Topic 6I - Solubility Equilibria

Thermodynamics of Solutions

Enthalpy of Solution

Depends on balance between Lattice Enthalpy [energy required to separate solute species (atoms, ions, molecules) from lattice] and Hydration Enthalpy (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:

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

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

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

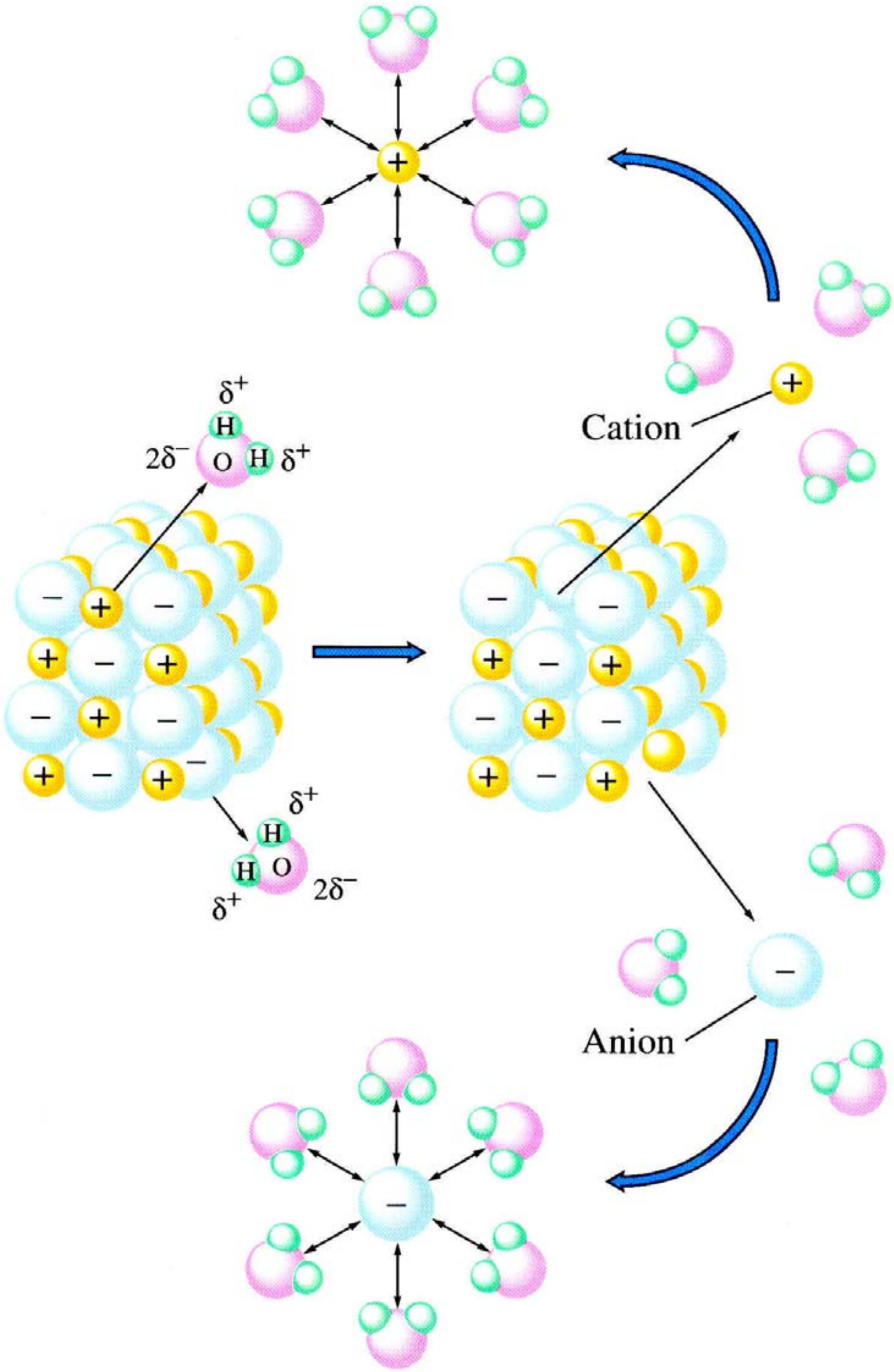

Figure 4.2
Ionic solid dissolving in water

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

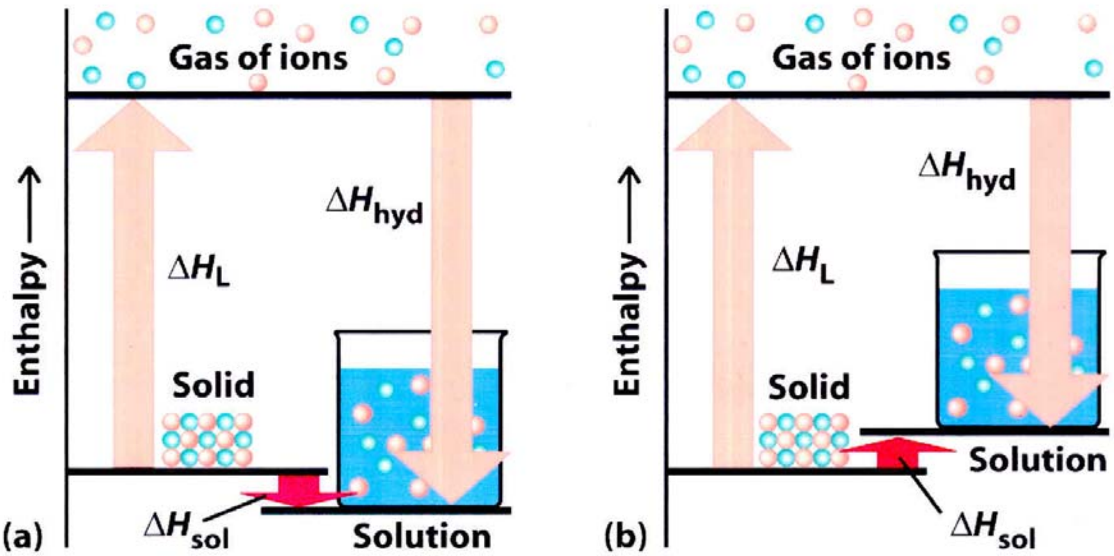

FIGURE 8.23 The enthalpy of solution, ΔH_{sol}, is the sum of the enthalpy change required to separate the molecules or ions of the solute, the lattice enthalpy, ΔH_L (step 1 in Fig. 8.16), and the enthalpy change accompanying their hydration, ΔH_{hyd} (steps 2 and 3 in Fig. 8.16). The outcome is finely balanced: (a) in some cases, it is exothermic; (b) in others, it is endothermic. For gaseous solutes, the lattice enthalpy is zero because the molecules are already widely separated.

TABLE 8.5 Lattice Enthalpies at 25 °C ($kJ \cdot mol^{-1}$) = 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
Sulfides							
MgS	3406	CaS	3119	SrS	2974	BaS	2832

TABLE 10.7 Enthalpies of Hydration, ΔH_{hyd}, at 25 °C, of Some Halides, in kilojoules per mole* = ΔH_{hyd}

	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 entry where the row labeled Na^+ intersects the column labeled Cl^-, for instance, is the enthalpy change, $-784\ kJ \cdot mol^{-1}$, for the process $Na^+(g) + Cl^-(g) \rightarrow Na^+(aq) + Cl^-(aq)$; 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*

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

	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 value for silver iodide, for example, is the entry found where the row labeled "silver" intersects the column labeled "iodide."

Table 7-1 Solubilities of Ionic Compounds in Water

Anion	Soluble[†]	Slightly Soluble	Insoluble
NO_3^- (nitrate)	All	—	—
CH_3COO^- (acetate)	Most	—	$Be(CH_3COO)_2$
ClO_3^- (chlorate)	All	—	—
ClO_4^- (perchlorate)	Most	$KClO_4$	—
F^- (fluoride)	Group I, AgF, BeF_2	SrF_2, BaF_2, PbF_2	MgF_2, CaF_2
Cl^- (chloride)	Most	$PbCl_2$	AgCl, Hg_2Cl_2
Br^- (bromide)	Most	$PbBr_2$, $HgBr_2$	AgBr, Hg_2Br_2
I^- (iodide)	Most	—	AgI, Hg_2I_2, PbI_2, HgI_2
SO_4^{2-} (sulfate)	Most	$CaSO_4$, Ag_2SO_4, Hg_2SO_4	$SrSO_4$, $BaSO_4$, $PbSO_4$
S^{2-} (sulfide)	Groups I and II, $(NH_4)_2S$	—	Most
CO_3^{2-} (carbonate)	Group I, $(NH_4)_2CO_3$	—	Most
SO_3^{2-} (sulfite)	Group I, $(NH_4)_2SO_3$	—	Most
PO_4^{3-} (phosphate)	Group I, $(NH_4)_3PO_4$	—	Most
OH^- (hydroxide)	Group I, $Ba(OH)_2$	$Sr(OH)_2$, $Ca(OH)_2$	Most

[†] Soluble compounds are defined as those that dissolve to the extent of 10 or more grams per liter; slightly soluble compounds, 0.1 to 10 grams per liter; and insoluble compounds, less than 0.1 gram per liter at room temperature.

Solubility Equilibria

Solubility Product

For ionic solids in saturated solutions:

$$A_x^{m+}B_y^{n-}\ (s) \rightleftarrows xA^{m+}\ (aq) + yB^{n-}\ (aq)$$

for which

$$K_c = K_{sp} = a(A^{m+})^x \times a(B^{n-})^y \approx [A^{m+}]^x[B^{n-}]^y$$

Examples:

$PbI_2\ (s) \rightleftarrows Pb^{2+}\ (aq) + 2\ I^-\ (aq)$

$K_{sp} = [Pb^{2+}][I^-]^2 = 1.39 \times 10^{-8}$ ($[Pb^{2+}] = 1.5 \times 10^{-3}$ M)

$Fe(OH)_3\ (s) \rightleftarrows Fe^{3+}\ (aq) + 3\ OH^-\ (aq)$

$K_{sp} = [Fe^{3+}][OH^-]^3 = 1.1 \times 10^{-36}$ ($[Fe^{3+}] = 4.5 \times 10^{-10}$ M)

The concept of solubility product and K_{sp} is meaningful only for sparingly soluble salts. At solution concentrations higher than ~0.01 M, effects such as ion-ion interactions and incomplete ionic dissolution become important. (*e.g.*, PbI^+, PbI_2 clusters, $Fe(OH)_2^+$, $Fe(OH)^{2+}$, *etc.*)

Table 12.6: Solubility Product Constants

TABLE 12.6

Solubility product constants K_{sp} at 25°C for sparingly soluble salts

Formula	K_{sp}	Formula	K_{sp}	Formula	K_{sp}
Fluorides		**Hydroxides** (*continued*)		**Phosphates** (*continued*)	
MgF_2	7.4×10^{-11}	$Cu(OH)_2$	5.5×10^{-20}	$Ni_3(PO_4)_2$	4.7×10^{-32}
CaF_2	1.5×10^{-10}	$AgOH$	1.8×10^{-8}	$Cu_3(PO_4)_2$	1.4×10^{-37}
SrF_2	4.3×10^{-9}	$Zn(OH)_2$	7.7×10^{-17}	$Cd_3(PO_4)_2$	2.5×10^{-33}
BaF_2	1.8×10^{-7}	$Cd(OH)_2$	5.3×10^{-15}	**Carbonates**	
Hg_2F_2	3.1×10^{-6}	$Hg(OH)_2$	3.1×10^{-26}	$MgCO_3$	7.0×10^{-6}
PbF_2	7.1×10^{-7}	$Sn(OH)_2$	5.5×10^{-27}	$CaCO_3$	5.0×10^{-9}
Chlorides		$Pb(OH)_2$	1.4×10^{-20}	$SrCO_3$	5.4×10^{-10}
$CuCl$	1.7×10^{-7}	**Sulfides**		$BaCO_3$	2.6×10^{-9}
$AgCl$	1.8×10^{-10}	MnS	3.8×10^{-15}	$MnCO_3$	2.2×10^{-11}
Hg_2Cl_2	1.5×10^{-18}	FeS	1.3×10^{-20}	$FeCO_3$	3.1×10^{-11}
$PbCl_2$	1.2×10^{-5}	CoS	8.2×10^{-22}	$NiCO_3$	1.4×10^{-7}
Bromides		NiS	9.2×10^{-23}	$CuCO_3$	1.8×10^{-10}
$CuBr$	6.3×10^{-9}	CuS	1.1×10^{-37}	$ZnCO_3$	1.2×10^{-10}
$AgBr$	5.4×10^{-13}	Ag_2S	1.1×10^{-49}	$CdCO_3$	6.2×10^{-12}
Hg_2Br_2	6.4×10^{-23}	ZnS	2.5×10^{-26}	Hg_2CO_3	3.7×10^{-17}
$PbBr_2$	6.6×10^{-6}	CdS	1.2×10^{-30}	$PbCO_3$	1.5×10^{-13}
Iodides		HgS	5.4×10^{-54}	**Oxalates**	
CuI	1.3×10^{-12}	SnS	2.7×10^{-29}	$MgC_2O_4.2H_2O$	4.8×10^{-6}
AgI	8.5×10^{-17}	PbS	7.5×10^{-30}	$CaC_2O_4.H_2O$	2.3×10^{-9}
Hg_2I_2	5.3×10^{-29}	**Sulfates**		$MnC_2O_4.2H_2O$	1.7×10^{-7}
PbI_2	8.5×10^{-9}	$CaSO_4$	7.1×10^{-5}	CuC_2O_4	4.4×10^{-10}
Hydroxides		$SrSO_4$	3.4×10^{-7}	$Ag_2C_2O_4$	5.4×10^{-12}
$Mg(OH)_2$	5.6×10^{-12}	$BaSO_4$	1.1×10^{-10}	$ZnC_2O_4.2H_2O$	1.4×10^{-9}
$Al(OH)_3$	2.5×10^{-32}	Ag_2SO_4	1.2×10^{-5}	$CdC_2O_4.3H_2O$	1.4×10^{-8}
$Ca(OH)_2$	4.7×10^{-6}	$PbSO_4$	1.8×10^{-8}	$Hg_2C_2O_4$	1.8×10^{-13}
$Cr(OH)_3$	4.7×10^{-38}	**Phosphates**		PbC_2O_4	8.5×10^{-10}
$Mn(OH)_2$	2.1×10^{-13}	$Mg_3(PO_4)_2$	9.9×10^{-25}	**Chromates**	
$Fe(OH)_2$	4.9×10^{-17}	$AlPO_4$	9.8×10^{-21}	$BaCrO_4$	1.2×10^{-10}
$Fe(OH)_3$	2.6×10^{-39}	$Ca_3(PO_4)_2$	2.1×10^{-33}	Ag_2CrO_4	1.1×10^{-12}
$Co(OH)_2$	1.1×10^{-15}	$FePO_4.2H_2O$	9.9×10^{-29}	$PbCrO_4$	2.8×10^{-13}
$Ni(OH)_2$	5.6×10^{-16}	$Co_3(PO_4)_2$	2.1×10^{-35}		

TABLE 11.2

Solubility Product Constants K_{sp} at 25°C

Iodates		**Fluorides**	
$AgIO_3$	$[Ag^+][IO_3^-] = 3.1 \times 10^{-8}$	BaF_2	$[Ba^{2+}][F^-]^2 = 1.7 \times 10^{-6}$
$CuIO_3$	$[Cu^+][IO_3^-] = 1.4 \times 10^{-7}$	CaF_2	$[Ca^{2+}][F^-]^2 = 3.9 \times 10^{-11}$
$Pb(IO_3)_2$	$[Pb^{2+}][IO_3^-]^2 = 2.6 \times 10^{-13}$	MgF_2	$[Mg^{2+}][F^-]^2 = 6.6 \times 10^{-9}$
		PbF_2	$[Pb^{2+}][F^-]^2 = 3.6 \times 10^{-8}$
		SrF_2	$[Sr^{2+}][F^-]^2 = 2.8 \times 10^{-9}$
Carbonates			
Ag_2CO_3	$[Ag^+]^2[CO_3^{2-}] = 6.2 \times 10^{-12}$		
$BaCO_3$	$[Ba^{2+}][CO_3^{2-}] = 8.1 \times 10^{-9}$		
		Chlorides	
$CaCO_3$	$[Ca^{2+}][CO_3^{2-}] = 8.7 \times 10^{-9}$	$AgCl$	$[Ag^+][Cl^-] = 1.6 \times 10^{-10}$
$PbCO_3$	$[Pb^{2+}][CO_3^{2-}] = 3.3 \times 10^{-14}$	$CuCl$	$[Cu^+][Cl^-] = 1.0 \times 10^{-6}$
$MgCO_3$	$[Mg^{2+}][CO_3^{2-}] = 4.0 \times 10^{-5}$	Hg_2Cl_2	$[Hg_2^{2+}][Cl^-]^2 = 2 \times 10^{-18}$
$SrCO_3$	$[Sr^{2+}][CO_3^{2-}] = 1.6 \times 10^{-9}$		
		Bromides	
		$AgBr$	$[Ag^+][Br^-] = 7.7 \times 10^{-13}$
Chromates			
Ag_2CrO_4	$[Ag^+]^2[CrO_4^{2-}] = 1.9 \times 10^{-12}$	$CuBr$	$[Cu^+][Br^-] = 4.2 \times 10^{-8}$
$BaCrO_4$	$[Ba^{2+}][CrO_4^{2-}] = 2.1 \times 10^{-10}$	Hg_2Br_2	$[Hg_2^{2+}][Br^-]^2 = 1.3 \times 10^{-21}$
$PbCrO_4$	$[Pb^{2+}][CrO_4^{2-}] = 1.8 \times 10^{-14}$		
Oxalates		**Iodides**	
CuC_2O_4	$[Cu^{2+}][C_2O_4^{2-}] = 2.9 \times 10^{-8}$	AgI	$[Ag^+][I^-] = 1.5 \times 10^{-16}$
FeC_2O_4	$[Fe^{2+}][C_2O_4^{2-}] = 2.1 \times 10^{-7}$	CuI	$[Cu^+][I^-] = 5.1 \times 10^{-12}$
MgC_2O_4	$[Mg^{2+}][C_2O_4^{2-}] = 8.6 \times 10^{-5}$	PbI_2	$[Pb^{2+}][I^-]^2 = 1.4 \times 10^{-8}$
PbC_2O_4	$[Pb^{2+}][C_2O_4^{2-}] = 2.7 \times 10^{-11}$	Hg_2I_2	$[Hg_2^{2+}][I^-]^2 = 1.2 \times 10^{-28}$
SrC_2O_4	$[Sr^{2+}][C_2O_4^{2-}] = 5.6 \times 10^{-8}$		
Sulfates		**Hydroxides**	
$BaSO_4$	$[Ba^{2+}][SO_4^{2-}] = 1.1 \times 10^{-10}$	$AgOH$	$[Ag^+][OH^-] = 1.5 \times 10^{-8}$
$CaSO_4$	$[Ca^{2+}][SO_4^{2-}] = 2.4 \times 10^{-5}$	$Al(OH)_3$	$[Al^{3+}][OH^-]^3 = 3.7 \times 10^{-15}$
$PbSO_4$	$[Pb^{2+}][SO_4^{2-}] = 1.1 \times 10^{-8}$	$Fe(OH)_3$	$[Fe^{3+}][OH^-]^3 = 1.1 \times 10^{-36}$
		$Fe(OH)_2$	$[Fe^{2+}][OH^-]^2 = 1.6 \times 10^{-14}$
		$Mg(OH)_2$	$[Mg^{2+}][OH^-]^2 = 1.2 \times 10^{-11}$
		$Mn(OH)_2$	$[Mn^{2+}][OH^-]^2 = 2 \times 10^{-13}$
		$Zn(OH)_2$	$[Zn^{2+}][OH^-]^2 = 4.5 \times 10^{-17}$

Common Ion Effect

Decrease in solubility of a salt due to the presence of a common ion from a second salt.

Application of LeChatlier's Principle.

Example: The solubility of AgCl is lower in a solution of NaCl than it is in pure water due to excess Cl^- ions:

$$AgCl\ (s) \rightleftharpoons Ag^+\ (aq) + \underset{\text{excess}}{Cl^-}\ (aq)$$

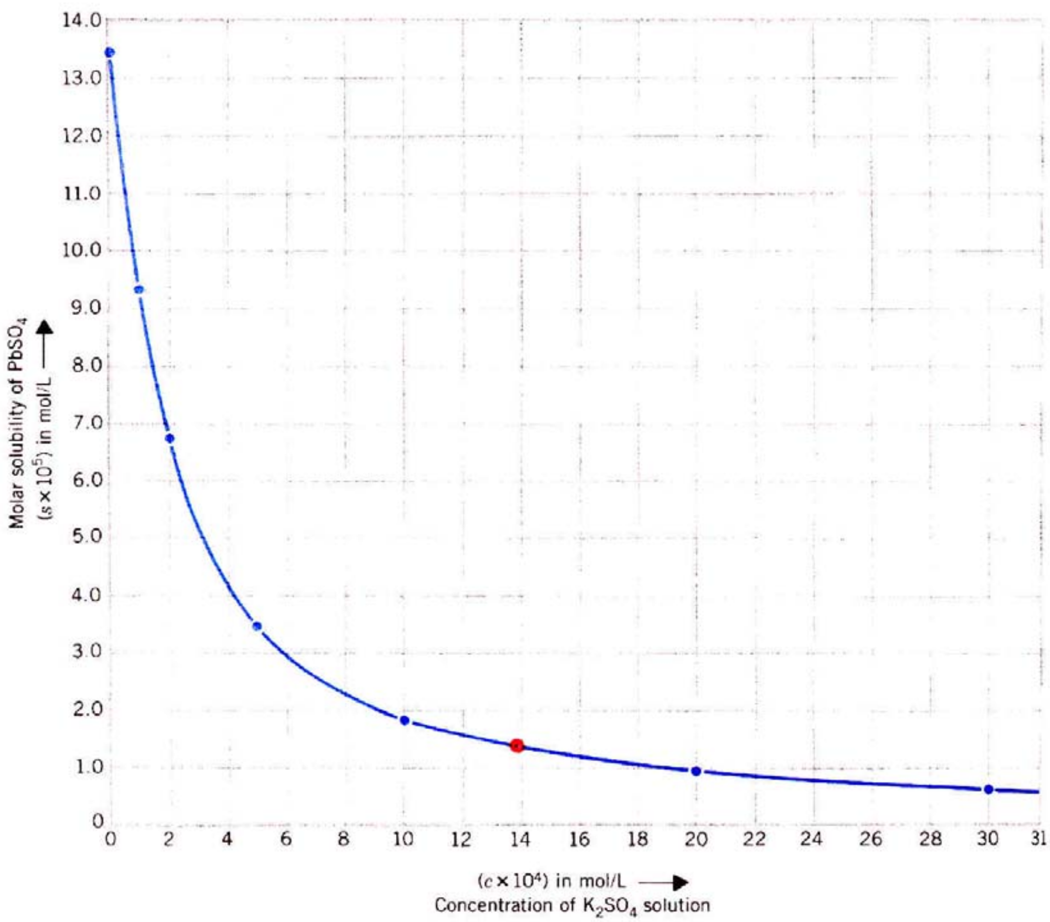

Fig. 11.1. The common ion effect. The molar solubility, s, of $PbSO_4$ in solutions containing K_2SO_4 is plotted as a function of the concentration, c, in moles per liter, of the K_2SO_4. The relationship between s and c is $s(c + s) = 1.8 \times 10^{-8} = K_{sp}(PbSO_4)$. Thus as c increases, s decreases.

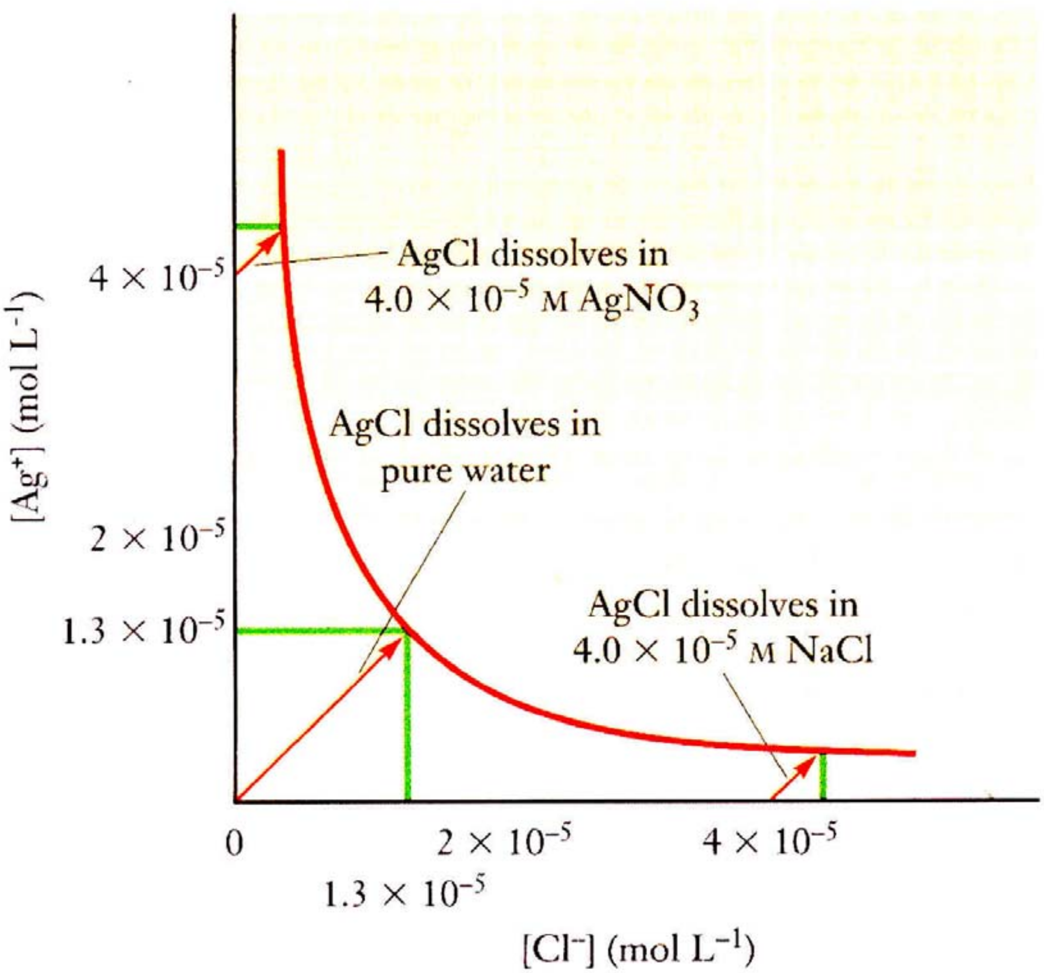

FIGURE 11.7 The presence of a dissolved common ion reduces the solubility of a salt in solution. As the AgCl dissolves, the concentrations of the ions follow the paths shown by the red arrows until they reach the red equilibrium curve. The molar solubilities are proportional to the lengths of the green lines: 1.3×10^{-5} mol L^{-1} for AgCl in pure water, but only 0.37×10^{-5} mol L^{-1} in either 4.0×10^{-5} M $AgNO_3$ or 4.0×10^{-5} M NaCl.