Solubility of ionic solids in water

Notes on General Chemistry

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■ Factors affecting solubility

The solubility of ionic solids in water depends of two things: (1) the energy change, $\Delta H_{\text{dissolve}}$, that occurs when the ionic solid goes into solution as hydrated ions, and (2) the affect of the hydrated ions on the arrangement of the surrounding water molecules, measured by the organizational energy, ΔH_{org}. These factors combine to determine the free energy change of dissolving,

$$\Delta G_{\text{dissolve}} = \Delta H_{\text{dissolve}} + \Delta H_{\text{org}}.$$

If the solution forms with a drop in free energy change of dissolving, $\Delta G_{\text{dissolve}} < 0$, the ionic solid is soluble.

If the solution forms with an increase in free energy change of dissolving, $\Delta G_{\text{dissolve}} > 0$, the ionic solid is insoluble.

Dissolving energy, $\Delta H_{\text{dissolve}}$

The energy change on formation of the solution is usually reported as the *dissolving energy*, $\Delta H_{\text{dissolve}}$. It is the difference,

$$\Delta H_{\text{dissolve}} = \Delta H_{\text{hydration}} - \Delta H_{\text{lattice}},$$

between the lattice energy, $\Delta H_{\text{lattice}}$, the energy required to break the ionic solid apart into separated ions, and the hydration energy, $\Delta H_{\text{hydration}}$, the energy released when the separated ions become surrounded water molecules. If there is a net release of energy, that is, if more energy is released on hydration than is stored in the ionic solid lattice, then solubility is favored. If there is a net gain of energy, that is, if less energy is released on hydration than is stored in the ionic solid lattice, then solubility is unfavored.

Organization energy, $\Delta H_{\text{org}} = -T\,\Delta S_{\text{dissolve}}$

The effect of the hydrated ions on the arrangement of the surrounding water molecules can be quantified in terms of the *dissolving organization energy*, $\Delta H_{\text{org}} = -T\,\Delta S_{\text{dissolve}}$, where $\Delta S_{\text{dissolve}}$ is the difference,

$$\Delta S_{\text{dissolve}} = S_{\text{solution}} - S_{\text{solid}},$$

between the entropy of the solution and the entropy of the solid. Essentially, $\Delta S_{\text{dissolve}}$, reflects the change in *energy dispersal* that results when the ions in the solid are hydrated in solution. Since the ions in the solid are held in place by Coulombic attractions to neighboring, oppositely charged ions, the interaction energies are relatively undispersed in the solid.

Since ions in solution are separated from one another by water molecules, the energy of the ion-water interaction is *more dispersed* than the ion-ion interaction in the solid. However, since the ions in solution organize neighboring water molecules into a hydration shell, the energy of the water-water interaction is *less dispersed* than in pure water. The competition between these two effects means that energy dispersal in the solution can be either more or less than in the solid.

If the sheath of water molecules is weakly held, then the dispersal of the ions in water dominates, so that ΔH_{org} *is negative and solubility favored*. This is the case with large ions that have a single unit of charge. This is because the water molecules cannot get close enough to the ions to be tightly held and so the hydration shell is fragile.

If the sheath of water molecules is tightly held, then the reduction in dispersal of water-water interaction dominates, so that ΔH_{org} *is positive and solubility unfavored*. This is the case with small ions and ones that have multiple units of charge. This is because the water molecules are more strongly held by the ions, because they can get closer to the ion and they experience greater charge on the ion.The result is that the hydration shell is robust.

Predicting solubility from dissolving energy and organizational energy

If both the dissolving energy and the organization energy are both negative, that is, if solution formation is *exothermic* and if energy is *more dispersed* in the solution than in the solid, then the solubility will be high.

If both the dissolving energy and the organization energy are both positive, that is, if solution formation is *endothermic* and if energy is *less dispersed* in the solution than in the solid, then the solubility will be low.

If the dissolving energy and the organization energy have opposite signs, then their relative values determines whether the ionic solid will be soluble or not. To determine this, we need the lattice energy and hydration energy to evaluate the dissolving energy, and we need to know the contribution of the hydrated ions to the organizational energy to determine the overall organizational energy.

Here is the organizational energy contribution for common ions.

Li^+	Na^+	K^+	Rb^+	Cs^+
7.1	−1.3	−12.	−14.	−15.

Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
56.	38.	36.	25.

NH_4^+	Ag^+	Tl^+
−8.8	2.1	−8.4

Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}	Pb^{2+}
49.	61.	61.	68.	53.	56.	46.	25.

F^-	Cl^-	Br^-	I^-	OH^-
3.3	−12.	−16.	−21.	3.3

NO_3^-	MnO_4^-	ClO_3^-	ClO_4^-	BrO_3^-	IO_3^-	HCO_3^-
−26.	−30.	−25.	−28.	−22.	−7.9	−13.

SO_4^{2-}	CO_3^{2-}
6.7	21.

Organizational energy, $\Delta H_{\text{org}}(\text{ion}) = -T\Delta S_{\text{dissolve}}(\text{ion})$, values (kJ/mol) for individual ions (crystal → aqueous solution) at 25 °C. Adapted from Phillips and Williams, *Inorganic Chemistry*, Volume 1 (Oxford University Press, 1965), Table 7.XI, page 259.

> Does it make sense that the X^+ organizational energy becomes more negative with increasing atomic number?

> Propose why Li^+ has a positive organizational energy while the other X^+ ions have negative organizational energy.

> Does it make sense that the X^- organizational energy becomes more negative with increasing atomic number?

> Propose why F^- and OH^- have a positive organizational energy while the other X^- ions

> have negative organizational energy.

> Does it make sense that the X^{2+} organizational energy becomes less positive with increasing atomic number?

> Propose why CO_3^{2-} has a positive organizational energy while ClO_3^- has a negative organizational energy.

> Propose why SO_4^{2-} has a positive organizational energy while MnO_4^- has a negative organizational energy.

Example: NaCl

Sodium chloride is an example where even though the dissolving energy is endothermic, the organizational energy is sufficiently exothermic that the compound is *soluble*. Using values from J. Bell, *ACS Chemistry* (W. H. Freeman, 2005), Table 2.3, page 92, the dissolving energy evaluates to the *endothermic* value

$$\begin{aligned}\Delta H_{\text{dissolve}} &= \Delta H_{\text{hydration}}(\text{NaCl}) - \Delta H_{\text{lattice}}(\text{NaCl}) \\ &= (-784\ \text{kJ/mol}) + (+787\ \text{kJ/mol}) = +3\ \text{kJ/mol},\end{aligned}$$

which favors *insolubility*. Using the ion organizational energies, the organizational energy evaluates to the *exothermic* value

$$\begin{aligned}\Delta H_{\text{org}} &= \Delta H_{\text{org}}(\text{Na}^+) + \Delta H_{\text{org}}(\text{Cl}^-) \\ &= (-1.3\ \text{kJ/mol}) + (-12\ \text{kJ/mol}) = -13\ \text{kJ/mol},\end{aligned}$$

which favors *solubility*. The organizational energy is sufficiently exothermic that the free energy of dissolving is also exothermic,

$$\Delta G_{\text{dissolve}} = \Delta H_{\text{dissolve}} + \Delta H_{\text{org}} = +3\ \text{kJ/mol} - 13\ \text{kJ/mol} = -10\ \text{kJ/mol}.$$

This means the solubility of sodium chloride is due to energy being *more dispersed* in the solution than in the solid.

Example: $MgCO_3$

Magnesium carbonate is an example opposite to sodium chloride: Even though the dissolving energy is exothermic, the organizational energy is sufficiently endothermic that the compound is *insoluble*. Using values from J. Bell, *ACS Chemistry* (W. H. Freeman, 2005), Table 2.3, page 92, the dissolving energy evaluates to the *exothermic* value

$$\begin{aligned}\Delta H_{\text{dissolve}} &= \Delta H_{\text{hydration}}(\text{MgCO}_3) - \Delta H_{\text{lattice}}(\text{MgCO}_3) \\ &= (-3148\ \text{kJ/mol}) + (+3122\ \text{kJ/mol}) = -26\ \text{kJ/mol},\end{aligned}$$

which favors *solubility*. Using the ion organizational energies, the organizational energy evaluates to the *exothermic* value

$$\begin{aligned}\Delta H_{\text{org}} &= \Delta H_{\text{org}}\left(\text{Mg}^{2+}\right) + \Delta H_{\text{org}}\left(\text{CO}_3^{2-}\right) \\ &= (+56\ \text{kJ/mol}) + (-25\ \text{kJ/mol}) = +31\ \text{kJ/mol},\end{aligned}$$

which favors ins*olubility*. Because the endothermic organizational energy is so large, the free energy of dissolving is also endothermic,

$$\Delta G_{\text{dissolve}} = \Delta H_{\text{dissolve}} + \Delta H_{\text{org}} = -26\ \text{kJ/mol} + 31\ \text{kJ/mol} = +5\ \text{kJ/mol}.$$

This means that the insolubility of calcium carbonate is due to energy being *less dispersed* in the solution than in the solid.

■ Solubility rules for ionic solids in water

Here are rules that you can use to remember whether an ionic solid is soluble or not. The rules are consequences of the combined effect of dissolving energy and organizational energy.

Soluble in water

1. All sodium, potassium, and ammonium (NH_4^+) salts are soluble.

> Analyze whether the solubility of sodium, potassium, and ammonium salts is due to exothermicity of dissolving energy, exothermicity of organizational energy, or both.

2. All nitrates, acetates (CH_3CO^-) and perchlorates (ClO_4^-) are soluble.

> Analyze whether the solubility of nitrates, acetates and perchlorates is due to exothermicity of dissolving energy, exothermicity of organizational energy, or both.

3. All chlorides, bromides and iodides are soluble, except halide of Ag^+, Pb^{2+} and Hg_2^{2+}.

> Analyze whether the solubility of chlorides, bromides and iodides is due to exothermicity of dissolving energy, exothermicity of organizational energy, or both.

> Analyze whether the exceptions are due to exothermicity of dissolving energy, exothermicity of organizational energy, or both.

4. All sulfates are soluble, except sulfates of Ag^+, Pb^{2+}, Hg_2^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}.

> Determine whether the exceptions in the sulfate rule are due to exothermicity of dissolving energy or exothermicity of organizational energy.

> Analyze whether the exceptions are due to exothermicity of dissolving energy, exothermicity of organizational energy, or both.

Insoluble in water

5. All sulfides are insoluble, except sulfides of Ca^{2+}, Sr^{2+} and Ba^{2+}.

> Analyze whether the insolubility of sulfides is due to endothermicity of dissolving energy, endothermicity of organizational energy, or both.

> Analyze whether the exceptions are due to exothermicity of dissolving energy, exothermicity of organizational energy, or both.

6. All carbonates (CO_3^{2-}) and phosphates (PO_4^{3-}).

> Analyze whether the insolubility of carbonates and phosphates is due to endothermicity of dissolving energy, endothermicity of organizational energy, or both.

7. All hydroxides are insoluble, except hydroxides of Ca^{2+}, Sr^{2+} and Ba^{2+}.

> Analyze whether the insolubility of carbonates, sulfides, oxides and hydroxides is due to endothermicity of dissolving energy, endothermicity of organizational energy, or both.

8. All silver (Ag^{+}), lead(II) (Pb^{2+}) and mercury(I) (Hg_2^{2+}) salts are insoluble

> Analyze whether the insolubility of silver, lead(II) and mercury(I) salts is due to endothermicity of dissolving energy, endothermicity of organizational energy, or both.