Chem Factsheet

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Why do some Ionic Compounds Dissolve and Some do Not?

To succeed in this topic you need to:-

- Be familiar with basic enthalpy change definitions including lattice enthalpy, enthalpy change of solution and enthalpy change of hydration.
- Be familiar with trends in charge and size of simple ions.
- Be familiar with the concept of polarity as applied to water molecules.
- Be familiar with the concepts of Free Energy and Entropy.
- Be familiar with the relationship $\Delta G = \Delta H - T\Delta S$

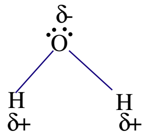
After working through this Factsheet you will:-

- Appreciate the factors involved in the dissolving of ionic compounds in water
- Understand that the overall outcome depends on a fine balance between a variety of factors.

This Factsheet will present an overview of the key factors involved in the dissolving of ionic compounds.

Dissolving

The relatively large difference in electronegativity between hydrogen and oxygen, together with the shape of the molecule, mean that a water molecule is very polar.



This means that water molecules can form strong electrostatic attractions with ions. For cations (+ve) the negative end of water's dipole will be attracted towards the ion and for anions (-ve) the positive end of water's dipole will be attracted.

In general, the greater the charge on an anion or cation and the smaller its size, the greater will be its attraction for water molecules. In other words, more charge dense ions attract water molecules more strongly.

The enthalpy of hydration, $\Delta H^\ominus_{hyd}$, of an ion is the enthalpy change when one mole of free gaseous ions is dissolved completely in water to form one mole of aqueous ions. As energy is released when bonds form, this is an exothermic process whose magnitude gives an indication of the strength of electrostatic attraction between the ions and water molecules.Some typical values of $\Delta H^\ominus_{hyd}$ are:

Ion	Ionic Radius / pm	$\Delta H^\ominus_{hyd}$ kJ mol^{-1}
Li^+	76	–538
Na^+	102	–424
K^+	138	–340
Be^{2+}	45	–2524
Mg^{2+}	72	–1963
Ca^{2+}	100	–1616
F^-	133	–504
Cl^-	181	–359
Br^-	196	–328

These values show the effect of increasing ion size, as, down either Group 1, 2 or 7, $\Delta H^\ominus_{hyd}$, becomes less exothermic. As well as having a higher charge, Group 2 ions are also smaller than their Group 1 counterparts, hence the much more negative values.

These values can be explained in terms of the fact that, the greater the charge and the smaller the size of an ion (i.e. the greater its *charge density*) the stronger the attraction between the ion and the polar water molecules.

It is also interesting to note that changing the charge has a much bigger impact on the magnitude of $\Delta H^\ominus_{hyd}$ than changing the size. e.g. approximately doubling the radius from Li^+ (76 pm) to K^+ (138 pm) changes the $\Delta H^\ominus_{hyd}$ from –538 to –340 but approximately doubling the charge (for similarly sized ions) from Na^+ (102 pm) to Ca^{2+} (100 pm) creates a much more dramatic change from –424 kJ mol^{-1} to –1616 kJ mol^{-1}.

It can, in fact, be shown that $\Delta H^\ominus_{hyd} \;\alpha\; \text{charge}^2/\text{radius}$.
When an ionic compound dissolves in water the overall enthalpy change can be thought of as depending on two processes.

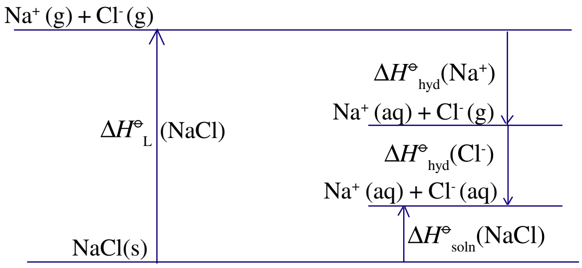
1. The ions in the ionic crystal lattice are separated from each other. This is an endothermic process, as very strong ionic bonds are being broken, and corresponds to the lattice dissociation enthalpy, $\Delta H^\ominus_L$.

2. The separate ions become surrounded by and attracted to water molecules. This is an exothermic process, as bonds are being formed, and corresponds to the enthalpy change of hydration.

   The overall process, corresponding to the enthalpy change of solution, $\Delta H^\ominus_{soln}$, depends on the balance between the enthalpy changes of hydration of the ions and the lattice dissociation enthalpy of the crystal lattice and can be exothermic or endothermic. This can be shown either as an enthalpy cycle diagram or an enthalpy level diagram.

$$\begin{tikzcd}
NaCl(s) + (aq) \arrow[rr, "\Delta H^\ominus_{soln}(NaCl)"] \arrow[dr, "\Delta H^\ominus_{L}(NaCl)"'] & & Na^+(aq) + Cl^-(aq) \\
& Na^+(g) + Cl^-(g) \arrow[ur, shift right, "\Delta H^\ominus_{hyd}(Na^+)"] \arrow[ur, shift left, "\Delta H^\ominus_{hyd}(Cl^-)"'] &
\end{tikzcd}$$

or



In general, the more exothermic the value of $\Delta H^\ominus_{soln}$ the more soluble a salt will be and the more endothermic the value, the less soluble the salt. However, as with any enthalpy change there is NO hard and fast rule to say that exothermic happens and endothermic doesn't!

In the case of sodium chloride the balance between the large endothermic lattice enthalpy and the large negative enthalpies of hydration is such that the overall enthalpy of solution is +4 kJ mol^{-1}
Whether or not a salt is soluble or not actually depends on a fine balance between several conflicting terms – especially as small, highly charged ions tend to give rise to both high lattice dissociation enthalpies **and** high enthalpies of hydration.

Entropy factors are also involved to further complicate the situation and it is hard to predict which of the several competing terms will be decisive in any given situation.

Overall we need to remember that an energetically favourable process is one for which ΔG is negative and that $\Delta G = \Delta H - T\Delta S$. ΔS for the dissociation of the lattice will be positive as the gaseous ions are much more disordered than the solid ionic lattice (making $-T\Delta S$ negative).

However, hydration of the ions is negative (making $-T\Delta S$ positive) as the hydrated ions are less disordered than the free gaseous ions. Overall, for sodium chloride, the negative $-T\Delta S$ for the dissociation of the lattice is more significant than the positive $-T\Delta S$ for the hydration of the ions such that the overall value of $-T\Delta S$ for the dissolving process is –12.9 kJ mol^{-1}.

Hence $\Delta G = +4 - 12.9 = -8.9$ kJ mol^{-1}
i.e. ΔG is favourable and we would expect Na*Cl* to be soluble.

If we compare the case for NaCl with that for LiF; the smaller ion sizes of Li^+ and F^- than those of Na^+ and Cl^- make the lattice dissociation energy of LiF more positive and the hydration energies more negative. In this case the balance is such that the overall enthalpy of solution is very slightly negative. However, in the case of LiF, the smaller ions means that they are more strongly solvated with the result that the negative ΔS for the hydration processes is more significant such that $-T\Delta S$ is, overall, positive on this occasion – more than cancelling out the slight negative ΔH, making ΔG positive, indicating that the salt is not soluble.

Practice Questions

1. (a) The standard enthalpies of hydration of the Mg^{2+} and the Cl^- ions are –1920 kJ mol^{-1} and –364 kJ mol^{-1}, respectively. Use this information, together with the fact that the enthalpy of lattice formation of magnesium chloride, $MgCl_2$, is –2493 kJ mol^{-1}, to calculate the enthalpy of solution of magnesium chloride.

   (b) Explain why ammonium chloride dissolves spontaneously in water even though its enthalpy of solution is +15 kJ mol^{-1}.

2. (a) Define the term **enthalpy of hydration**, ΔH_{hyd}, of an ion.
   (b) The table below gives some information about the sulfates of the Group 2 elements magnesium and barium.

sulfate lattice	lattice enthalpy of formation / kJ mol^{-1}	hydration enthalpy of cation / kJ mol^{-1}	solubility / mol dm^{-3}
$MgSO_4$	–2874	–1920	1.83
$BaSO_4$	–2374	–1360	1.43×10^{-6}

Use the lattice enthalpy and hydration enthalpy values to explain the difference in solubility.

Answers

1. (a) $\Delta H_{soln} = -\Delta H(\text{lattice formation}) + \Delta H(\text{hydration})$
   (or cycle with state symbols, (1) *numbers or labels)*
   = 2493 – 1920 – 2 × 364 (1)
   = -155 (1) (Note MgCl scores zero; +155 scores 1/3)

   (b) Increase in disorder on dissolving or ΔS positive (1)
   ΔG negative or $T\Delta S > \Delta H$ (1)

2. (a) Enthalpy change when 1 mol of gaseous ions **(1)** is dissolved such that further dilution causes no further heat change **(1)**
   (IGNORE "standard conditions")

   (b) **EITHER**
   $\Delta H_{soln} = -\Delta H(\text{lattice formation}) + \Delta H(\text{hydration})$ **(1)**
   Expression quoted or correctly used in at least one of the calculations below
   $\Delta H_{soln}\ MgSO_4 = -(-2874) + (-1920) = +954(kJ\ mol\ {-1})$ **(1)**
   $\Delta H_{soln}\ BaSO_4 = -(-2374) + (-1360) = +1014(kJ\ mol\ {-1})$ **(1)**

   Enthalpy of solution of $MgSO_4$ less endothermic/more exothermic/more negative than for $BaSO_4$, so $MgSO_4$ more soluble than $BaSO_4$ (or reverse argument) **(1)**

   OR
   (both) lattice energies **and** hydration enthalpies decrease from $MgSO_4$ to $BaSO_4$ (or down group) **(1)** (but) lattice energies change less **(1)**

   $\Delta H_{soln} = -\Delta H(\text{lattice formation}) + \Delta H(\text{hydration})$ **(1)** stated in words or symbols so ΔH_{soln} less exothermic/more endothermic/more positive for $BaSO_4$ so less soluble

   OR so ΔH_{soln} more exothermic/more negative/less endothermic for $MgSO_4$ so $MgSO_4$ more soluble **(1)**

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