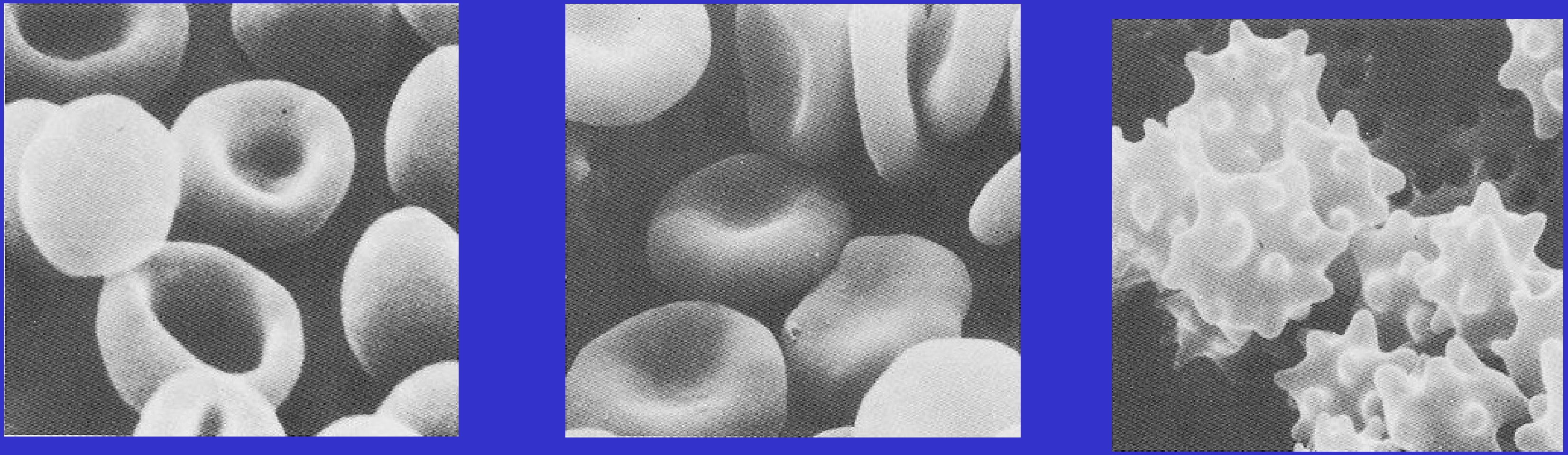
Osmosis

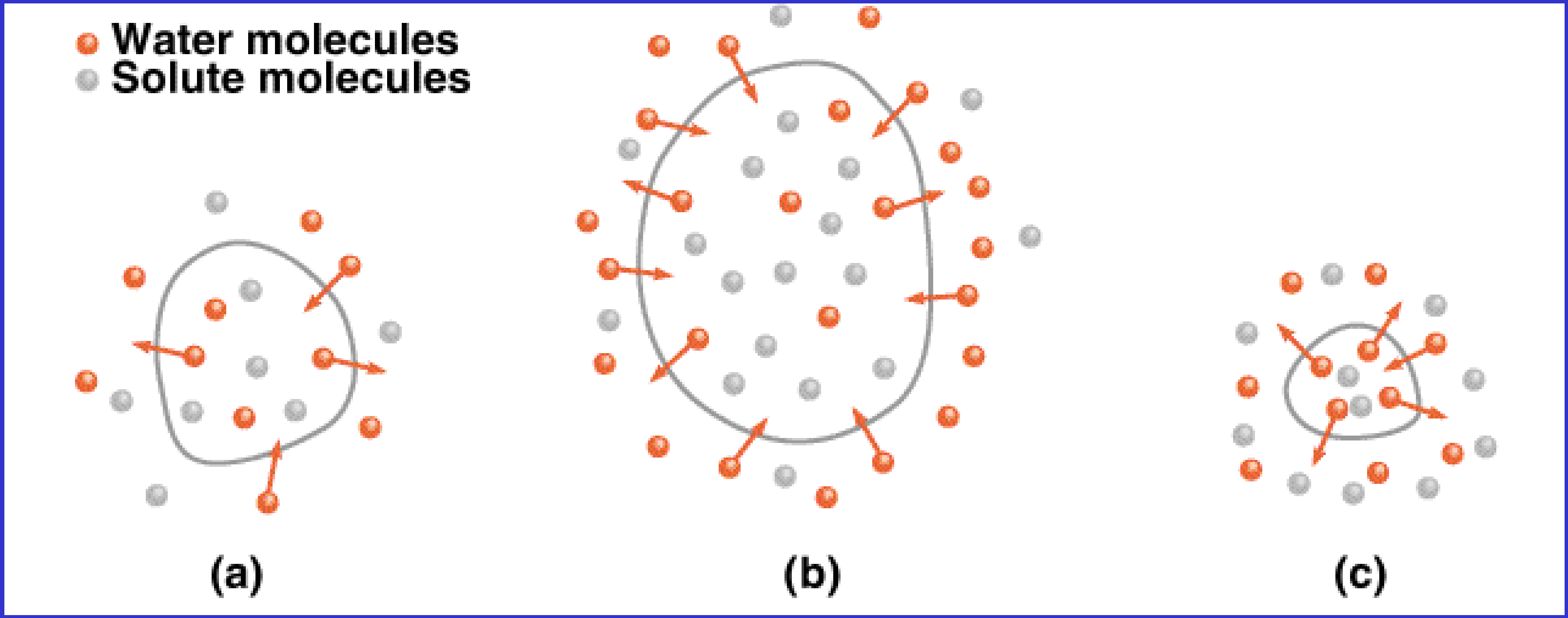
Dialysis – separation of large molecules from solution, small molecules pass through the membrane

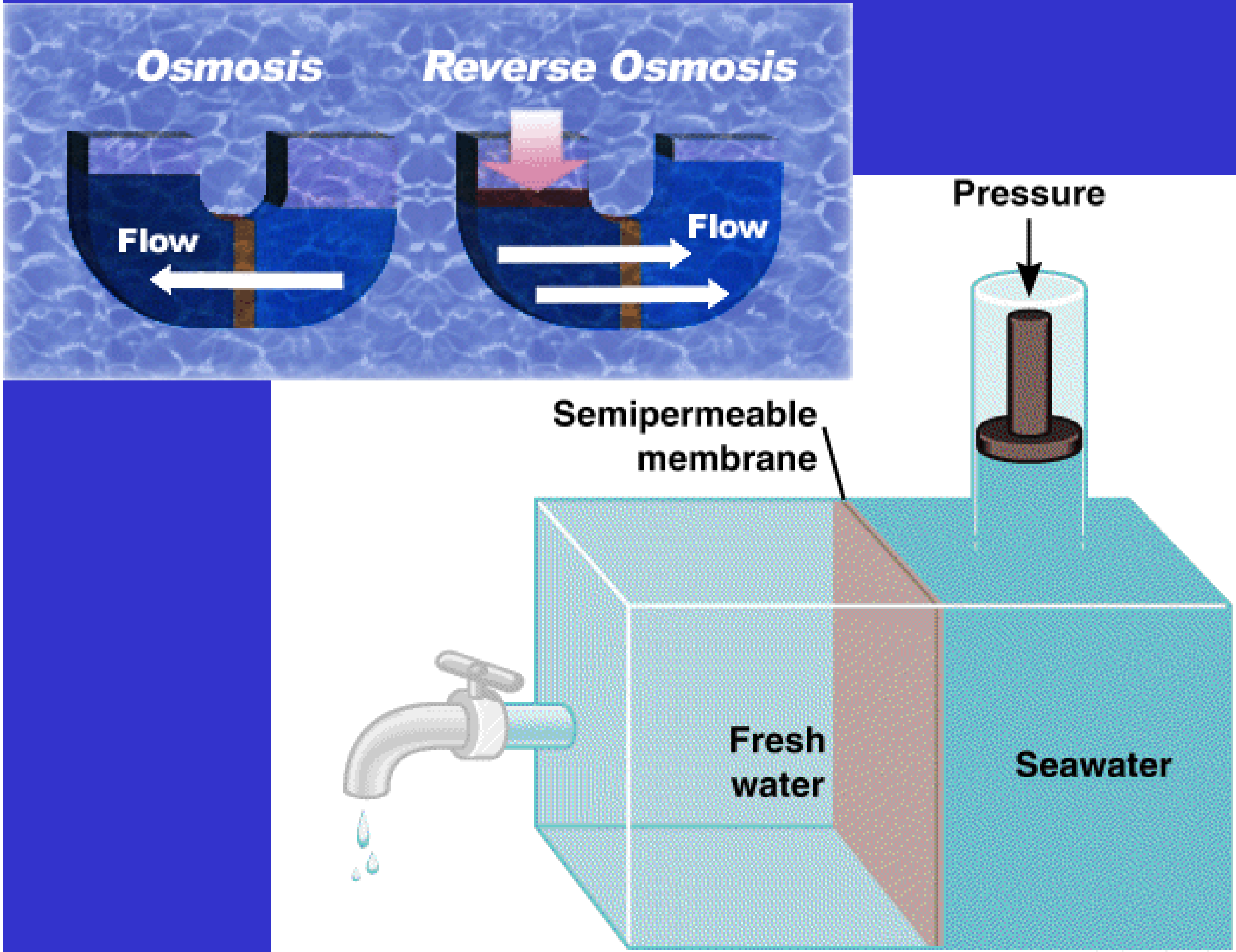
Isotonic solution

Hypotonic solution

Hypertonic solution



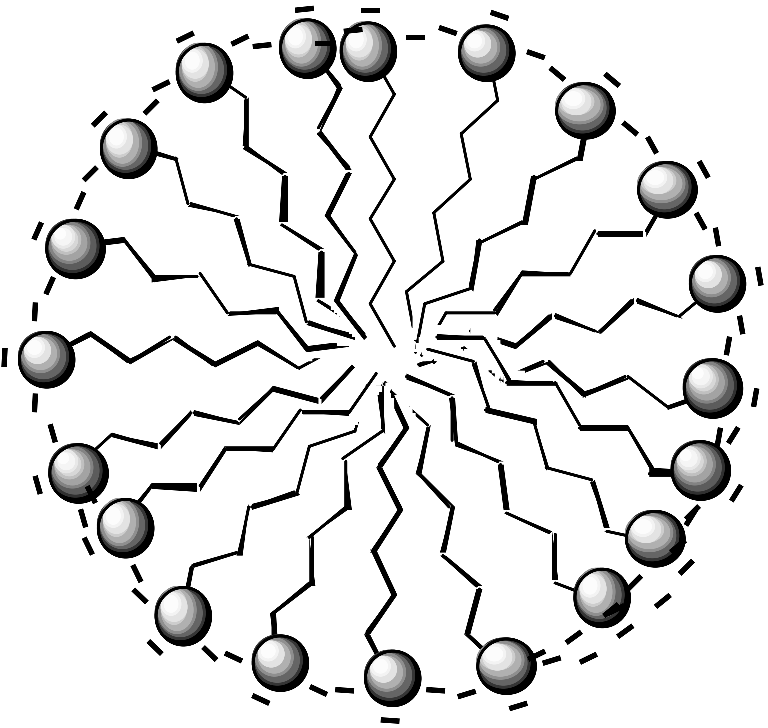

Water molecules
Solute molecules
(a)
(b)
(c)


Osmosis
Reverse Osmosis
Flow
Flow
Pressure
Semipermeable membrane
Fresh water
Seawater

Colloidal Systems

- Colloids are suspensions with particles larger than molecules, but small enough to resist gravitational precipitation. Size 10 tp 2000 Å.

- Types of colloids:
  - aerosols (g + l or s, fog, smoke)
  - foam (l + g, whip cream, beer foam
  - emulsion (l + l, milk)
  - sol (l + s, paint)
  - solid foam (s + g, marshmallow),
  - solid emulsion (s + l, butter),
  - solid sol (s + s, ruby glass).



Micell

Colloidal Systems

Lyophilic colloids, TD stable
High molecular weight (solution of polystyrene in acetone, solution protein or nucleic acid in water

Micellar
Aggregation of solute molecules – micells (10 - 1000 particles)

Lyophobic colloids, TD unstable
Must be stirred or protective micellar layer