

Factors affecting solubility

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Boston University

Solubility determined by (Dill/3e pp 208)

$$\Delta G_{\text{dissolve}} = \dots$$

$$\Delta E_{\text{dissolve}} (\text{surroundings}) + \Delta E_{\text{org}} (\text{system})$$

If $\Delta G_{\text{dissolve}} < 0 \rightarrow$ **soluble**

If $\Delta G_{\text{dissolve}} > 0 \rightarrow$ **insoluble**

We can predict $\Delta E_{\text{dissolve}}$

Table 2.3 Lattice and hydration energies (in kJ mol^{-1}) for some ionic compounds.

The entries where the cation row and anion columns intersect are $\Delta E_{\text{lattice}}$ and $\Delta E_{\text{hydration}}$ values for the compound. For example, 2440 kJ mol^{-1} is $\Delta E_{\text{lattice}}$ for MgBr_2 .

Cation	Anion					
	Cl^-		Br^-		I^-	
	$\Delta E_{\text{lattice}}$	$\Delta E_{\text{hydration}}$	$\Delta E_{\text{lattice}}$	$\Delta E_{\text{hydration}}$	$\Delta E_{\text{lattice}}$	$\Delta E_{\text{hydration}}$
Li^+	861	-898	818	-867	759	-822
Na^+	787	-784	751	-753	700	-708
K^+	717	-701	689	-670	645	-625
Ag^+	916	-850	903	-819	887	-774
Mg^{2+}	2524	-2679	2440	-2626	2327	-2540
Ca^{2+}	2260	-2337	2176	-2285	2074	-2194
Sr^{2+}	2153	-2205	2075	-2142	1963	-2053
	S^{2-}		CO_3^{2-}			
Mg^{2+}	3406	-3480	3122	-3148		
Ca^{2+}	3119	-3140	2804	-2817		
Sr^{2+}	2974	-3030	2720	-2725		

We can predict ΔE_{org} (ion)

Li^+ 7.1	Na^+ -1.3	K^+ -12.	Rb^+ -14.	Cs^+ -15.			
Mg^{2+} 56.	Ca^{2+} 38.	Sr^{2+} 36.	Ba^{2+} 25.				
NH_4^+ -8.8	Ag^+ 2.1	Tl^+ -8.4					
Mn^{2+} 49.	Fe^{2+} 61.	Co^{2+} 61.	Ni^{2+} 68.	Cu^{2+} 53.	Zn^{2+} 56.	Cd^{2+} 46.	Pb^{2+} 25.
F^- 3.3	Cl^- -12.	Br^- -16.	I^- -21.	OH^- 3.3			
NO_3^- -26.	MnO_4^- -30.	ClO_3^- -25.	ClO_4^- -28.	BrO_3^- -22.	IO_3^- -7.9	HCO_3^- -13.	
SO_4^{2-} 6.7	CO_3^{2-} 21.						

Dill/3e p 211

 MgCO_3 : ΔE_{org} makes $\Delta G_{\text{dissolve}} > 0$

$$\begin{aligned} \Delta E_{\text{dissolve}} &= \Delta E_{\text{lattice}} + \Delta E_{\text{hydration}} \\ &= + 3122 \text{ kJ/mol} - 3148 \text{ kJ/mol} \\ &= - 26 \text{ kJ/mol} \end{aligned}$$

$$\begin{aligned} \Delta E_{\text{org}} &= \Delta E_{\text{org}} (\text{Mg}^{2+}) + \Delta E_{\text{org}} (\text{CO}_3^{2-}) \\ &= + 56 \text{ kJ/mol} + 21 \text{ kJ/mol} \\ &= + 77 \text{ kJ/mol} \end{aligned}$$

$$\begin{aligned} \Delta G_{\text{dissolve}} &= \Delta E_{\text{dissolve}} + \Delta E_{\text{org}} \\ &= - 26 \text{ kJ/mol} + 77 \text{ kJ/mol} \\ &= + 51 \text{ kJ/mol} \rightarrow \text{insoluble!!!} \end{aligned}$$

 AgCl : $\Delta E_{\text{dissolve}}$ makes $\Delta G_{\text{dissolve}} > 0$

$$\begin{aligned} \Delta E_{\text{dissolve}} &= \Delta E_{\text{lattice}} + \Delta E_{\text{hydration}} \\ &= + 916 \text{ kJ/mol} - 850 \text{ kJ/mol} \\ &= + 66 \text{ kJ/mol} \end{aligned}$$

$$\begin{aligned} \Delta E_{\text{org}} &= \Delta E_{\text{org}} (\text{Ag}^+) + \Delta E_{\text{org}} (\text{Cl}^-) \\ &= + 2.1 \text{ kJ/mol} - 12 \text{ kJ/mol} \\ &= - 10 \text{ kJ/mol} \end{aligned}$$

$$\begin{aligned} \Delta G_{\text{dissolve}} &= \Delta E_{\text{dissolve}} + \Delta E_{\text{org}} \\ &= + 66 \text{ kJ/mol} - 10 \text{ kJ/mol} \\ &= + 56 \text{ kJ/mol} \rightarrow \text{insoluble!!!} \end{aligned}$$

Solubility “rules”

Soluble compounds

- Na^+ , K^+ , and NH_4^+
- NO_3^- , CH_3COO^- , ClO_4^-
- Cl^- , Br^- , I^- , except with Ag^+ , Pb^{2+} , Hg_2^{2+}
- SO_4^{2-} , except with Ag^+ , Pb^{2+} , Hg_2^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+}

Insoluble compounds

- CO_3^{2-} , S^{2-} , and PO_4^{3-} , except with Na^+ , K^+ , and NH_4^+
- Ag^+ , Pb^{2+} , Hg_2^{2+}
- OH^- , except with NH_4^+ , Na^+ , K^+ , Ba^{2+}

Solubility data

- Rules: Dill/3e pp 211–212 and, e.g., <http://snipurl.com/j7aej>
- Chart: <http://snipurl.com/j5l77>
- Table: <http://snipurl.com/j5l8m>