Module 4

Solutions

Session Slides with Notes

Solvent	Solute
gas	gas
liquid	gas
liquid	liquid
liquid	solid
solid	solid

Solutions
- homogeneous

vs

suspensions, emulsions, colloids, gels, sols

- heterogenous phase spaces

$$\text{Concentration} = \frac{\text{amount of solute}}{\text{amount of solvent or solution}}$$

Mole fraction:

gaseous solutions

partial pressure = mole fraction

fraction

$$X_A = \frac{n_A}{n_A + n_B + \ldots}$$

Raoult's Law

$P_{vap} = X P^{\circ}_{vap}$

Percent by mass and volume:

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

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

Practical measurement

lab protocols

Molarity

reaction quotients
equilibrium constants
rate expressions

$$M = \frac{\text{moles of solute}}{\text{liter of solution}}$$

Molality

$$m = \frac{\text{moles of solute}}{\text{kilograms of solvent}}$$

Colligative properties
- BP elevation
- FP depression

400mL of 0.2 M NaOH solution
How many moles?

$(0.2 \frac{mol}{L})(.4L) = 0.08$ mol

6.0 g NaCl (MW 58.4) in water
makes 250mL of solution. Molarity?

58.4 g/mol

$\left(\frac{1 mol}{58.4 g}\right)(6g) = 0.1$ mol

$\frac{0.1 mol}{.25 L} = 0.4$ M

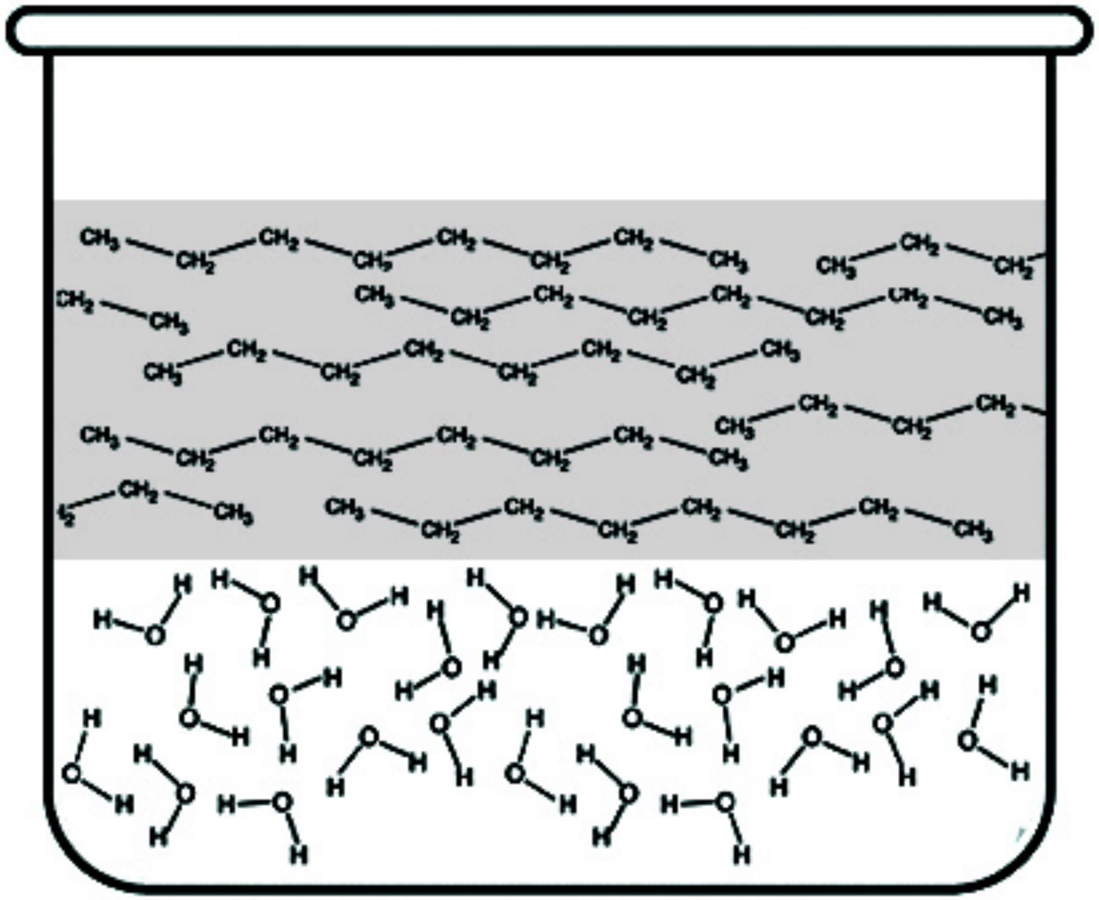
undissolved $\rightleftharpoons$ dissolved

Like Dissolves Like

$+\Delta G$

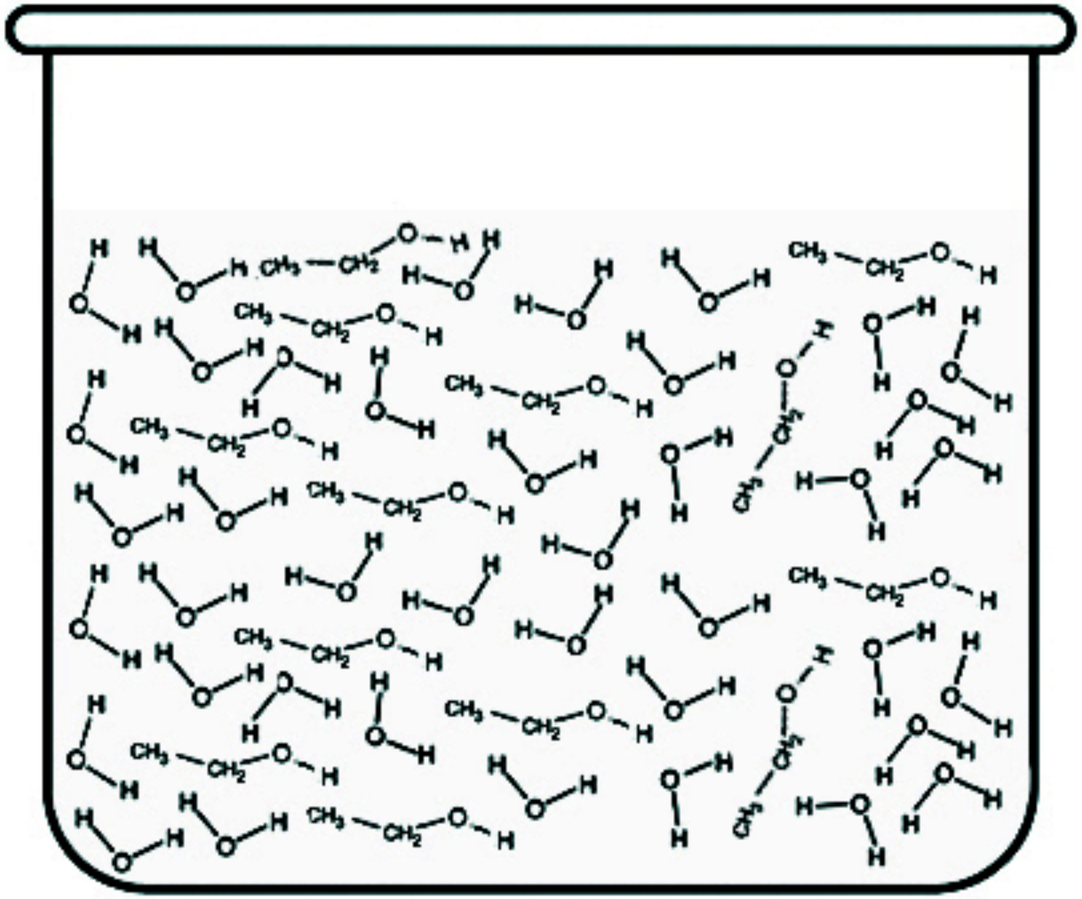
$+\Delta H$

$+\Delta U$

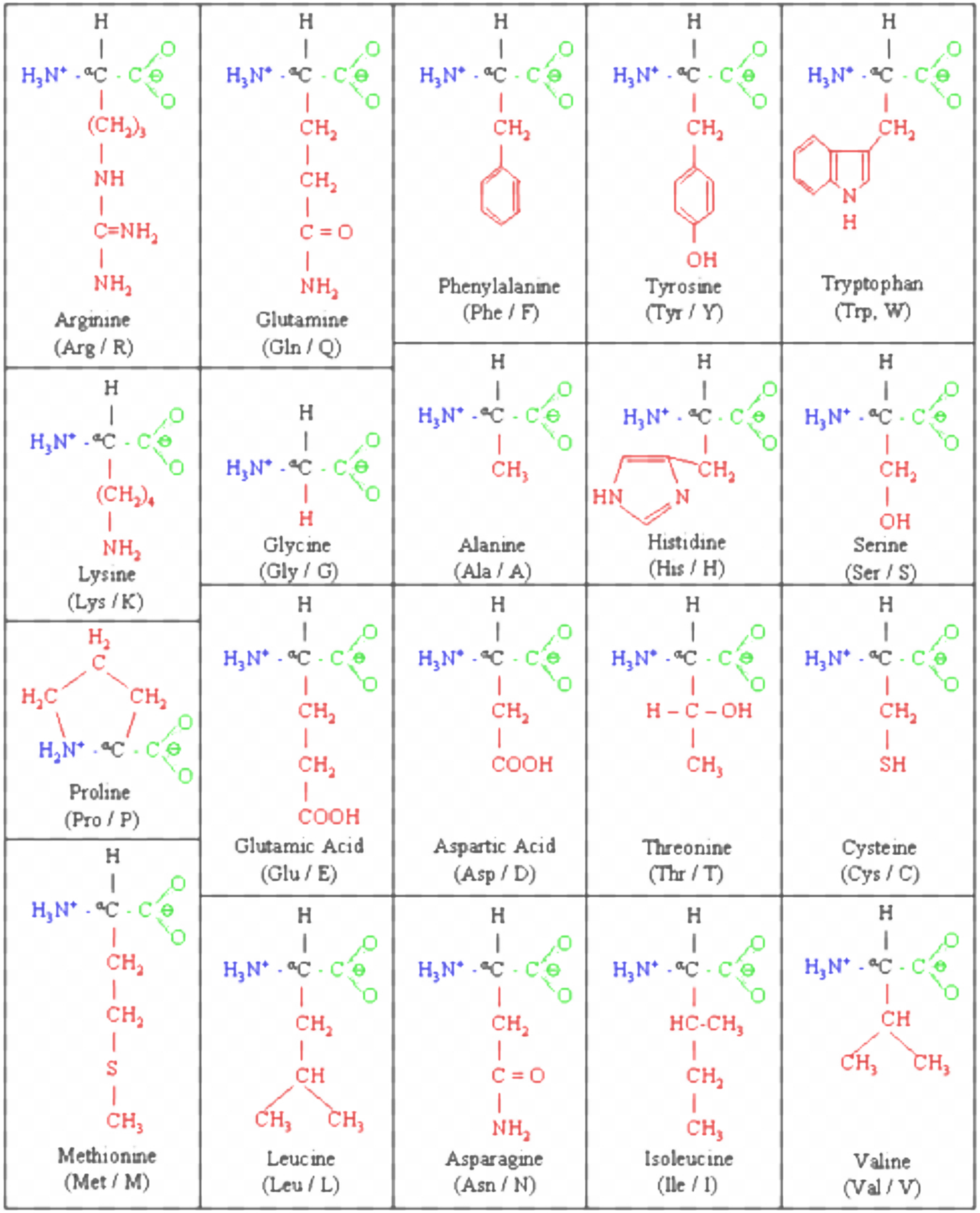


Solubility in Water

Methanol	infinite
Ethanol	infinite
Propanol	infinite
Butanol	90g/kg
Pentanol	2.7g/kg

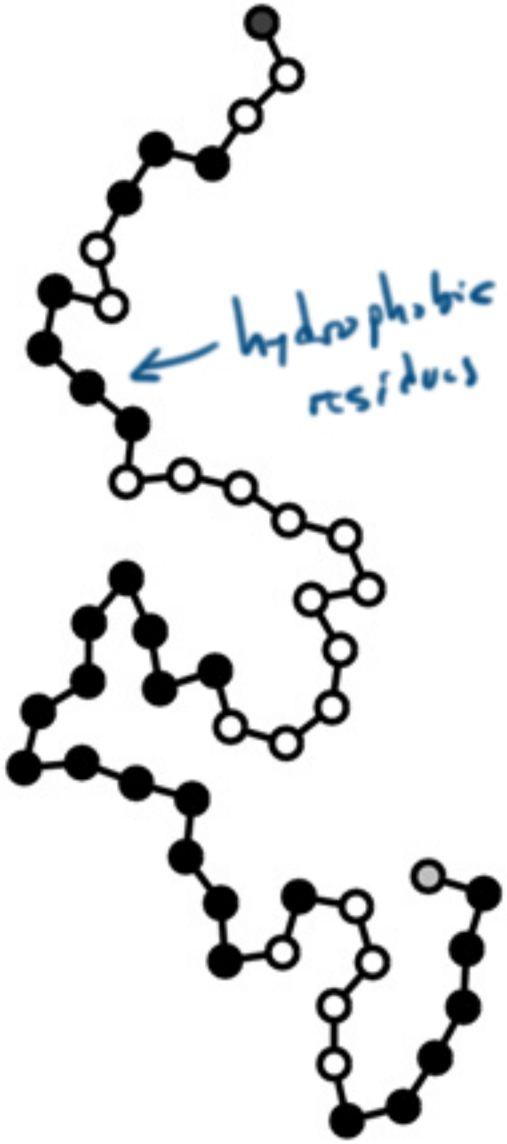


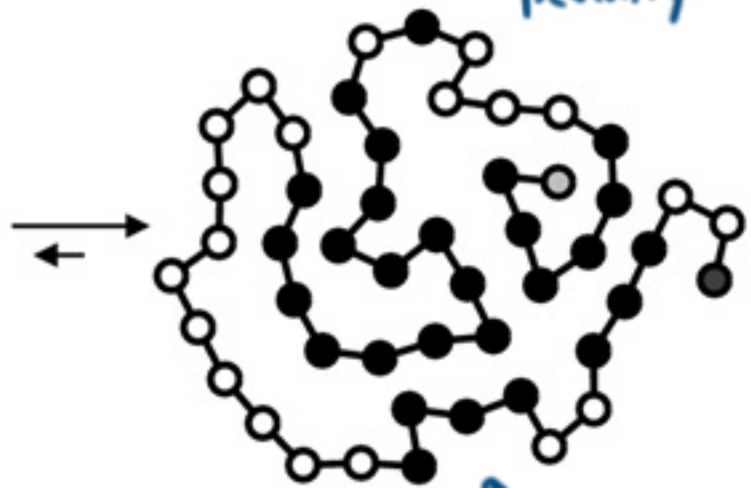
Note: at about 5:1 hydrocarbon to polar group it becomes insoluble.

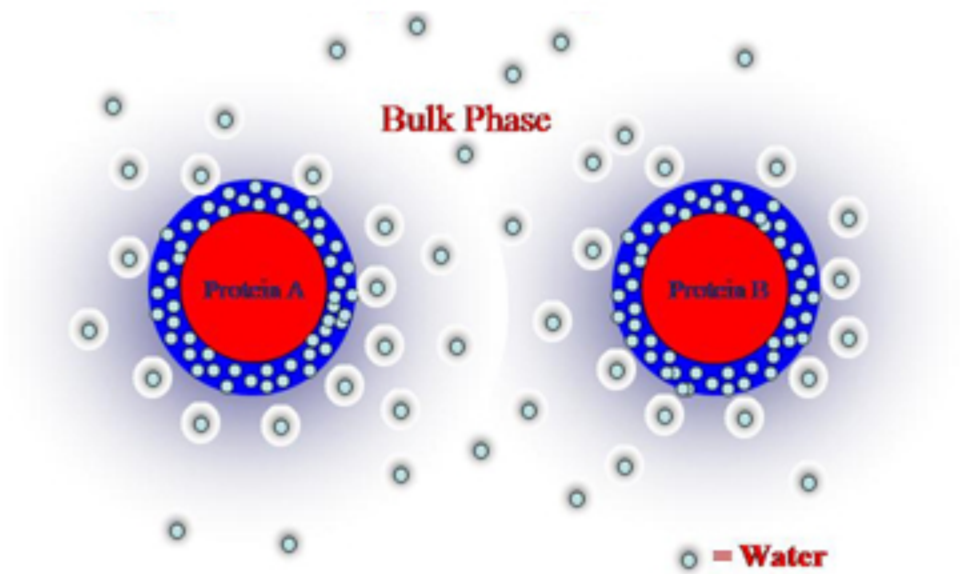


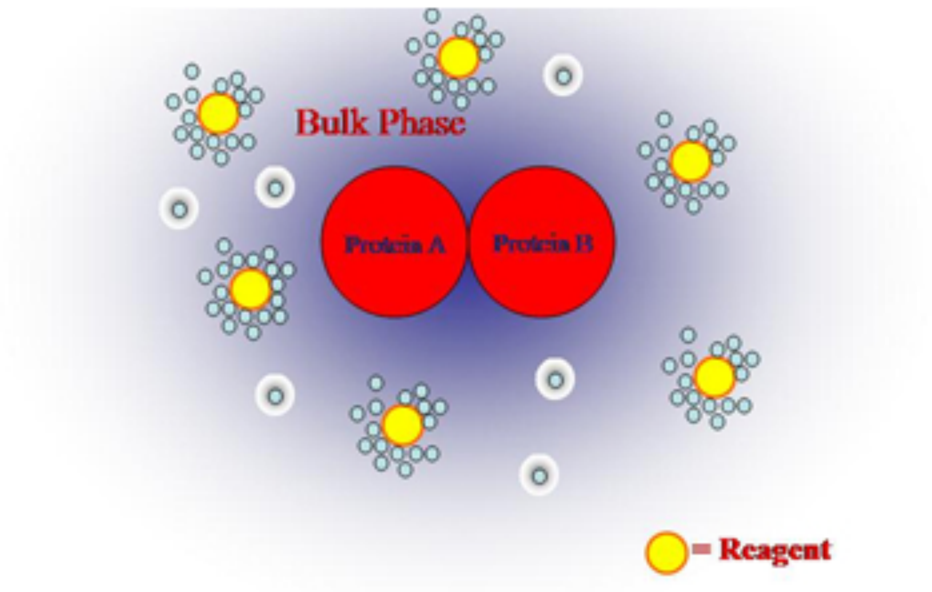
Arginine
(Arg / R)
Glutamine
(Gln / Q)
Phenylalanine
(Phe / F)
Tyrosine
(Tyr / Y)
Tryptophan
(Trp, W)
Lysine
(Lys / K)
Glycine
(Gly / G)
Alanine
(Ala / A)
Histidine
(His / H)
Serine
(Ser / S)
Proline
(Pro / P)
Glutamic Acid
(Glu / E)
Aspartic Acid
(Asp / D)
Threonine
(Thr / T)
Cysteine
(Cys / C)
Methionine
(Met / M)
Leucine
(Leu / L)
Asparagine
(Asn / N)
Isoleucine
(Ile / I)
Valine
(Val / V)

- Driven by enthalpy in self association of water
- also driven by entropic penalty







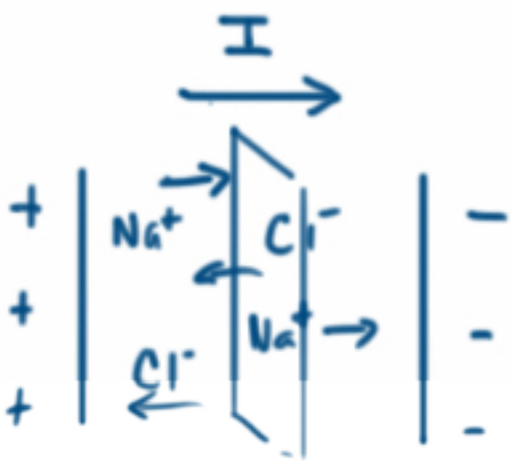


Hofmeister Series

$$F^- \approx SO_4^{2-} > HPO_4^{2-} > \text{acetate} > Cl^- > NO_3^- > Br^- > ClO_3^- > I^- > ClO_4^- > SCN^-$$

$$NH_4^+ > K^+ > Na^+ > Li^+ > Mg^{2+} > Ca^{2+} > \text{guanidinium}$$

Electrolytes



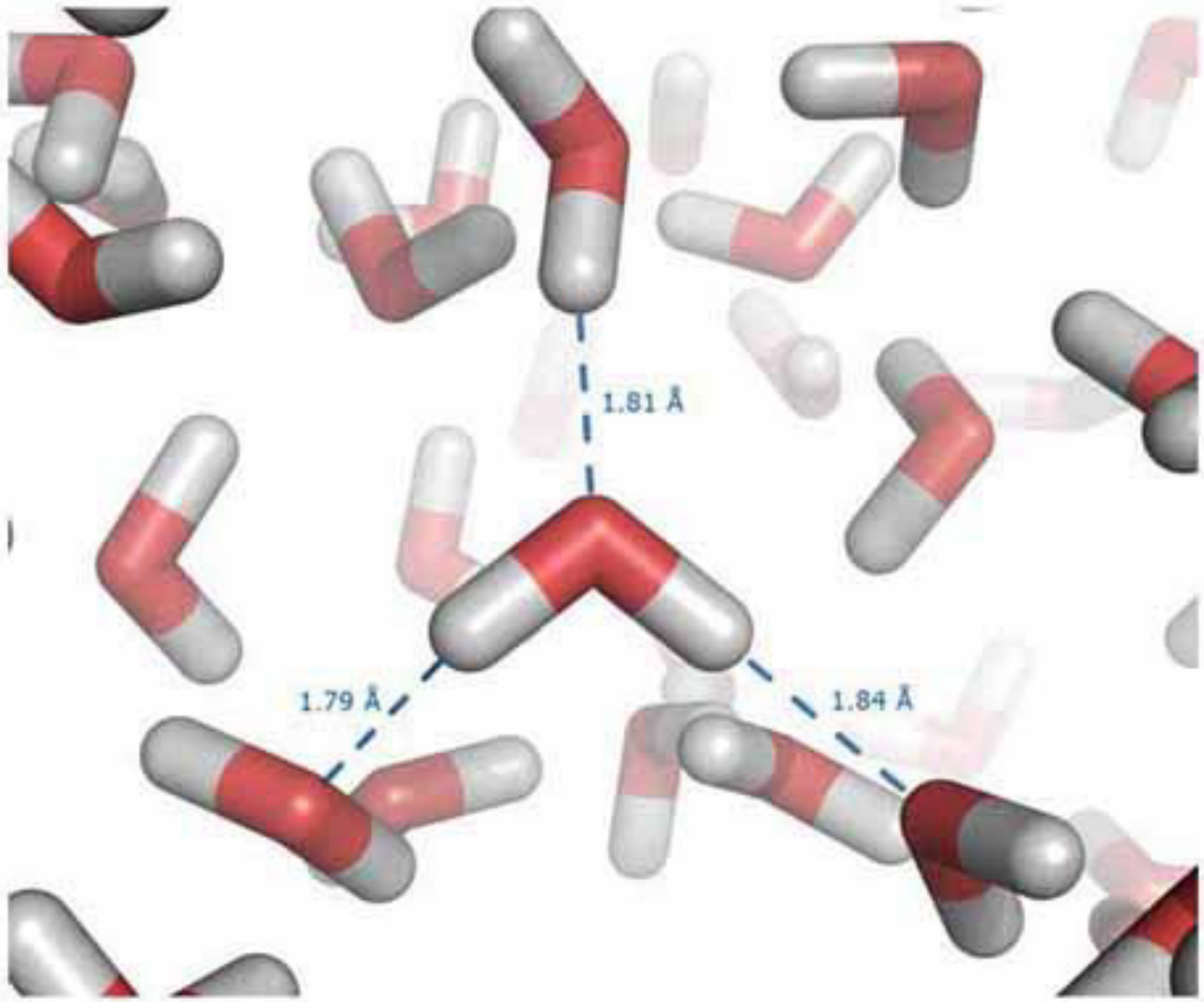
Strong

$NaCl(s) \longrightarrow Na^+(aq) + Cl^-(aq)$

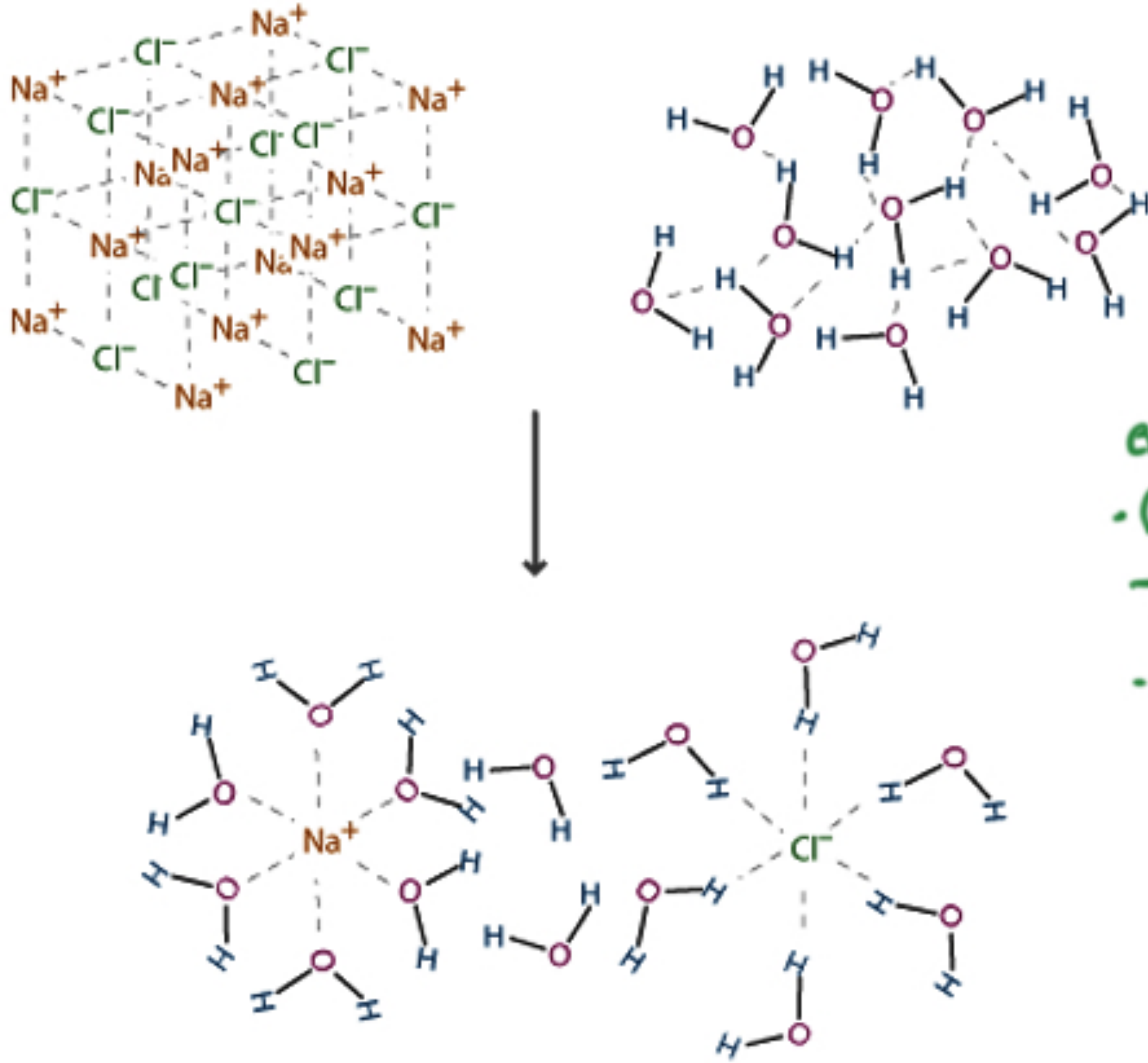
Weak ← sparingly soluble "insoluble"

$PbSO_4(s) \rightleftharpoons Pb^{2+}(aq) + SO_4^{2-}(aq)$

Heterogeneous Solution Equilibria (K_{sp})



1.81 Å
1.79 Å
1.84 Å



enthalpy change ΔH

- for NaCl · increasing T increases solubility
- solution process is endothermic

ΔH consists of

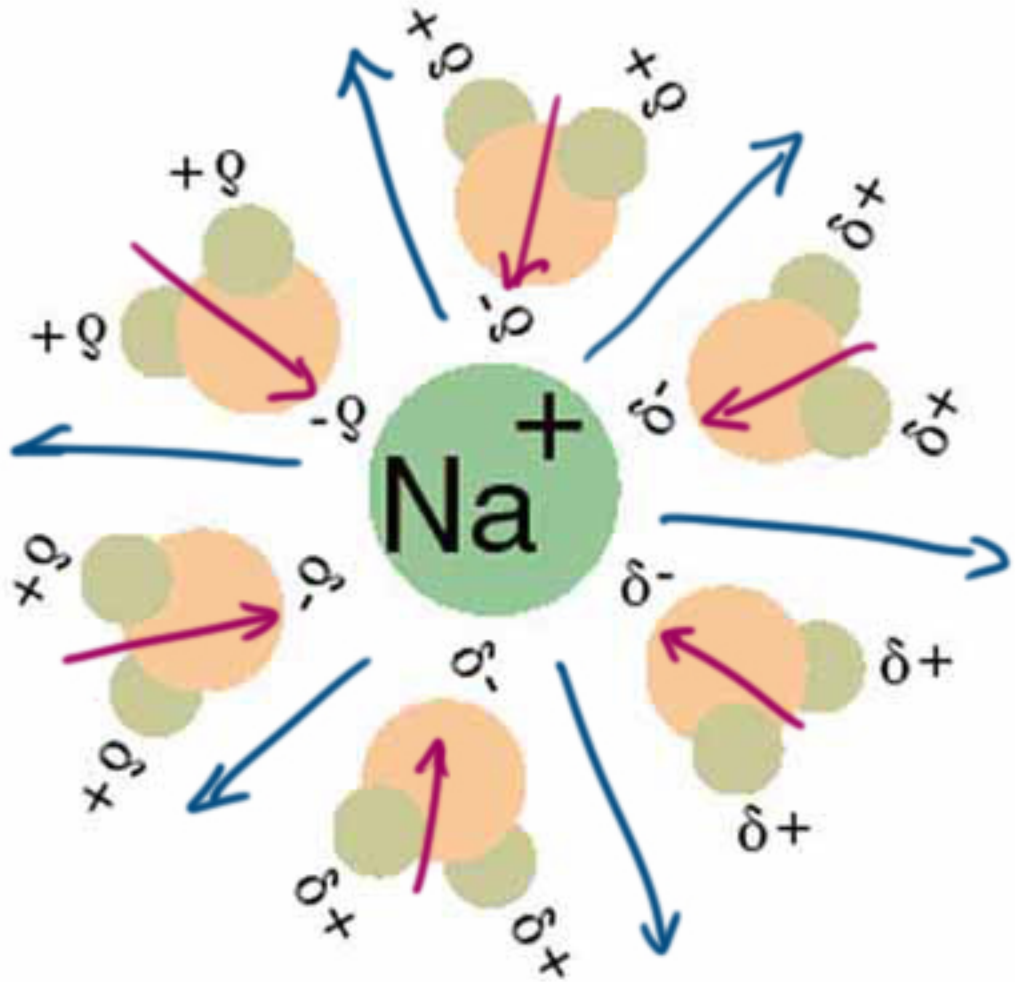
lattice energy $\oplus \Delta H$

enthalpy of hydration $\ominus \Delta H$

also entropic penalty

$$F = \frac{k q_1 q_2}{r^2 d_{H_2O}}$$

$d_{H_2O} \leftarrow$ dielectric constant ~ 80



Cl^-

Endothermic solution process - positive ΔH

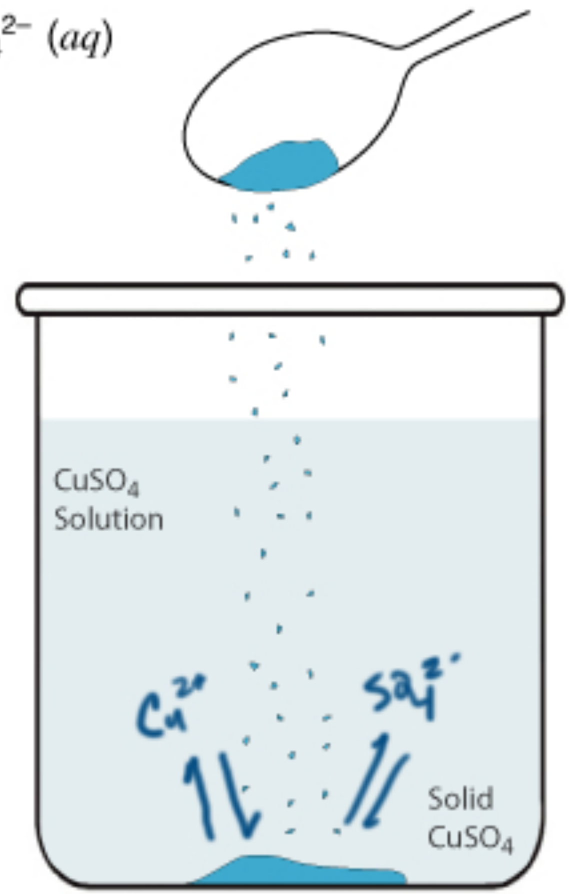
$$\text{heat} + \text{solvent} + \text{solute} \rightleftharpoons \text{solution}$$

Exothermic solution process - negative ΔH

$$\text{solvent} + \text{solute} \rightleftharpoons \text{solution} + \text{heat}$$

$$CuSO_4(s) \longrightarrow Cu^{2+}(aq) + SO_4^{2-}(aq)$$

$$CuSO_4(s) \rightleftharpoons Cu^{2+}(aq) + SO_4^{2-}(aq)$$



In solution chemistry the equilibrium state is the saturated solution.

SOLUBLE

Na^+, K^+, NH_4^+

NO_3^-

F⁻ tend to be insoluble

Cl^-, Br^-, I^-

(except with Pb^{2+}, Hg_2^{2+}, Ag^+ & Cu^+)

SO_4^{2-}

(except with Ba^{2+}, Sr^{2+}, Pb^{2+}, Hg_2^{2+}, Ca^{2+} & Ag_2^{2+})

Don't worry about all the nitty gritty details.

INSOLUBLE

S_2^-

(except with Na^+, K^+, NH_4^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Sr^{2+})

O_2^-

(except with Na^+, K^+, Ba^{2+}, Sr^{2+})

OH^- ★

(except with Na^+, K^+, Ca^{2+}, Ba^{2+}, Sr^{2+})

CrO_4^{2-}

(except with Na^+, K^+, Mg^{2+}, NH_4^+)

★ PO_4^{3-} & CO_3^{2-} ★

(except with Na^+, K^+, NH_4^+)

Testing an Aqueous Solution for the Presence of Flouride

$$CaCl_2\,(s) \longrightarrow Ca^{2+}\,(aq) + 2\,Cl^-\,(aq)$$

common ion

$$Ca^{2+}\,(aq) + 2\,F^-\,(aq) \longrightarrow CaF_2\,(s)$$

$CaCl_2 \leftarrow$ soluble

$CaF_2 \leftarrow$ insoluble

$$PbSO_4\,(s) \rightleftharpoons Pb^{2+}\,(aq) + SO_4^{2-}\,(aq)$$

$$K = \frac{[Pb^{2+}][SO_4^{2-}]}{\cancel{[PbSO_4]}}$$

$$K_{sp} = [Pb^{2+}][SO_4^{2-}] \leftarrow \text{solubility product}$$

$$= 2.53 \times 10^{-8}$$

$Q_{sp} \rightarrow$ ion product

If $Q_{sp} < K_{sp}$ more can dissolve

If $Q_{sp} > K_{sp}$ precipitation

If $Q_{sp} = K_{sp}$ saturated

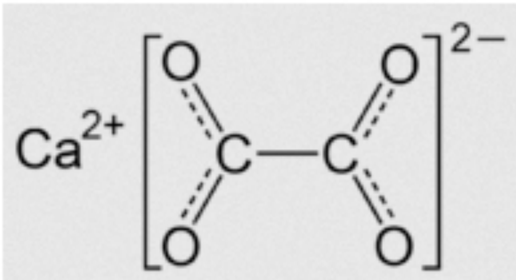
$$A_pB_q\,(s) \rightleftharpoons P\,A^{x+}\,(aq) \quad + \quad Q\,B^{y-}\,(aq)$$

$$K_{sp} = [A^{x+}]^P\,[B^{y-}]^Q$$

$$CaF_2\,(s) \rightleftharpoons Ca^{2+}\,(aq) \quad + \quad 2\,F^{-}\,(aq)$$

$$K_{sp} = [Ca^{2+}]\,[F^{-}]^2$$

		K_{sp}
Calcium oxalate	CaC_2O_4	2.7×10^{-9}

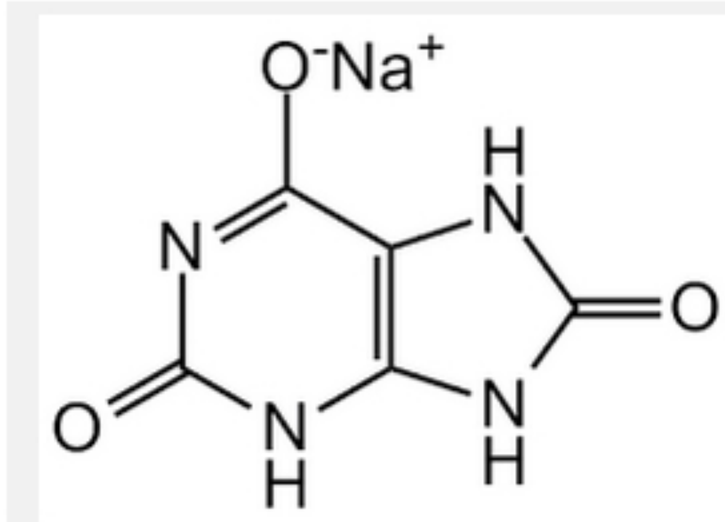


Most common type of kidney stone

Gout is associated with the appearance of crystals of monosodium urate monohydrate (hereafter called sodium urate) in the synovial fluid, causing an inflammatory reaction. There is a good correlation between the incidence of gout and raised serum uric acid concentrations. In particular the occurrence of gout increases rapidly with concentration above the saturation solubility of sodium urate in physiological saline, about 0·4 mmol/l (7 mg/100 ml). Apparently we can view the development of gout as stemming simply from the process of precipitation from a supersaturated solution.

What is the K_{sp} of sodium urate?

(Concentration of physiological saline: 150mM NaCl)



$$K_{sp} = [Na^+][\text{urate}]$$

$$= (1.5 \times 10^{-1})(4 \times 10^{-4})$$

$$= 6 \times 10^{-5}$$

$$PbSO_4\,(s) \rightleftharpoons Pb^{2+}\,(aq) + SO_4^{2-}\,(aq)$$

$$K_{sp} = 2.53 \text{ X } 10^{-8}$$

x^2 type

What is the molar solubility of $PbSO_4$?

at saturation

$[Pb^{2+}][SO_4^{2-}] = 2.5 \times 10^{-8}$

in pure H_2O $[Pb^{2+}] = [SO_4^{2-}]$

call $[Pb^{2+}] = x$

$x^2 = 2.5 \times 10^{-8}$

$x = 1.6 \times 10^{-4}$

1.6×10^{-4} M

What is the molar solubility of $PbSO_4$ in a 0.1 M solution of Na_2SO_4?

at saturation $[SO_4^{2-}] \sim 0.1$

$[Pb^{2+}][0.1] = 2.5 \times 10^{-8}$

$[Pb^{2+}] = 2.5 \times 10^{-7}$ M

2.5×10^{-7} M

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\,F^-(aq)$$

1 liter of saturated CaF_2 solution was evaporated at room temperature, leaving 0.017 g (2.2 X 10^{-4} mol) which was collected as a residue. Calculate the K_{sp} of CaF_2 at room temperature.

at saturation $[Ca^{2+}] = 2.2 \times 10^{-4}$ mol/L

$[F^-] = 4.4 \times 10^{-4}$ mol/L

$$K_{sp} = [Ca^{2+}][F^-]^2$$

$$(2.2 \times 10^{-4})(4.4 \times 10^{-4})^2$$

$$\downarrow$$

$$20 \times 10^{-8}$$

$$\downarrow$$

$$(2 \times 10^{-4})(2 \times 10^{-7}) = 4 \times 10^{-11}$$

$4x^3$
type

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\,F^-(aq)$$

The solubility product of CaF_2 is 3.5 X 10^{-11}, calculate the molar solubility of CaF_2 at room temperature.

$K_{sp} = [Ca^{2+}][F^-]^2 = 3.5 \times 10^{-11}$

call $[Ca^{2+}] = x$

$[F^-] = 2x$

$4x^3 = 3.5 \times 10^{-11}$

$x^3 = 0.9 \times 10^{-11}$

$x^3 = 9 \times 10^{-12}$

$x = 2.1 \times 10^{-4}$

Which is more soluble in water?

Tricky!

$CaCO_3$	$K_{sp} = 4.8 \times 10^{-9}$
✓ Ag_2CO_3	$K_{sp} = 4.8 \times 10^{-12}$

$x^2 = 4.8 \times 10^{-9}$

$x = 7 \times 10^{-5}$

$4x^3 = 4.8 \times 10^{-12}$

$= 1 \times 10^{-4}$

Which precipitates first when concentrated Na_2CO_3 is added to a solution 0.1M for both Ca^{2+} and Ag^{+}?

$(0.1)[CO_3^{2-}] = 4.8 \times 10^{-9}$

$[CO_3^{2-}] = 4.8 \times 10^{-8}$

✓

$(0.1)^2[CO_3^{2-}] = 4.8 \times 10^{-12}$

$[CO_3^{2-}] = 4.8 \times 10^{-10}$

MCAT like

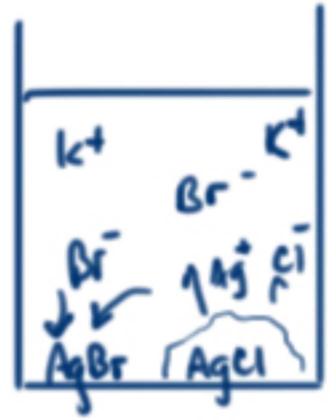
The solubility product constants of AgCl, AgBr, and AgI are, respectively, 1.7×10^{-10}, 4.1×10^{-13}, and 1.5×10^{-16}. If a concentrated solution containing KBr is stirred with solid AgCl

A. silver will be oxidized

B. AgCl will dissolve and solid AgBr will precipitate

C. no reaction will occur

D. silver will be reduced



Add ammonia (imagine the problem had Zn^{2+})

the $ZnBr_2$ all dissolved and the solution turned purple

+2

complex ion

$$AgCl \rightleftharpoons Ag^+ + Cl^-$$

$$Ag^+ + Br^- \rightleftharpoons AgBr$$

$$AgCl + Br^- \longrightarrow AgBr + Cl^-$$

Metathesis reaction toward the least soluble

The K_{sp} of FeS is 8 X 10^{-19}. The K_{sp} of PbS is 3 X 10^{-28}. In a solution containing 0.1 mM concentrations of both Fe^{2+} and Pb^{2+}, which will precipitate first upon dropwise addition of 0.01mM Na_2S?

What is the lowest concentration of Pb^{2+} obtainable before FeS begins to precipitate?

When the anion is a weak base. !

$$MgF_2\,(s) \rightleftharpoons Mg^{2+}\,(aq) + 2\,F^-\,(aq)$$

$$H^+\,(aq) + F^-\,(aq) \rightleftharpoons HF\,(aq)$$

How will lowering pH affect the solubility of MgF_2?

Often the problem involves carbonate

$$CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-}$$

$CO_3^{2-} + H^+ \rightleftharpoons HCO_3^-$ ← bicarbonate

$HCO_3^- + H^+ \rightleftharpoons H_2CO_3$ ← carbonic acid

remember $H_2CO_3 \rightleftharpoons H_2O + CO_2$

Many hydroxide salts are insoluble.

What effect will ~~changing~~ lowering pH have on Lead(II) solubility ?

$$Pb(OH)_2 \quad K_{sp} = 1.4 \times 10^{-20}$$

More could dissolve.

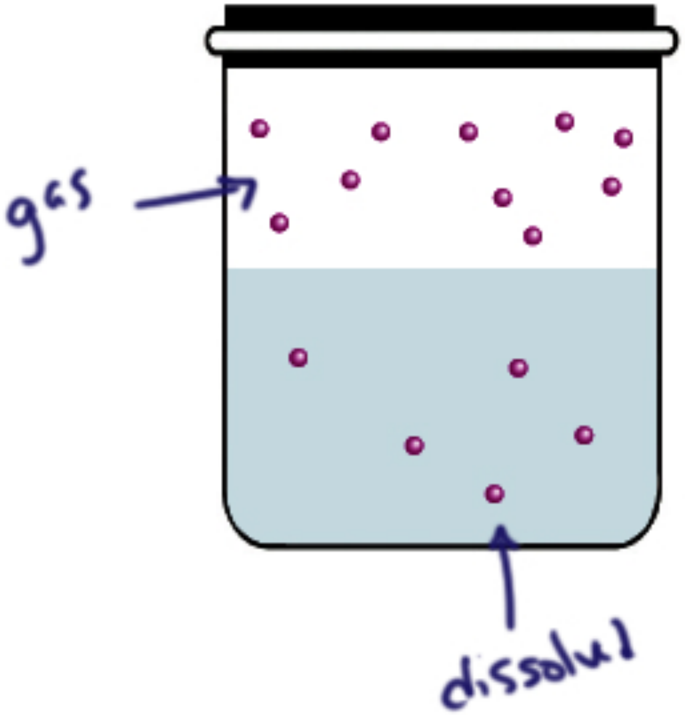
$$H^+ + \underset{\substack{\uparrow \\ \text{lowering } OH^-}}{OH^-} \rightleftharpoons H_2O$$

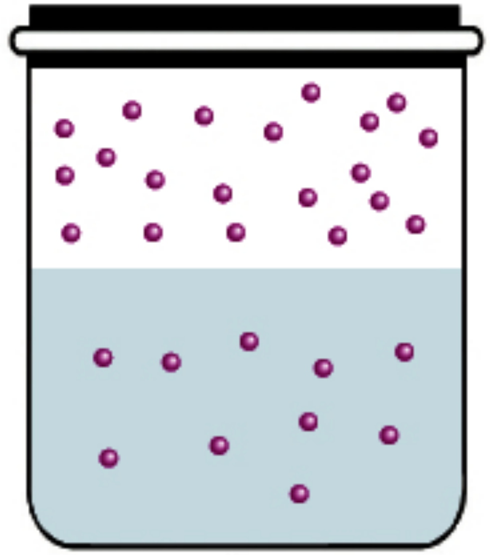
Henry's Law

$$C_A = k\,p_A$$

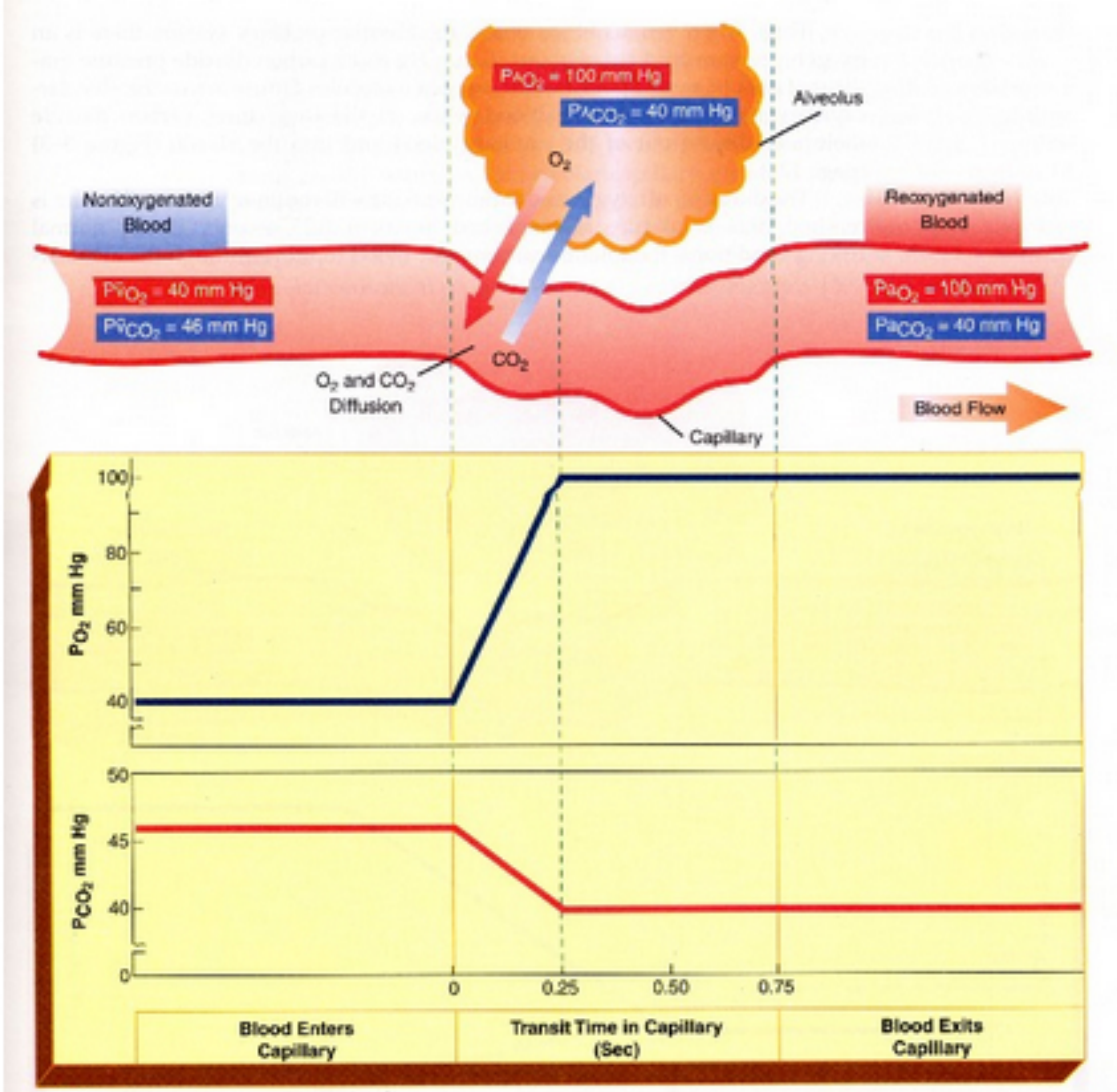
C_A: concentration

p_A: partial pressure of gas





In blood - concentrations of O_2 and CO_2 are referenced by Henry's Law equilibrium pressure.



PAO2 = 100 mm Hg
PACO2 = 40 mm Hg
Alveolus
O2
Nonoxygenated Blood
Reoxygenated Blood
Pv̄O2 = 40 mm Hg
Pv̄CO2 = 46 mm Hg
PaO2 = 100 mm Hg
PaCO2 = 40 mm Hg
CO2
O2 and CO2 Diffusion
Capillary
Blood Flow
PO2 mm Hg
100
80
60
40
PCO2 mm Hg
50
45
40
0
0
0.25
0.50
0.75
Blood Enters Capillary
Transit Time in Capillary (Sec)
Blood Exits Capillary

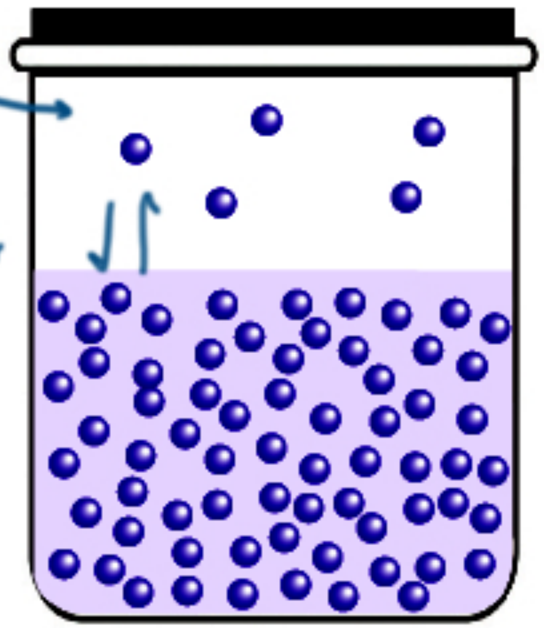
Rault's Law

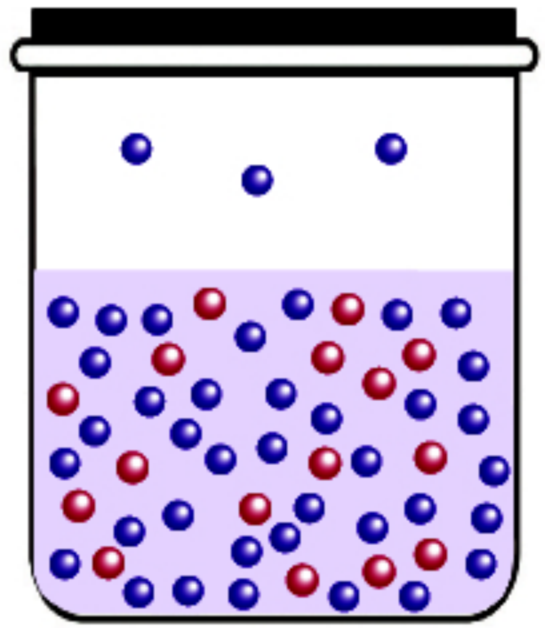
$$p_A = X_A p_A^o$$

mole fraction of solvent

vapor pressure p_A^o

pure solvent

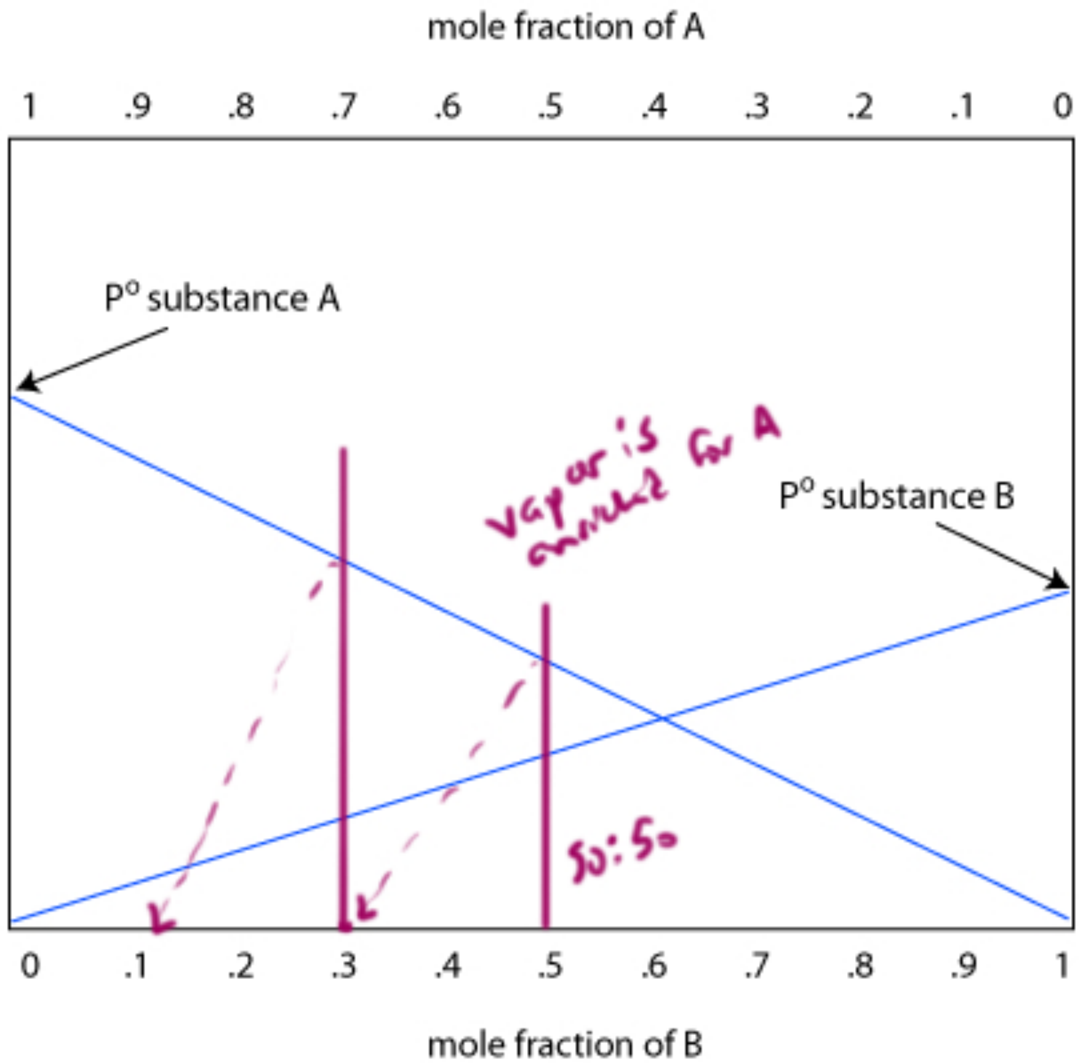




Ideal solutions obey Rault's Law.

An ideal solution

Distillation



If the solution is not ideal - may form an azeotrope. (constant boiling mixture)

vapor has the same composition as the mixture.

Colligative
Properties

Freezing Point Depression and Boiling Point Elevation

Use 2 for NaCl

molality

FP depression

$$\Delta T_{FP} = k_f\,(i)\;m$$

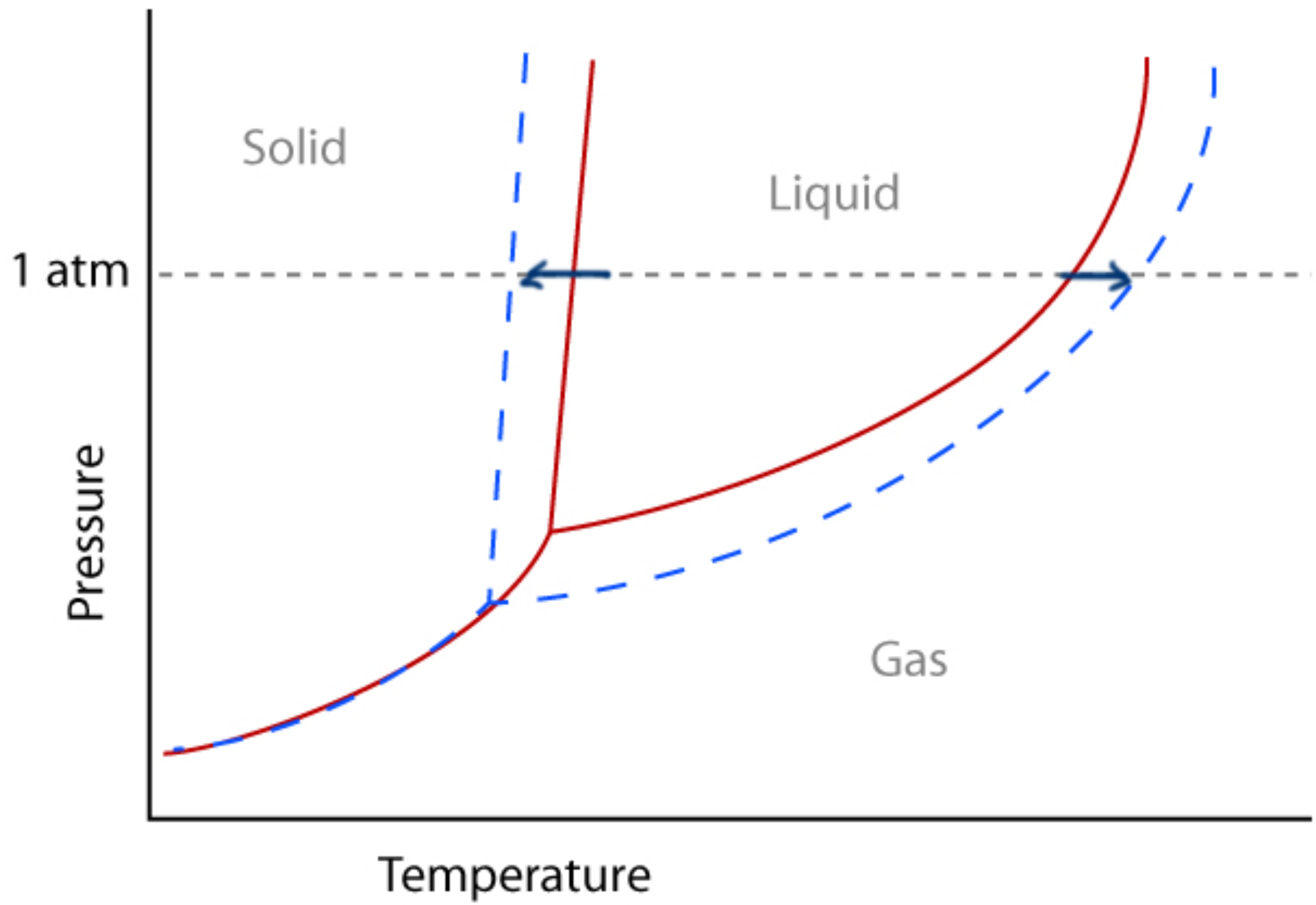
$\frac{\text{mol}}{\text{kg solvent}}$

BP elevation

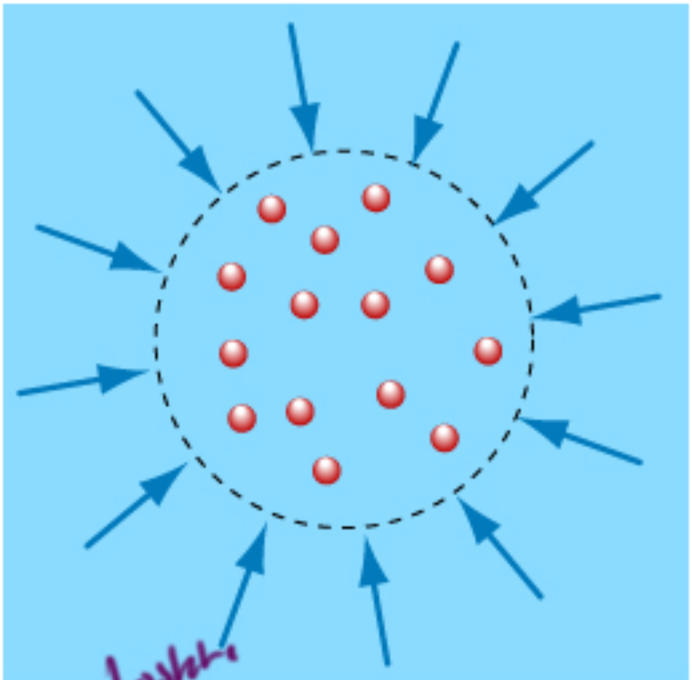
$$\Delta T_{BP} = k_b\,(i)\;m$$

For water, $k_f = -1.85\ \mathrm{K\ L^{-1}\ mol^{-1}}$

For water, $k_b = 0.51\ \mathrm{K\ L^{-1}\ mol^{-1}}$


Solid
Liquid
1 atm
Pressure
Gas
Temperature

The osmotic pressure Π in a solution of volume V liters containing n moles of solvent is given by the *van't Hoff* equation:



$$\Pi V = nRT$$