Topic 5C. Phase Equilibria in Two-Component Systems

5C.1 The Vapor Pressure of Mixtures

5C.2 Binary Liquid Mixtures

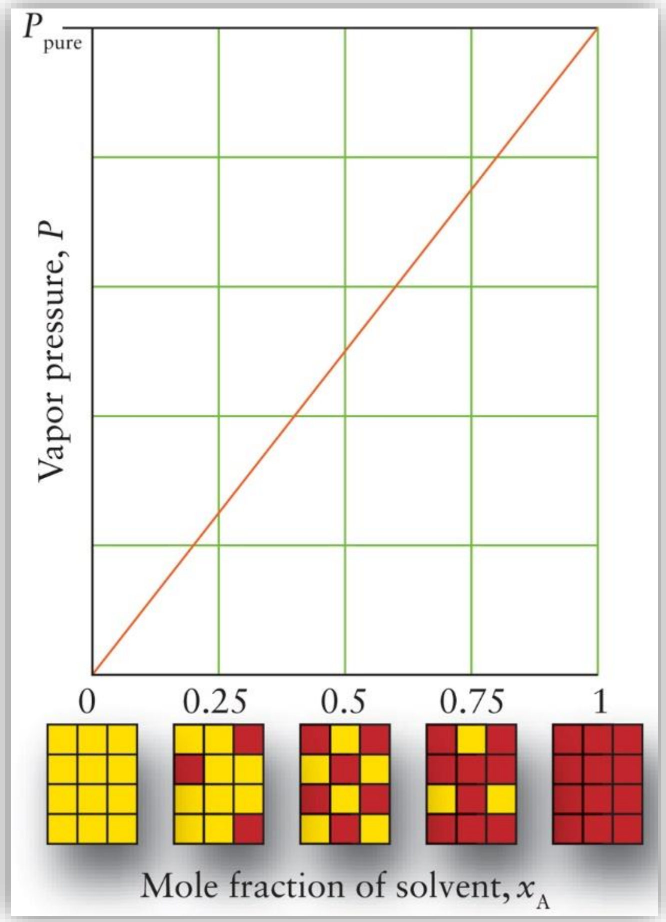
5C.3 Distillation

5C.4 Azeotropes

Vapor Pressure of Mixture

- Raoult's Law: The vapor pressure of a liquid is proportional to its mole fraction.

$$P_A = \frac{n_A}{n_A + n_B} P_A^* = x_A P_A^*$$



Vapor Pressure of Mixture

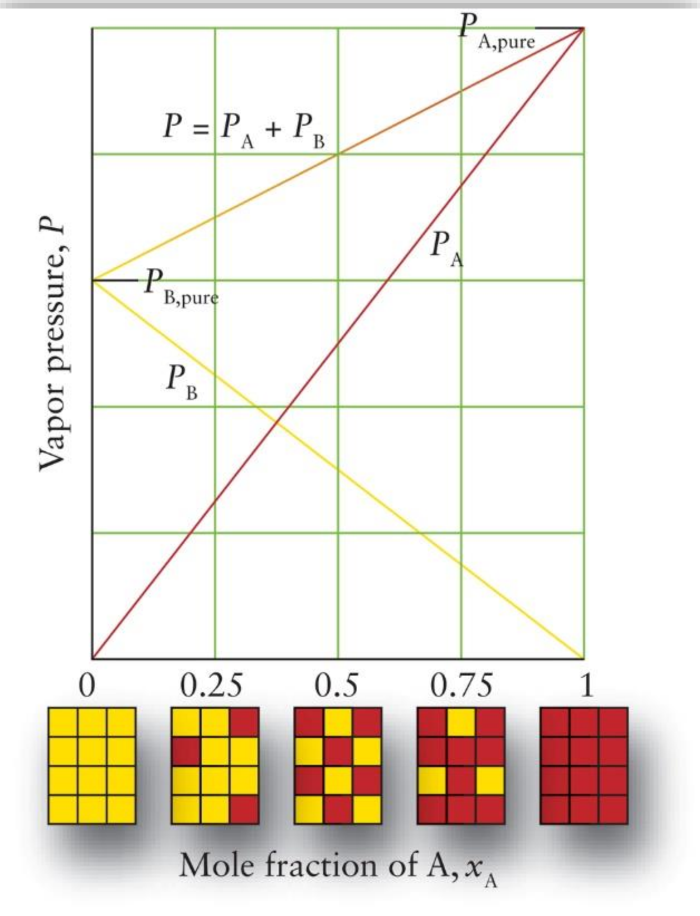
- Raoult's Law: the vapor pressure of a liquid is proportional to its mole fraction.

$$P_A = \frac{n_A}{n_A + n_B} P_A^* = x_A P_A^*$$

$$P_B = \frac{n_B}{n_A + n_B} P_B^* = x_B P_B^*$$

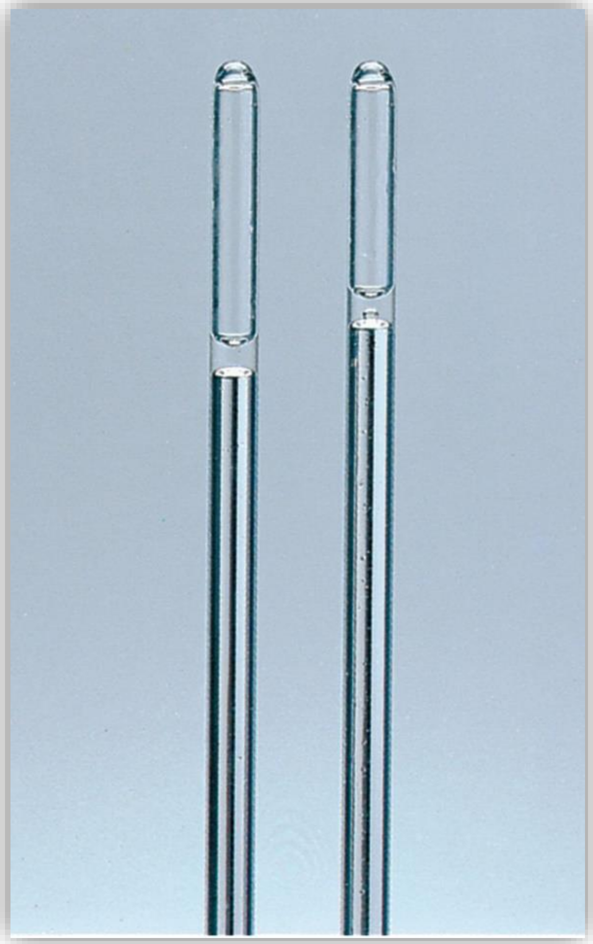
$$P_{TOT} = x_A P_A^* + x_B P_B^* = x_A P_A^* + (1 - x_A) P_B^*$$

- Ideal solution: a hypothetical mixture in which both volatile components obey Raoult's law.
  → A–A, B–B, and A–B interactions are the same.



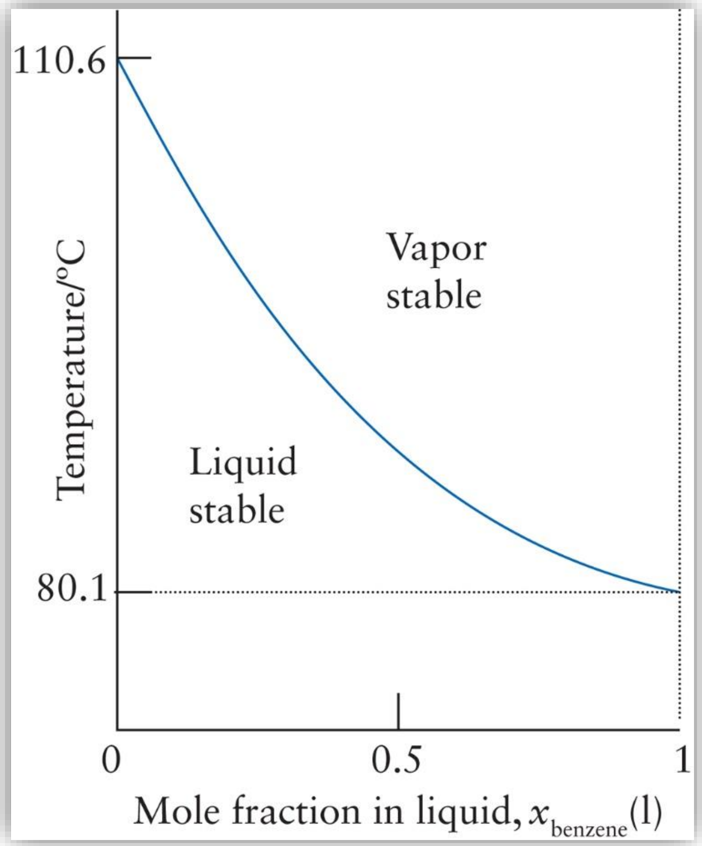
Vapor Pressure of Mixture

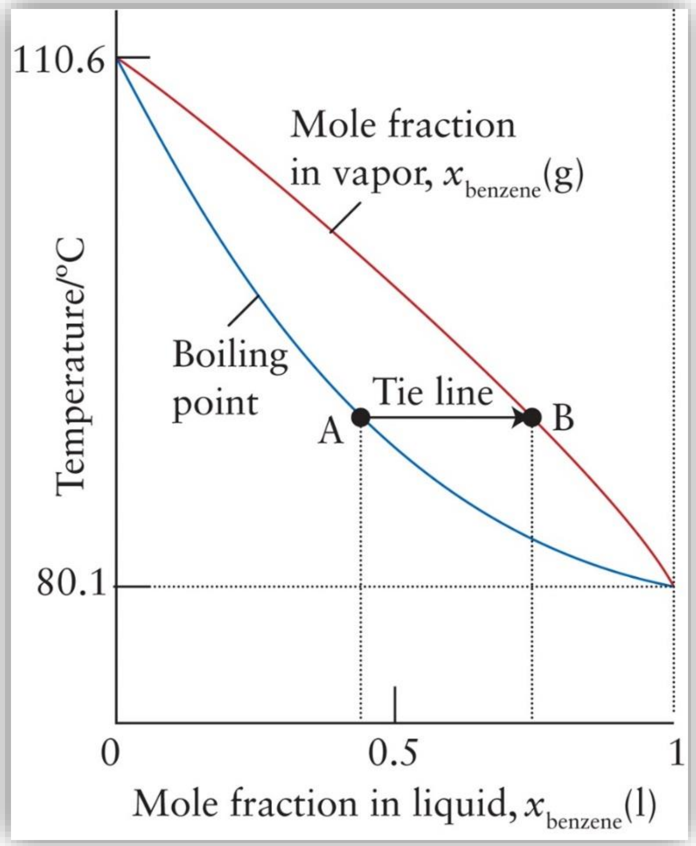
- Difference in vapor pressure in the absence and presence of a solute.



Binary Liquid Mixtures

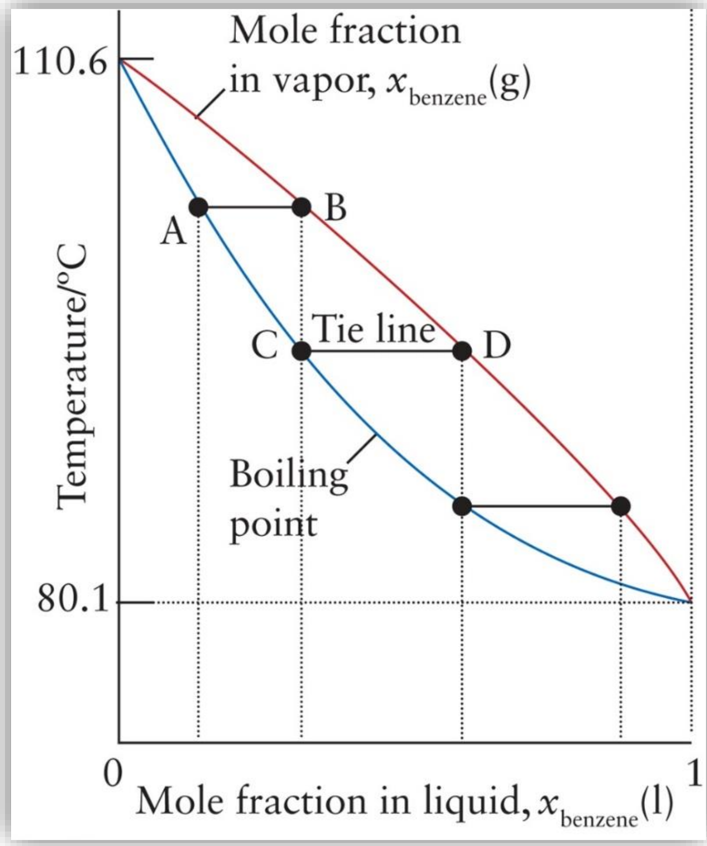
- Phase diagram of a mixture of benzene and toluene

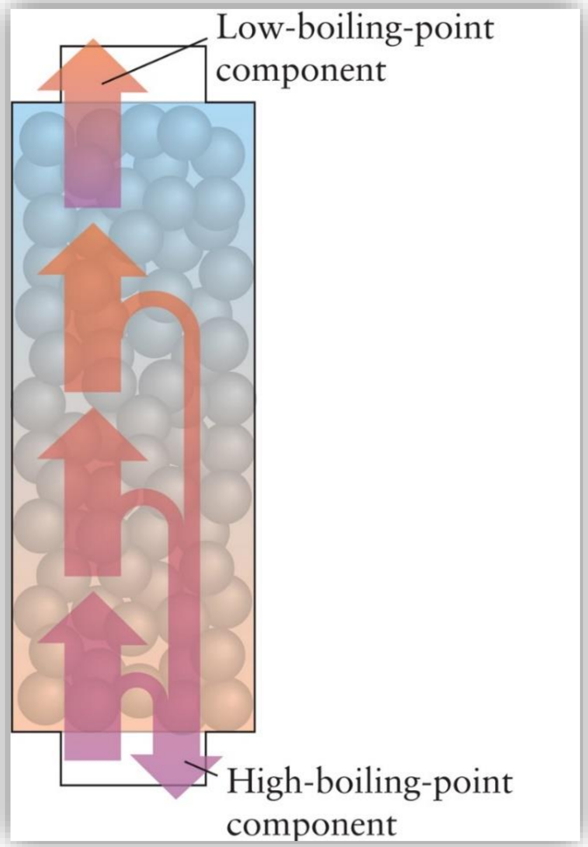




Distillation

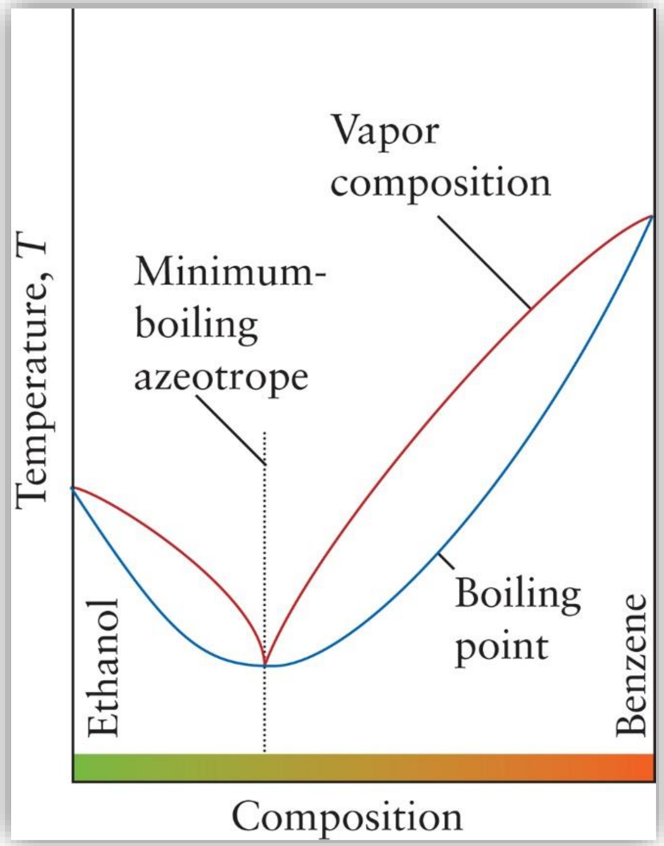
- Distillation
- Fractional distillation

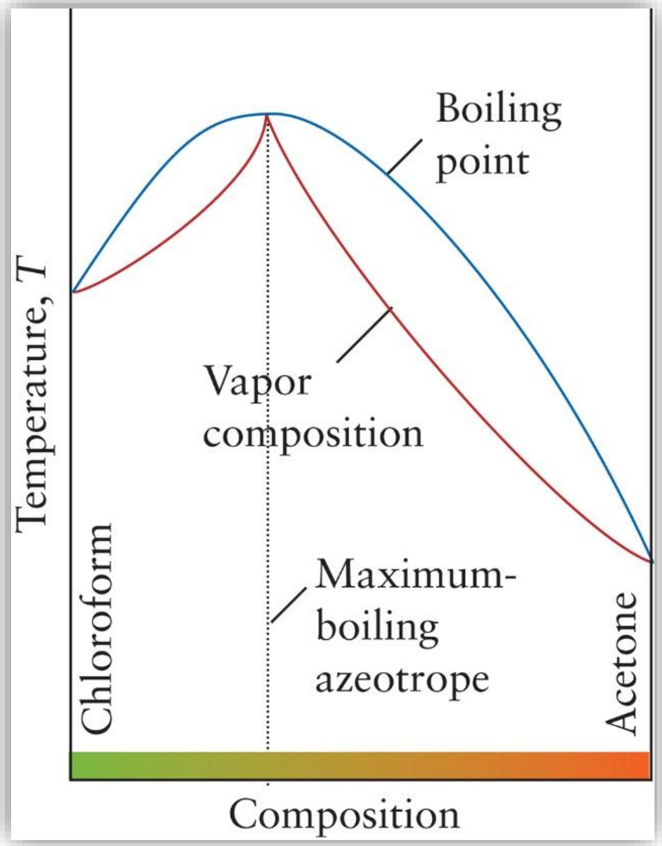




Azeotropes

- Enthalpy of mixing leads to a deviation from Raoult's law.
- Azeotropes





Topic 5D. Solubility

5D.1 The Limits of Solubility

5D.2 The Like-Dissolves-Like Rule

5D.3 Pressure and Gas Solubility

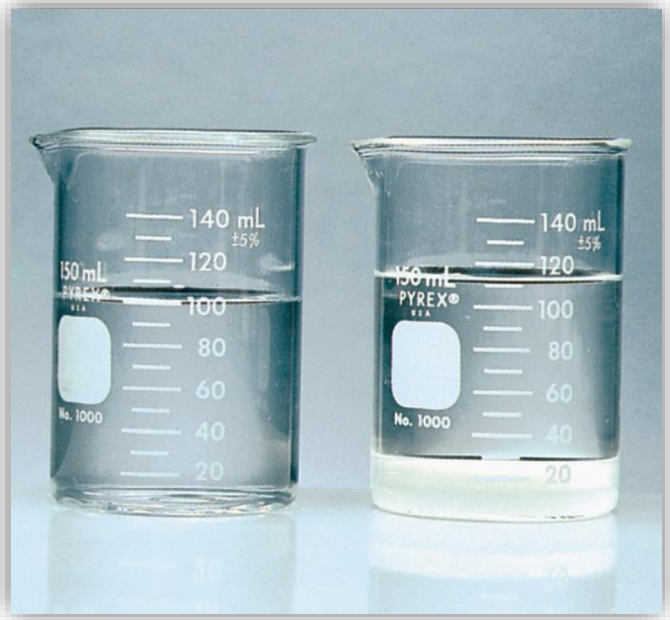
5D.4 Temperature and Solubility

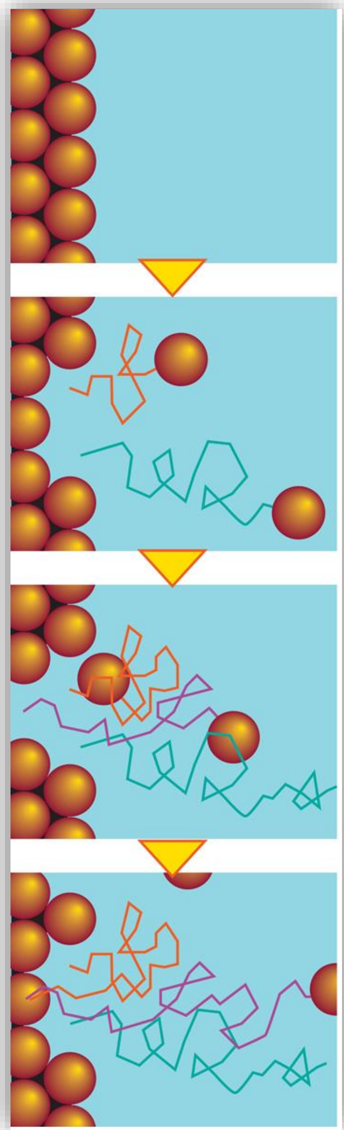
5D.5 The Thermodynamics of Dissolving

5D.6 Colloids

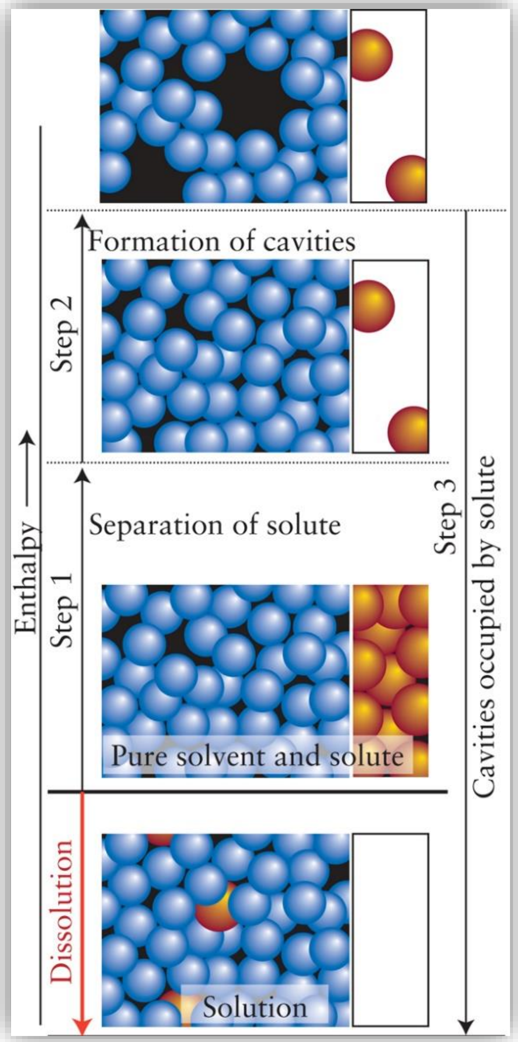
Limits of Solubility

- Molar solubility: substance's molar concentration in a saturated solution; the limit of its ability to dissolve in a given quantity of solvent.
- Dynamic equilibrium of solute in a saturation solution.

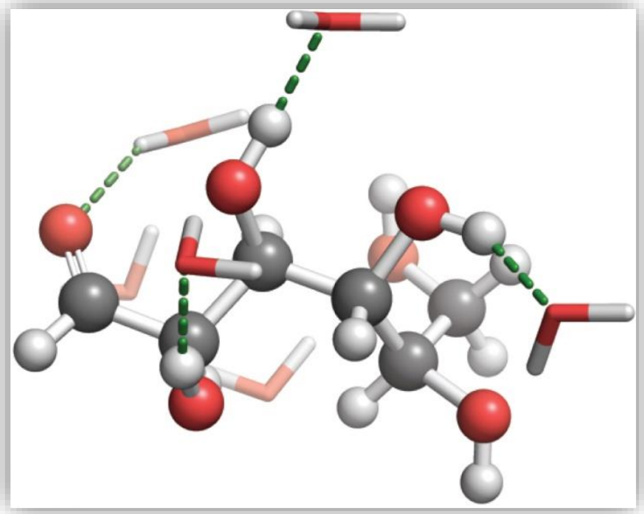




Dissolution Process

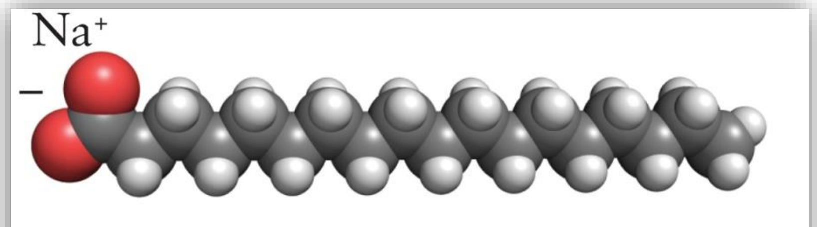


- For a dissolution process takes place
  → Solute–solute attraction must be replaced by solute–solvent attractions.

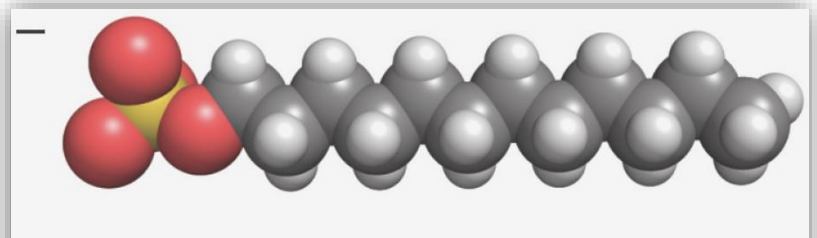


Like-Dissolves-Like Rule

- "Like-dissolves-like" rule
  - Polar liquids are good solvents for ionic or polar solutes.
  - Nonpolar liquids are good solvents for nonpolar solutes.
- Soap and surfactant: amphiphilic character

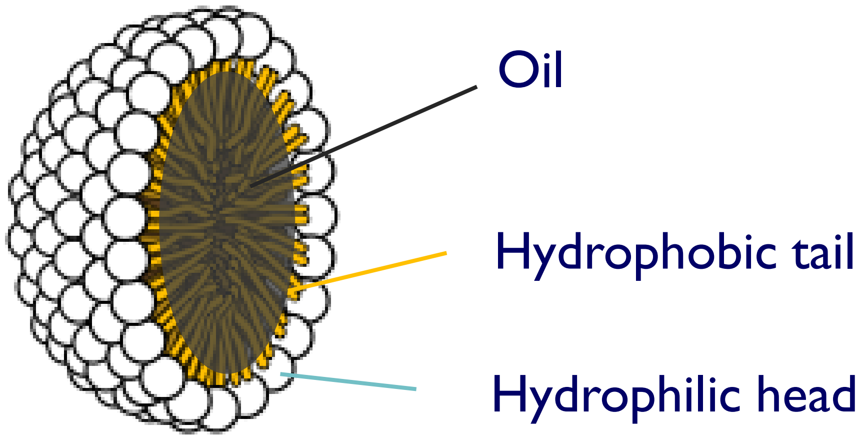


1 Sodium stearate, $NaCH_3(CH_2)_{16}CO_2$



2 A typical surfactant ion

Micelle structure



Pressure and Gas Solubility

- Henry's Law: $s = k_H P$

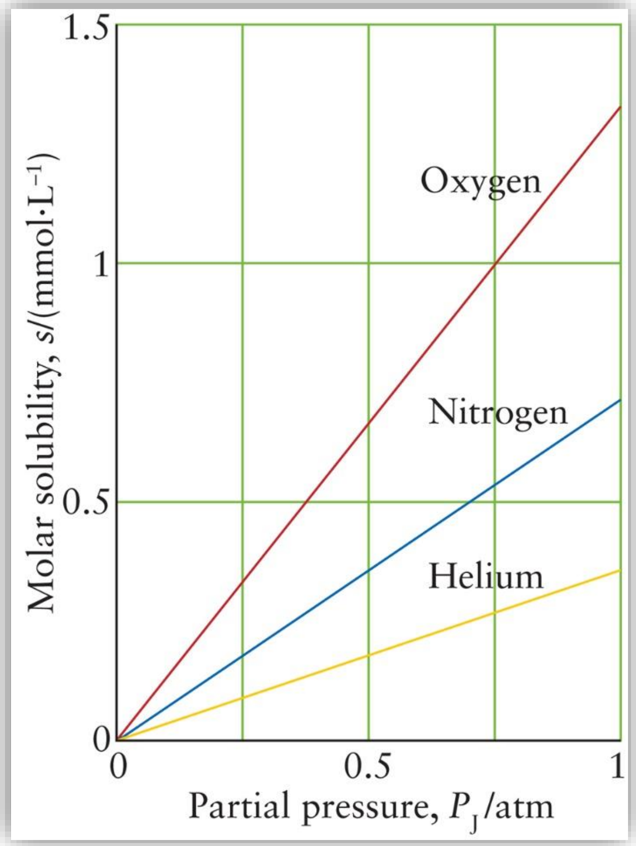
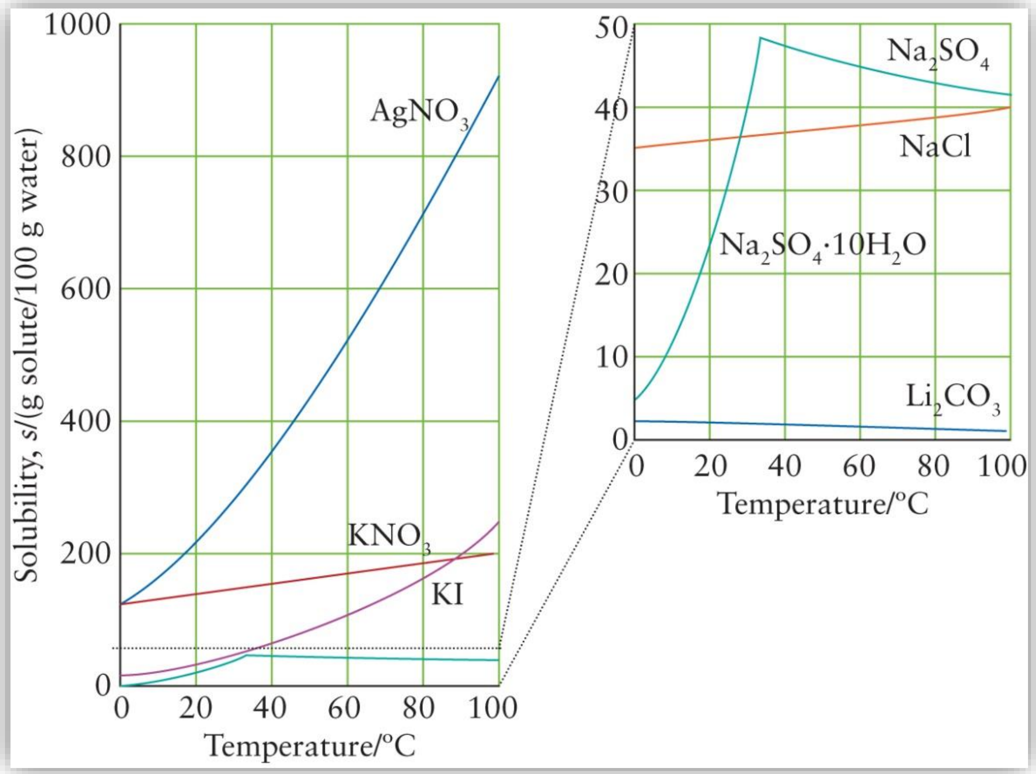


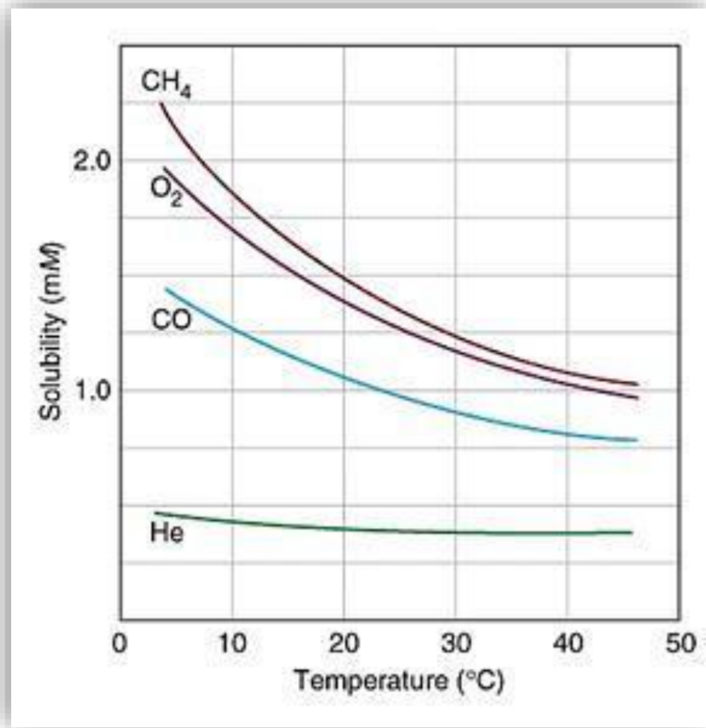
TABLE 5D.2 Henry's Constants for Gases in Water at 20 °C

Gas	$k_H/(\text{mol}\cdot\text{L}^{-1}\cdot\text{atm}^{-1})$
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}

Temperature and Solubility

- Solubility of a solid: endothermic; generally, increases with temperature
- Solubility of a gas: exothermic; generally, decreases with temperature
- Many exceptions exist





Thermodynamics of Dissolving

- A simple thermodynamic approach
- Gibbs Free Energy of solution

  $$\Delta G_{sol} = \Delta H_{sol} - T\Delta S_{sol}$$

- For liquid or solid solutes, $\Delta S_{sol} > 0$

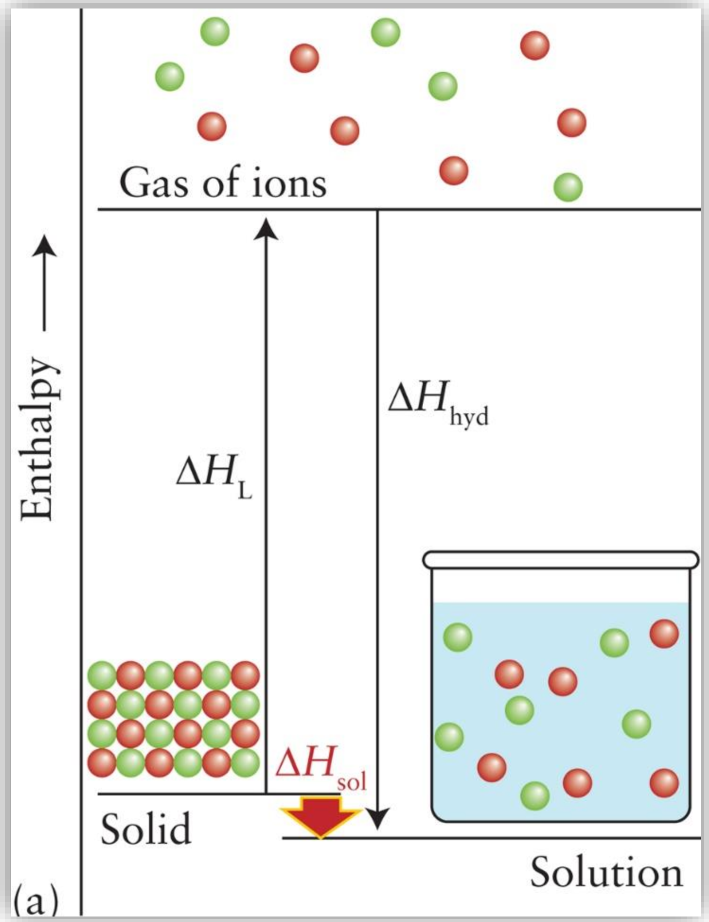
  $\Delta H_{sol} < 0 \rightarrow$ generally soluble

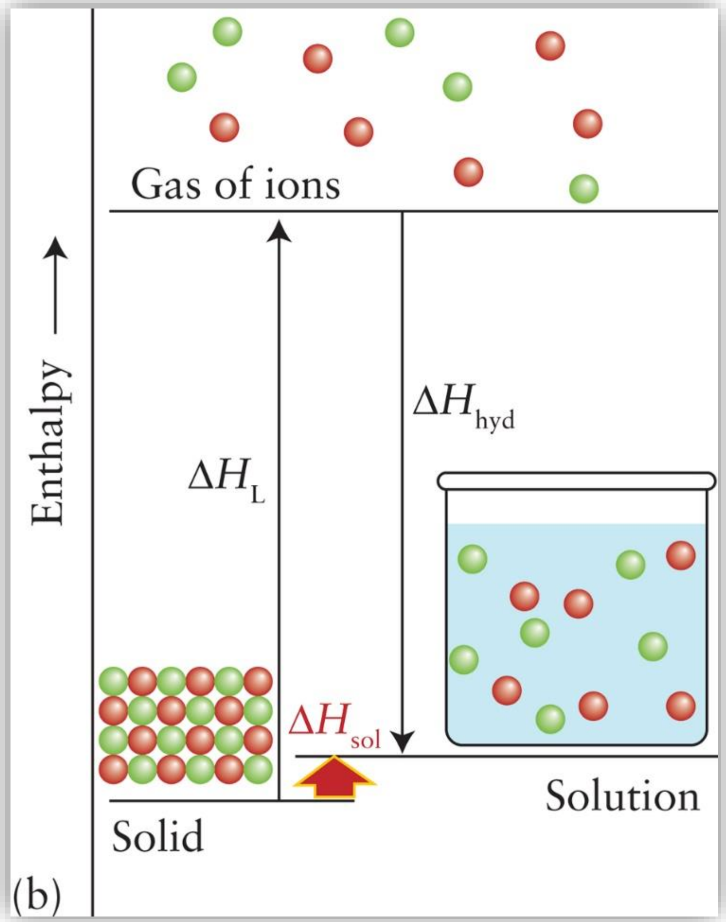
  $\Delta H_{sol} > 0 \rightarrow$ soluble with highly positive ΔS_{sol}

- For gaseous solutes, $\Delta S_{sol} < 0$

  ΔG_{sol} increases with T

Thermodynamics of Dissolving





Thermodynamics of Dissolving

TABLE 5D.3 Limiting Enthalpies of Solution, $\Delta H_{sol}/(kJ\cdot mol^{-1})$, at 25 °C*

	Anion							
Cation	**fluoride**	**chloride**	**bromide**	**iodide**	**hydroxide**	**carbonate**	**sulfate**	**nitrate**
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

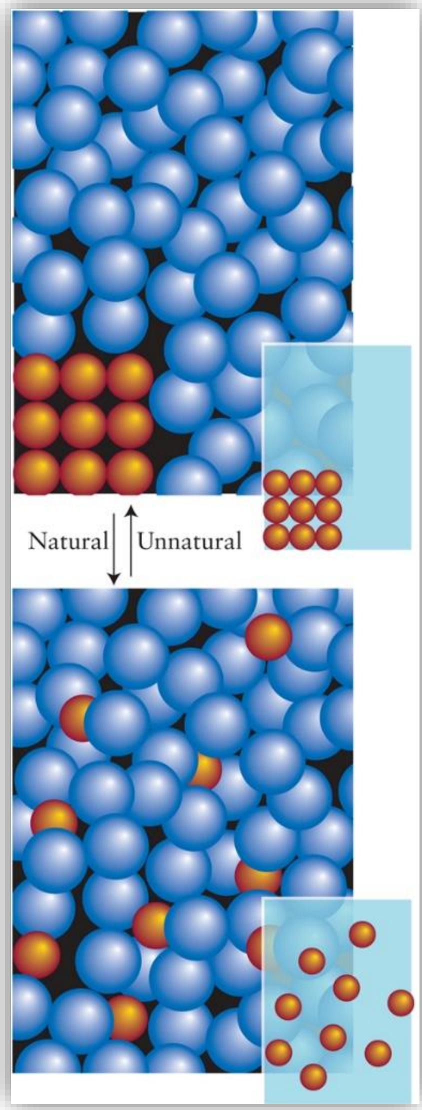
*The limiting enthalpy of solution value for silver iodide, ΔH_{sol}, for example, is the entry found where the row labeled "silver" intersects the column labeled "iodide," and it is +112.2 $kJ\cdot mol^{-1}$.

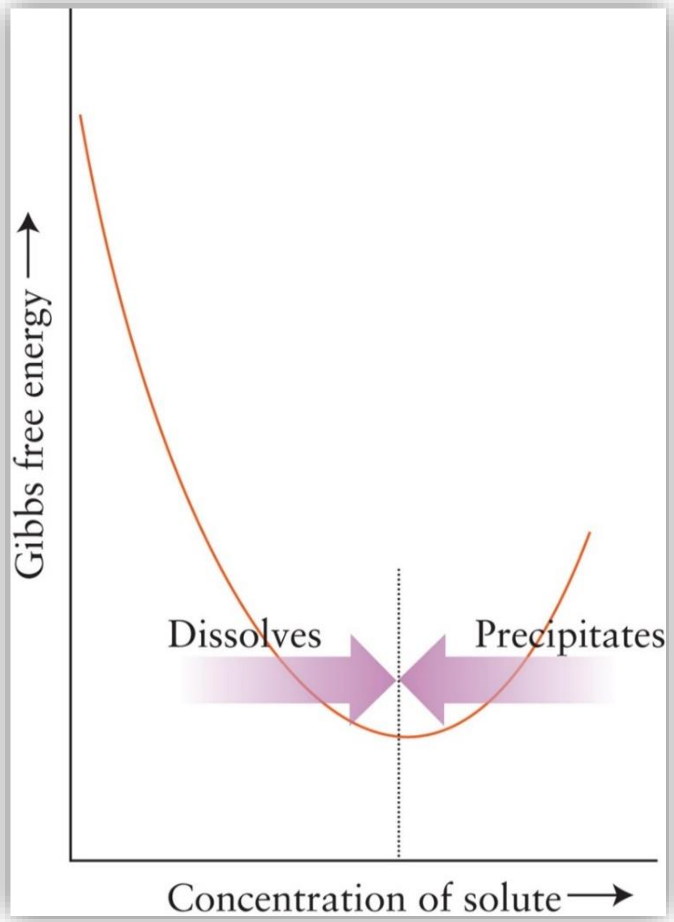
TABLE 5D.4 Limiting Enthalpies of Hydration, $\Delta H_{hyd}/(kJ\cdot mol^{-1})$, at 25 °C, of Some Halides*

	Anion			
Cation	F^-	Cl^-	Br^-	I^-
H^+	−1613	−1470	−1439	−1426
Li^+	−1041	−898	−867	−854
Na^+	−927	−784	−753	−740
K^+	−844	−701	−670	−657
Ag^+	−993	−850	−819	−806
Ca^{2+}	—	−2337	—	—

*The enthalpy of hydration for NaCl, ΔH_{hyd} for example, is the entry where the row labeled Na^+ intersects the column labeled Cl^-. The resulting value, −784 $kJ\cdot mol^{-1}$, is for the process $Na^+(g) + Cl^-(g) \rightarrow Na^+(aq) + Cl^-(aq)$ when the resulting solution is very dilute.

Thermodynamics of Dissolving





Colloids

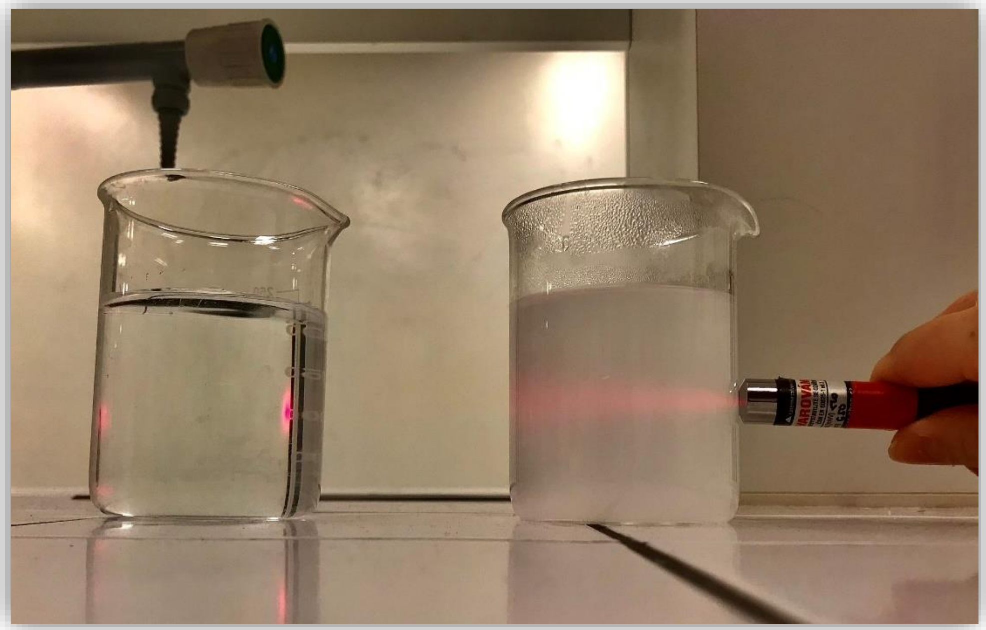
- Colloid: a dispersion of large particles from 1 nm to 1 μm
→ Properties between homogeneous solution and heterogeneous mixture

TABLE 5D.5 The Classification of Colloids*

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).

Colloids



https://en.wikipedia.org/wiki/Tyndall_effect