

Topic 5D - Solubility

Solutions

Dissolution Process

Competing Interactions:

Solute-solute (= 0 for Gases)
Solvent-solvent
Solute-solvent (must be sufficiently favorable for dissolution to occur)

Saturation Equilibrium

Rate of Dissolution = Rate of Precipitation
Limiting solubility

Effect of Pressure

Negligible for solid and liquid solutes
Important for gaseous solutes

Henry's Law: **Solubility = $k_H P$**

Effect of Temperature

Rate of dissolution increases with increasing temp., but saturation solubility does not necessarily increase with increasing temp.

Saturation solubility of gaseous solutes always decreases with increasing temp.

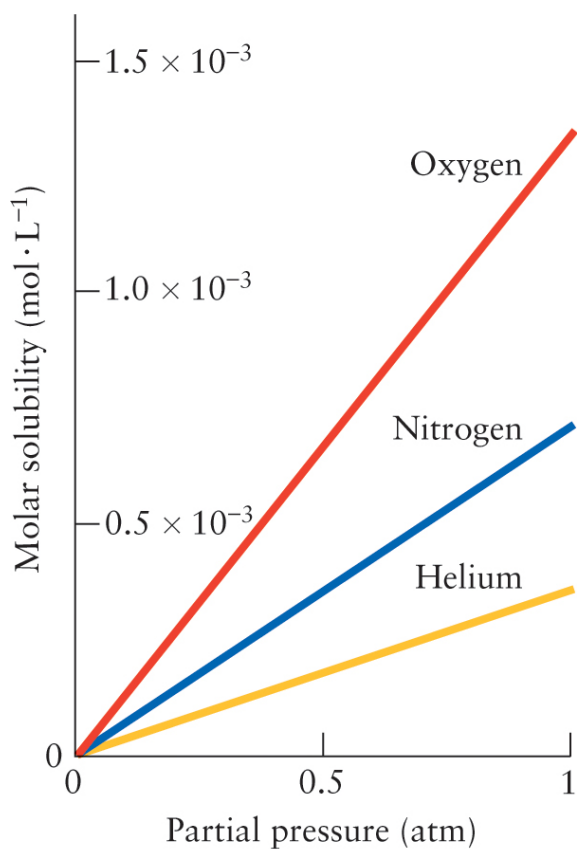


FIGURE 10.22 The variation of the molar solubilities of oxygen, nitrogen, and helium gases with partial pressure. Note that the solubility of each gas doubles when its partial pressure is doubled.

TABLE 10.5 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}

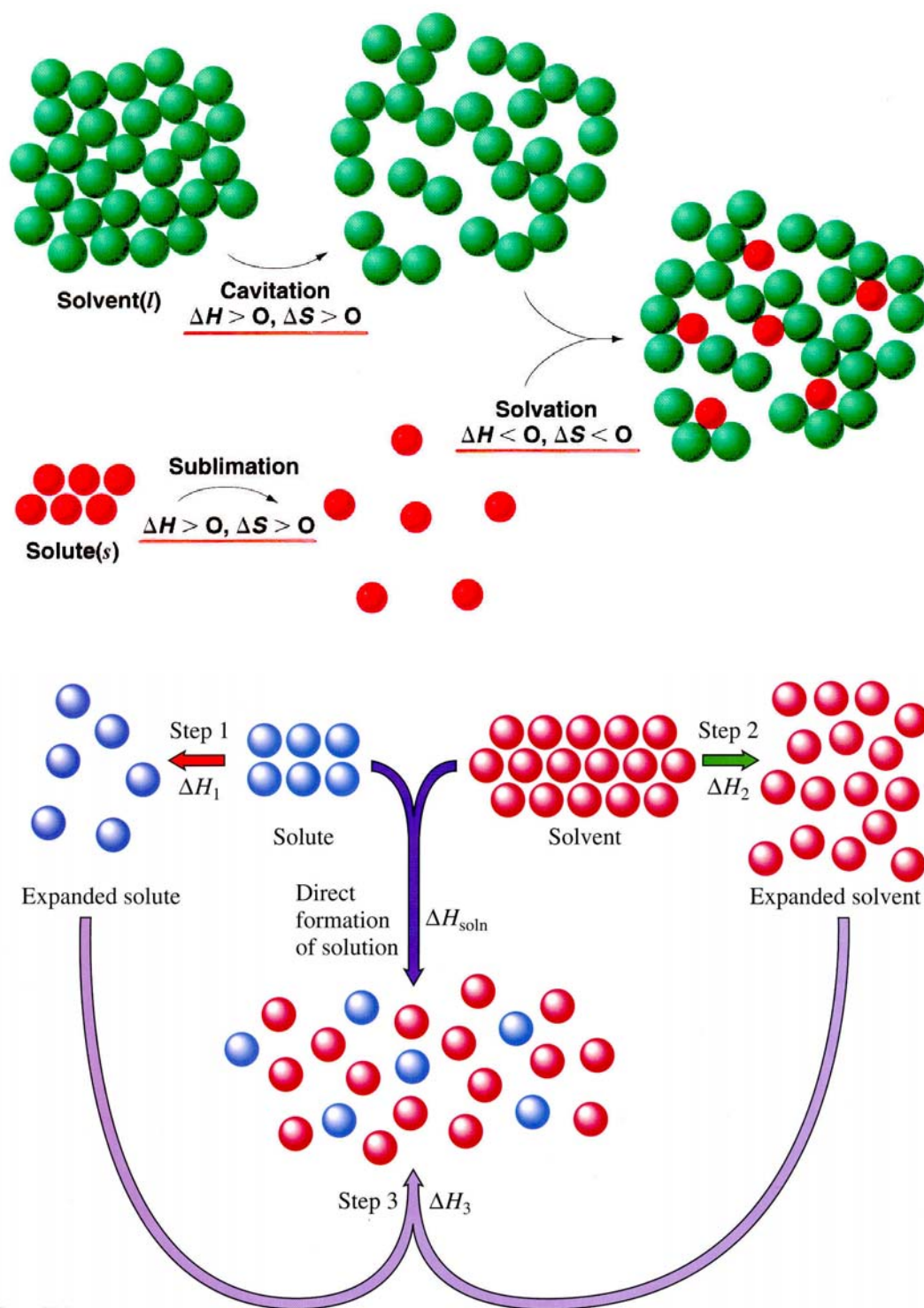
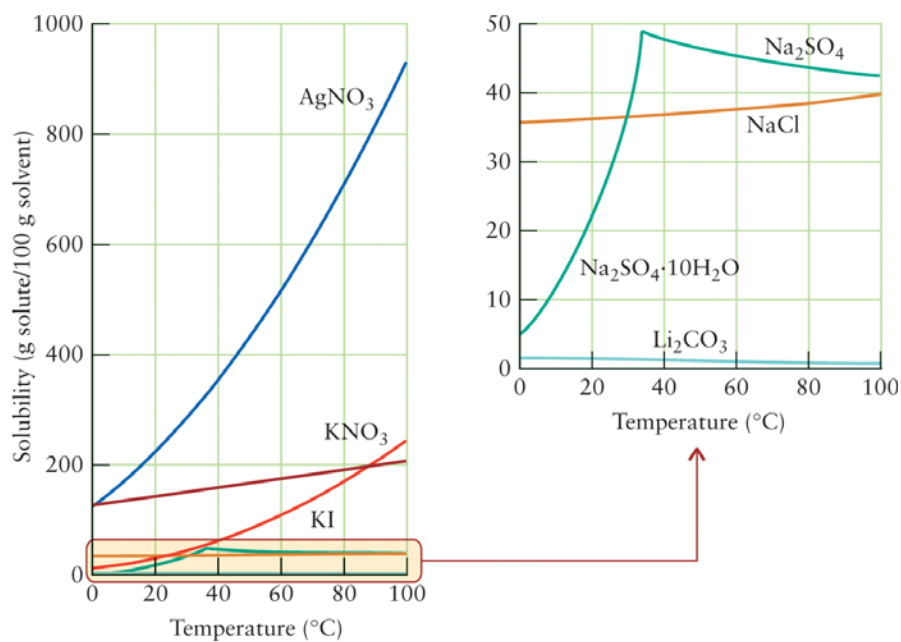
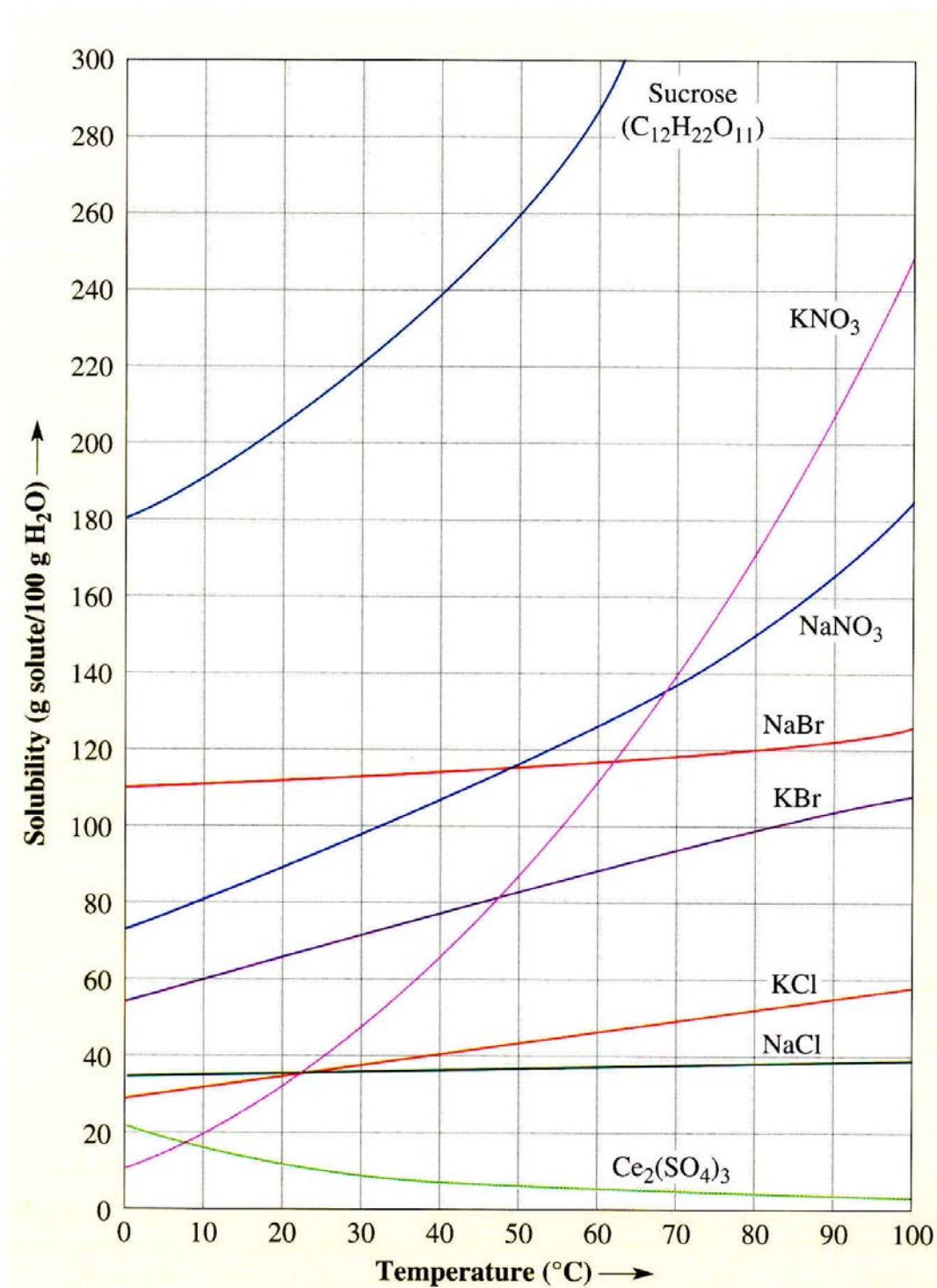


Figure 11.1
The steps in the dissolving process

FIGURE 10.23 The variation with temperature of the solubilities of six substances in water. The graph on the right is expanded vertically to show the variation in solubilities of three ionic compounds more clearly.



Solubility vs Temperature for Various Solutes in Water

Thermodynamics of Solutions

Enthalpy of Solution

Depends on the balance between **Lattice Enthalpy, ΔH_L** , [energy required to separate solute species (atoms, ions, molecules) from lattice] and **Hydration Enthalpy, ΔH_{hyd}** , (energy released when separated solute particles become dissolved).

$$\Delta H_{sol} = \Delta H_L + \Delta H_{hyd}$$

where

$$\Delta H_L \text{ is always } > 0$$

and

$$\Delta H_{hyd} \text{ is always } < 0$$

Free Energy of Solution

for most solutions:

$$\Delta S_{sol} \text{ is usually } > 0$$

Thus, the sign of ΔG_{sol} is usually determined by the sign of ΔH_{sol} , and ΔG_{sol} usually decreases with increasing temperature.

At saturation, G is a minimum, and $\Delta G = 0$.

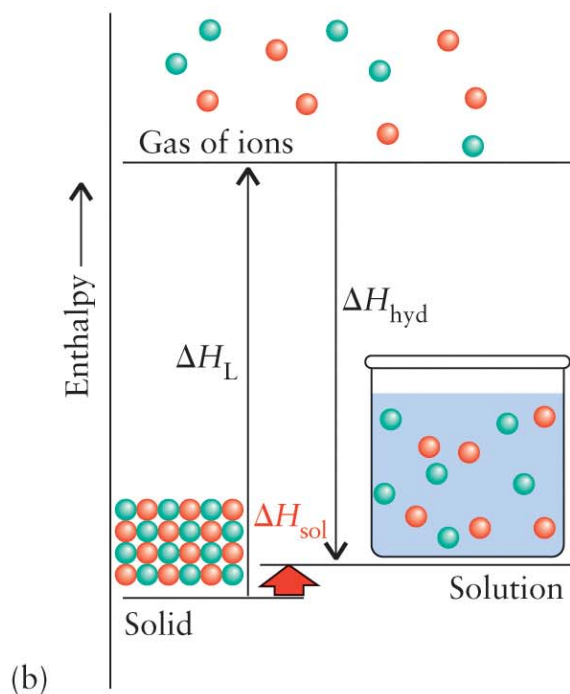
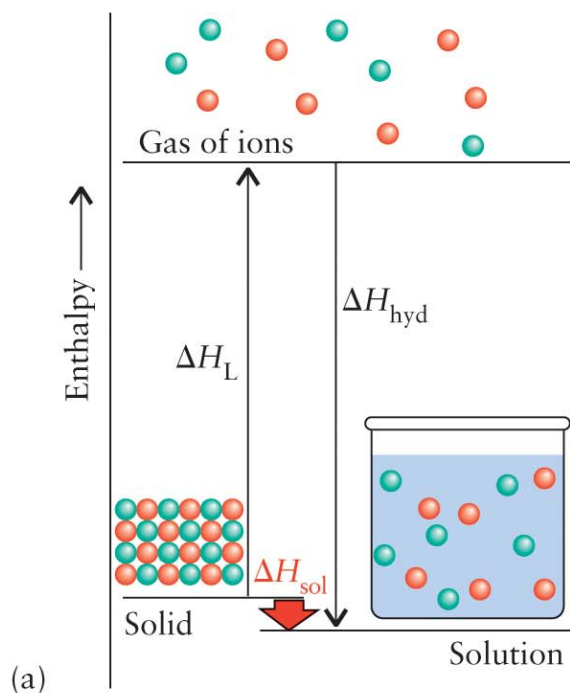


FIGURE 10.24 The enthalpy of solution, ΔH_{sol} , is the sum of the enthalpy change required to separate the molecules or ions of the solute (the lattice enthalpy, ΔH_L ; step 1 in Fig. 10.19), and the enthalpy change accompanying their hydration (ΔH_{hyd} ; steps 2 and 3 in Fig. 10.19). The outcome is finely balanced: (a) in some cases, it is exothermic; (b) in others, it

TABLE 8.5 Lattice Enthalpies at 25 °C ($\text{kJ}\cdot\text{mol}^{-1}$) = ΔH_{L} **Halides**

LiF	1046	LiCl	861	LiBr	818	LiI	759
NaF	929	NaCl	787	NaBr	751	NaI	700.
KF	826	KCl	717	KBr	689	KI	645
AgF	971	AgCl	916	AgBr	903	AgI	887
BeCl ₂	3017	MgCl ₂	2524	CaCl ₂	2260.	SrCl ₂	2153
		MgF ₂	2961	CaBr ₂	1984		

Oxides

MgO	3850.	CaO	3461	SrO	3283	BaO	3114
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Sulfides

MgS	3406	CaS	3119	SrS	2974	BaS	2832
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TABLE 10.7 Enthalpies of Hydration, ΔH_{hyd} , at 25 °C, of Some Halides, in kilojoules per mole* = ΔH_{hyd}

Cation	Anion			
	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 entry where the row labeled Na⁺ intersects the column labeled Cl⁻, for instance, is the enthalpy change, $-784 \text{ kJ}\cdot\text{mol}^{-1}$, for the process $\text{Na}^+(\text{g}) + \text{Cl}^-(\text{g}) \rightarrow \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq})$; the values here apply only when the resulting solution is very dilute.

TABLE 10.6 Limiting Enthalpies of Solution, ΔH_{sol} , at 25 °C, in kilojoules per mole*

Cation	Anion $\Delta H_{\text{sol}} = \Delta H_{\text{L}} + \Delta H_{\text{hyd}}$							
	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 value for silver iodide, for example, is the entry found where the row labeled “silver” intersects the column labeled “iodide.”

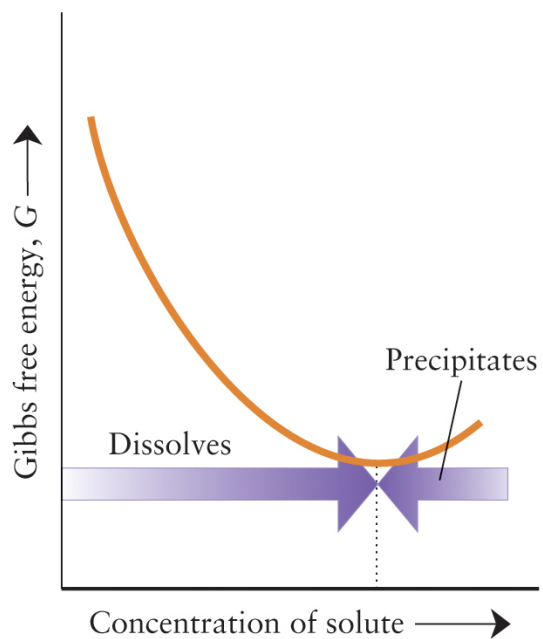


FIGURE 10.26 At low concentrations of solute, dissolving is accompanied by a decrease in Gibbs free energy of the system, so it is spontaneous. At high concentrations, dissolving is accompanied by an increase in Gibbs free energy, so the reverse process, precipitation, is spontaneous. The concentration of a saturated solution corresponds to the state of lowest Gibbs free energy at the temperature of the experiment.