11 Properties of solutions

臺灣大學化學系 NTU CHEMISTRY

※ Concentration

Molarity (*M*; 體積莫耳濃度)

➪ mol/L (mol of solute/volume of solution)

Mole fraction (莫耳分率)

➪mole fraction of **A** = $n_A/n_T = X_A$

(n_A：mole of **A**; n_T：mole of total)

Molality (*m*; 重量莫耳濃度)

➪ mol/Kg (mole of solute/weight of solvent)

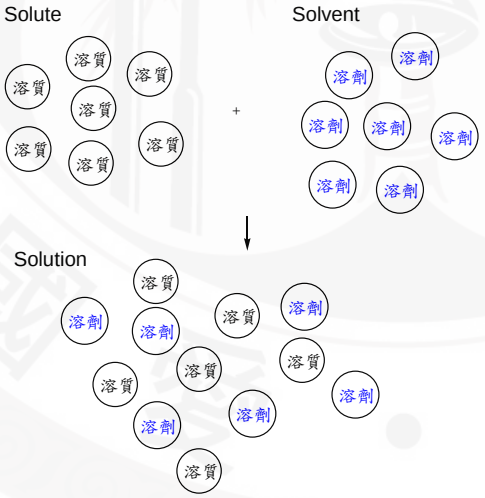
Mass percent or weight percent (重量百分濃度)

➪ mass percent of **A** = $(W_A/W_T) \times 100\%$

(W_A：weight of **A**; W_T：total weight)

臺灣大學化學系 NTU CHEMISTRY

※ The energies of solution formation



sloute-solute

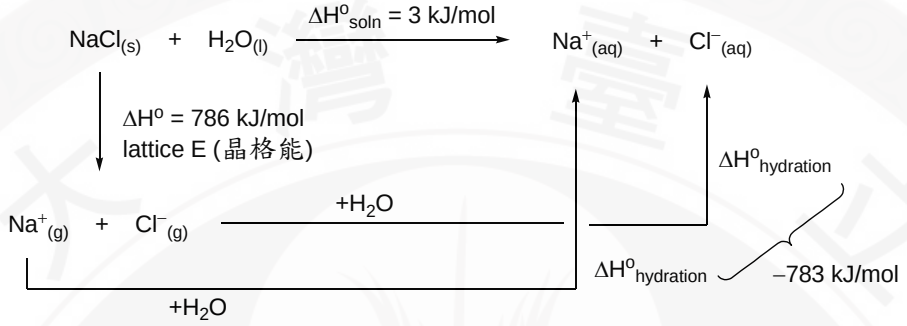
solvent-solvent

⬇

solute-solvent

Solvation E involved
(溶劑合)

Ex.



Free energy determines the direction:

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

↑ usually positive

Conclusion

solubility is difficult to predict

General rule

like dissolves like

polar compound dissolves in polar compound

nonpolar compound dissolves in nonpolar compound

※ Factors affecting solubility

◎ Structure effects

◎ Pressure effects

Little effects on *s* and *l*

For gas:

Governed by Henry's law $C = kP$

A constant

Concentration in M

Partial pressure

Obeyed most accurately under
- dilute condition
- solute does not dissociate
- solute does not react with solvent

◎ Temperature effects

Difficult to predict

Usually decreases for gas (negative ΔH, negative ΔS)

Ex. $CO_3^{2-}(aq) + CO_2(aq) + H_2O(l) \leftrightarrows 2HCO_3^-(aq)$

In hard water: $Ca(HCO_3)_2$ soluble
$CaCO_3$ insoluble

T ↑ → $[CO_2(aq)]$ ↓

⇨ equlibrium ←
⇨ $CO_3^{2-}(aq)$ ↑
⇨ $CaCO_3(s)$ ↓

※ The vapor pressures of solutions

◎ Raoult's law (拉午耳定律)

For a nonvolatile solute

$P_{soln} = X_{solv}P^{o}_{solv}$

P_{soln}: vapor pressure of the soln

X_{solv}: the mole fraction of solv

P^{o}_{solv}: vapor pressure of the pure solv

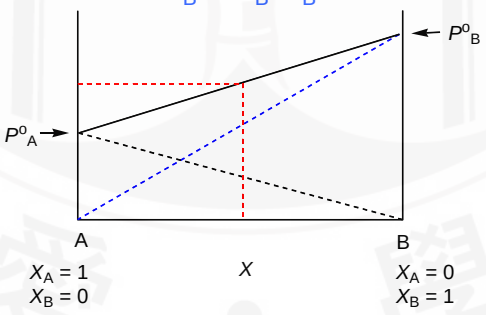
A model:

◎ When solute is also volatile

For ideal solution: follows Raoult's law

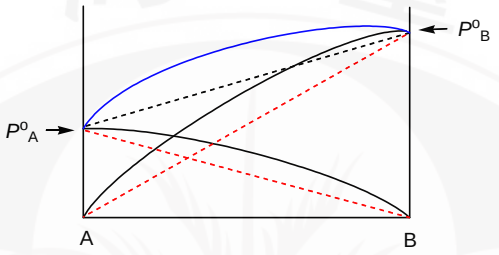
$P_A = X_A P^{o}_A$

$P_B = X_B P^{o}_B$

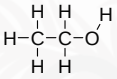


◎ Nonideal solutions

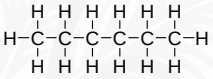
▸ With positive deviation
weak solute-solvent interactions



Ex.

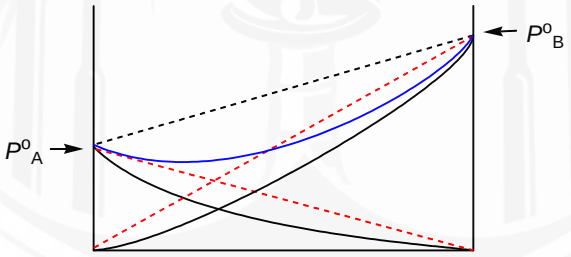


ethanol

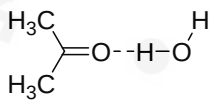


hexane

▸ Negative deviation
strong solute-solvent interactions



Ex.

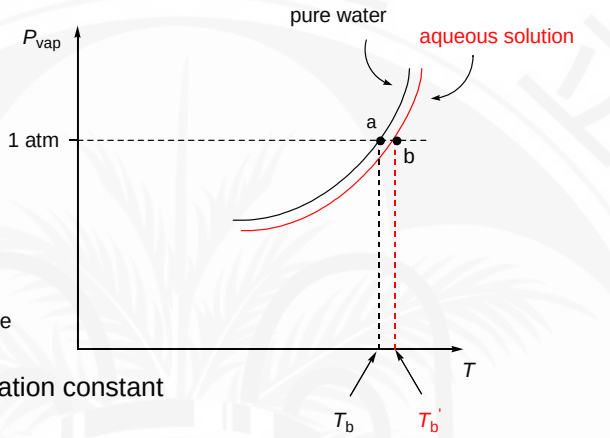


acetone

※ Boiling-point elevation and freezing-point depression

▸ Boiling-point elevation

Ex. Aqueous solution of a nonvolatile solute

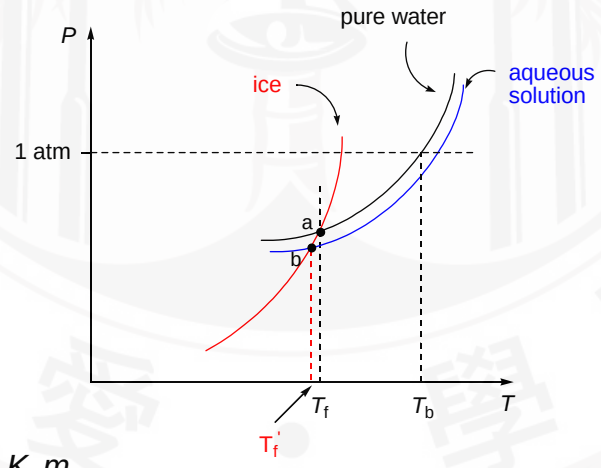


$\Delta T_b = T_b' - T_b$

$\Delta T_b = K_b\, m_{solute}$

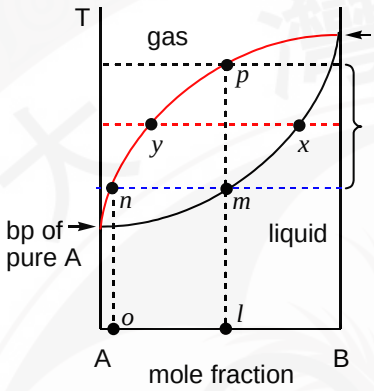
molal boiling-point elevation constant

▸ Freezing-point depression



$\Delta T_m = K_f\, m_{solute}$

※ Distillation of a mixture



下方為液態
上方為氣態
兩個弧線中間是氣態與液態平衡共存的區域

*l*點的液體加熱在*m*點開始沸騰
一直到*p*點才完全氣化

*m*點的液體與*n*點的氣體平衡共存
*n*點的氣體含有較多低沸點的A

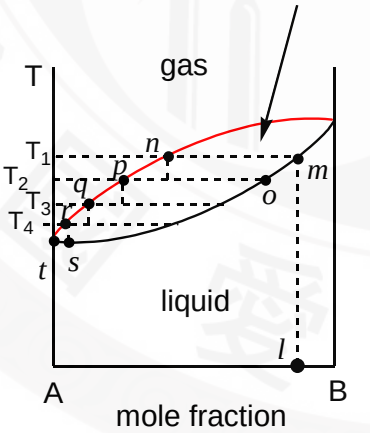
*m*點到*p*點都是氣態與液態平衡的狀態
隨著溫度的不同氣態與液態的成分會有所不同

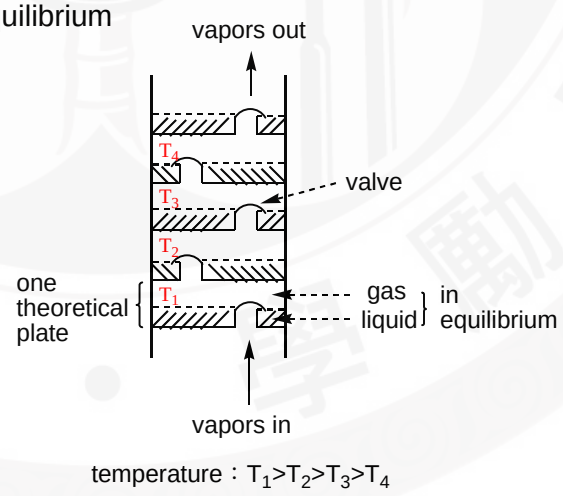
一個純的物質具有單一的沸點;一個混合物具有一個沸點的範圍

※ Fractional distillation

Distilled through a fractionating column

gas and liquid in equilibrium

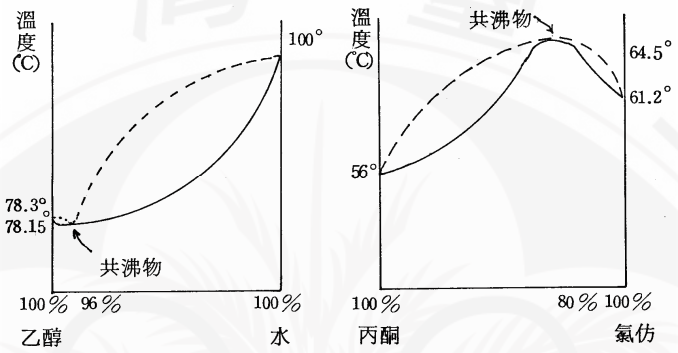




temperature：$T_1>T_2>T_3>T_4$

◎ Azeotropes (共沸物)

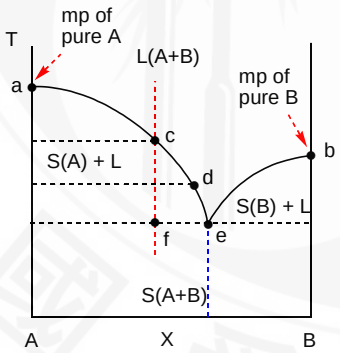
A minimum or maximum
in the boiling point-composition diagram



Can not be separated by ordinary distillation process

臺灣大學化學系 NTU CHEMISTRY

※ Solid mixtures



純物質具有單一的熔點
混合物具有一個熔點的範圍

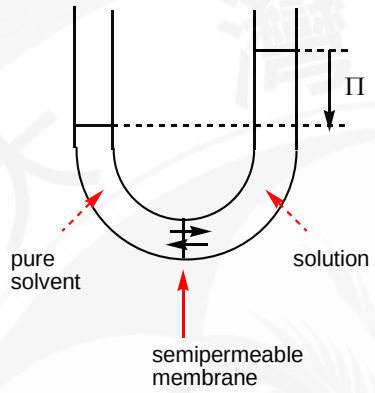
沿紅線由上而下
到達c點時固體A開始產生

溫度繼續下降時更多的A結晶出來
留在液體的部分含B的量就增加
因此隨著溫度的下降
液體的成分沿著c-d-e的弧線下降

待溫度降至f 點時B固體也開始結晶出來，

在f-e 的水平線下是固體
c-f 之間是固體與液體共存的平衡區(此混合物的熔點範圍)
e點的組成具有單一的熔點，稱為共熔點(eutectic point)

※ Osmotic pressure



$\Pi = MRT$
(M: molarity; T in K)

A good way to determine MW

Ex. 1.00×10^{-3} g of a protein in 1.00 mL water
Π = 1.12 torr, at 25.0 °C

Ans

$$\Pi = \frac{1.12 \text{ torr}}{760 \text{ torr/atm}}$$
$$= 1.47 \times 10^{-3} \text{ atm}$$
$$= M(0.08206)(25.0 + 273)$$

Isotonic solutions (等滲壓溶液):
having identical Π

※ The colligative properties (依數性)

P_{vap}
ΔT_b
ΔT_b
Π
} Depend on concentration only: colligative property

✓ Electrolyte solution
may not dissociate completely
forms ion pair

$$\text{van't Hoff factor } i = \frac{\text{moles of particles in soln}}{\text{moles of solute dissolved}}$$

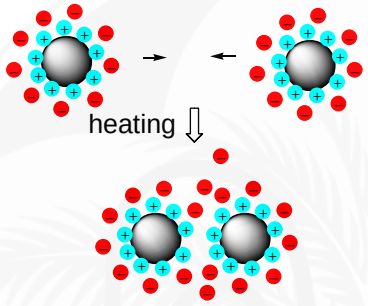
Ex. 0.10 *m* NaCl(*aq*) → i = 1.87 (from experiment)

$\Delta T = imK$ $\Pi = iMRT$

※ Colloids (膠體)

A suspension of tiny particles in a medium
(1-1000 nm)

Tyndall effect
light scattering by these particles



Major stabilizing factor:
electrostatic repulsion

To destroy:
- heating
- add electrolytes
  (neutralize the charge)
- discharge through electrodes

Examples of colloids			Type
Fog	liq	in gas	aerosol (氣溶膠；霧劑)
Smoke	s	in gas	aerosol
Whipped cream	g	in liq	foam
Milk	liq	in liq	emulsion
Paint, gel	s	in liq	sol
Polystyrene foam	g	in solid	foam
Cheese	liq	in solid	emulsion
Ruby glass	s	in solid	sol