

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 on two things: (1) the energy change, $\Delta E_{\text{dissolve}}$, that occurs when the ionic solid goes into solution as hydrated ions, and (2) the effect of the hydrated ions on the arrangement of the surrounding water molecules, measured by the organization energy, ΔE_{org} . These factors combine to determine the total energy change of dissolving,

$$\Delta E_{\text{total}} = \Delta E_{\text{dissolve}} + \Delta E_{\text{org}}.$$

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

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

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

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

$$\Delta E_{\text{dissolve}} = \Delta E_{\text{hydration}} + \Delta E_{\text{lattice}},$$

of the lattice energy, $\Delta E_{\text{lattice}}$, the energy required to break the ionic solid apart into separated ions, and the hydration energy, $\Delta E_{\text{hydration}}$, the energy released when the separated ions become surrounded by 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, ΔE_{org}

The effect of the hydrated ions on the arrangement of the surrounding water molecules can be quantified in terms of the *dissolving organization energy*, ΔE_{org} . Essentially, ΔE_{org} 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 oppositely charged neighbors, the interaction energies are relatively undispersed in the solid.

Since ions in solution are separated from one another by the 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 liquid 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 ΔE_{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 ΔE_{org} is *positive and solubility unfavored*. This is the case with small ions 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 organization 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 determine 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 organization energy to determine the overall organization energy.

Here is the organization 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.						

Organization energy, $\Delta E_{\text{org}}(\text{ion})$, values (kJ/mol) for individual ions (crystal \rightarrow 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^+ organization energy becomes more negative with increasing atomic number?

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

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

Propose why F^- and OH^- have a positive organization energy while the other X^- ions have negative organization energy.

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

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

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

Example: NaCl

Sodium chloride is an example where even though the dissolving energy is endothermic, the organization 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

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

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

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

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

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

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 organization energy is sufficiently endothermic that the compound is *insoluble*. The dissolving energy evaluates to the *exothermic* value

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

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

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

which favors *insolubility*. Because the endothermic organization energy is so large, the total energy of dissolving is also endothermic,

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

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 organization 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 organization 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 organization energy, or both.

3. All chlorides, bromides and iodides are soluble, except halides 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 organization energy, or both.

Analyze whether the exceptions are due to exothermicity of dissolving energy, exothermicity of organization 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 organization energy.

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

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

■ Solubility of salts in non-aqueous media

Professor Linda Doerrer kindly points out in the following that in non-aqueous solvents, solubilities are very different, and that this is especially important in organic chemistry.

“Although water is the first and most common solvent encountered in our experiences with solubility and studies of matter, it is not the only important solvent. Solvents such as chloroform, alcohols, and alkanes are commonly used in research and industrial laboratories.

“In non-aqueous or hydrophobic environments, the relative stabilities of ions as dissolved or precipitated changes dramatically. For example, one cannot dissolve table salt (NaCl) in oil (general formula $\text{C}_n\text{H}_{2n+2}$) for cooking. If you study organic chemistry, you will use the radically different behavior of such salts in an advantageous way.

“One can precipitate NaCl from a non-polar solvent, just the way PbI_2 precipitates from water. This formation of a precipitate is often an important factor in favoring a particular reaction and is used consciously by chemists to “stack the deck” in designing reactions.

“Magnesium sulfate, MgSO_4 , dissolves in water. When the salt is placed in a chloroform (CHCl_3) solution, we take advantage of the salt's affinity for water. The MgSO_4 is insoluble in chloroform but it can pull water molecules away from the chloroform and effectively dehydrate an organic solution. This drying technique is often used in organic chemistry after extracting a particular molecule into an aprotic, non-hydrogen bonding, organic solvent.