Chem Factsheet

www.curriculum-press.co.uk Number 94

Enthalpies of Solution

To succeed in this topic you need to understand:
- standard enthalpy changes (covered in Factsheet 08);
- Hess's law (covered in Factsheet 08);
- lattice energy (covered in Factsheets 28 and 29);
- how lattice energy values vary with ionic charge and radius (covered in Factsheets 28 and 29).

After working through this Factsheet you will be able to:
- define standard enthalpy of solution;
- construct energy cycles to relate lattice energy , enthalpies of hydration and enthalpy of solution;
- calculate enthalpies of solution by applying Hess's Law to such energy cycles;
- comment on the likelihood of solubility based on enthalpy of solution data
- comment on solubility trends in terms of variations in lattice energy and enthalpies of hydration.

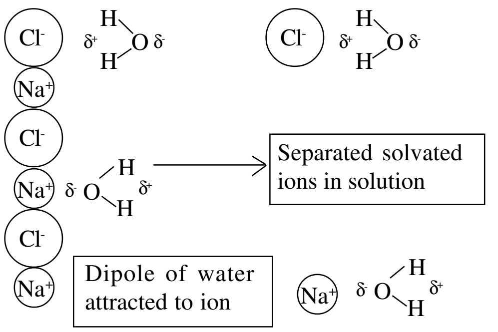
Water is probably the most common solvent used in chemistry and every day life. When water "dissolves" another substance (the solute) they form a homogeneous mixture (the solution) at a molecular or ionic level and, by various means, water molecules are found to bond to the solute particles. The solute particles are said to become *solvated* or *hydrated*.

However, observations tell us that not all substances will dissolve in water. For example, at room temperature, silicon dioxide (sand) is insoluble whereas ethanol ("alcohol") is infinitely soluble and sodium chloride (salt) is only moderately soluble, soon becoming saturated.

Here, you will study what happens at a molecular and ionic level when an *ionic* substance (e.g. sodium chloride, $Na^+Cl^-(s)$) dissolves in water and you will examine the energy changes involved at each stage in order to develop a means of explaining why some ionic compounds are soluble and some are insoluble. It will also allow you to explain trends in solubility. For instance, why do the group II sulphates become less soluble down the group whereas the hydroxides become more soluble?

As illustrated in fig. 1, when a crystal of sodium chloride is added to water, either end of the polar water molecules are attracted to the oppositely charged ions at the surface of the crystal forming *ion-dipole bonds*.

Fig 1



This bond formation is an exothermic process and the energy released is sufficient to overcome the ionic bonding forces holding the ions in their lattice positions. Hence, the hydrated ions detach from the crystal surface and diffuse away resulting in solution formation. This means other water molecules can bond to the ions in the newly exposed crystal surface and the processes of hydration, detachment and diffusion can repeat until the whole crystal has dissolved or the solution reaches saturation.

This is usually represented by an equation of the form:

$NaCl(s) + aq \rightarrow Na^+(aq) + Cl^-(aq)$

Conversely for some other ionic compounds, if the energy released by ion hydration is insufficient to overcome the electrostatic forces between ions, the solute will generally be less likely to dissolve.

In essence, an ionic solute is likely to be water soluble if the energy required to break up the ionic lattice is exceeded (or very nearly so) by the energy released by ion hydration. In short, if the overall process is exothermic (or only slightly endothermic) solubility is likely.

Before looking at the quantitative energetics of the dissolving process we need to define the relevant standard enthalpy changes. These are:

1. Lattice Dissociation Energy, ΔH°_{latt} :
this is the ***energy REQUIRED when ONE MOLE of a SOLID IONIC compound is converted to its CONSTITUENT GASEOUS IONS, measured under standard conditions of temperature and pressure (10^5 Pa and 298K).***

e.g. $NaCl(s) \rightarrow Na^+(g) + Cl^-(g)$; +780 kJ mole^{-1}
$MgO(s) \rightarrow Mg^{2+}(g) + O^{2-}(g)$; +3607 kJ mole^{-1}

(These are ALWAYS endothermic changes because bonds are being broken.)

2. Enthalpy of Hydration, ΔH°_{hydn} :
this is the ***energy RELEASED when ONE MOLE of GASEOUS IONS dissolve in EXCESS water, measured under standard conditions of temperature and pressure (10^5 Pa and 298K).***

eg $K^+(g) + (aq) \rightarrow K^+(aq)$; -305 kJ mol^{-1}
$Cl^-(g) + (aq) \rightarrow Cl^-(aq)$; -381 kJ mol^{-1}

(These are ALWAYS exothermic changes because bonds are being formed.)

3. Enthalpy of Solution, ΔH°_{soln} :
This is the **energy change which occurs when ONE MOLE of a substance DISSOLVES IN EXCESS WATER, measured under standard conditions of temperature and pressure (10^5 Pa and 298K).**

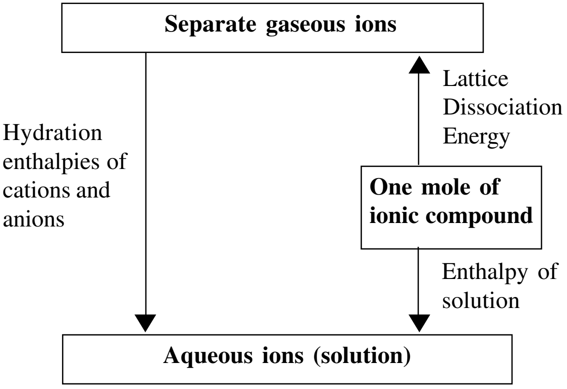
e.g. $CaCl_2(s) + (aq) \rightarrow Ca^{2+}(aq) + 2Cl^-(aq)$; -83 kJ mole^{-1}
$NaCl(s) + (aq) \rightarrow Na^+(aq) + Cl^-(aq)$; +10 kJ mole^{-1}

(These may be exothermic or slightly endothermic changes .)

***Exam Hint** : Many marks are lost by incomplete or inaccurate definitions of standard enthalpy changes. Each definition should include three elements; quantity, process and conditions.*

These three quantities can be connected in an energy cycle as shown in Fig 2.

Fig 2



Hess's Law can then be applied giving :

Enthalpy of Solution = **Lattice Dissociation Energy** + **Sum of the Hydration Enthalpies of ALL ions**

This is a *general* energy cycle which can be used to calculate ΔH°_{soln} , ΔH°_{hydn} of anion or cation or ΔH°_{latt} provided all other values are available.

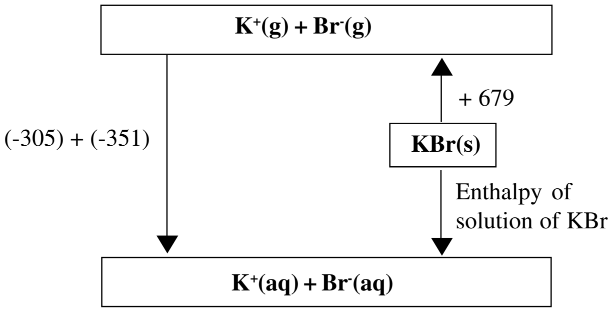
Exam Hint : *To avoid errors in applying Hess's Law, a simple device is to use the fact that the* ***sum of the clockwise enthalpy changes must equal the sum of the anti-clockwise enthalpy changes****.*

Data:

HYDRATION ENTHALPIES (/kJ mole^{-1})				**LATTICE DISSOCIATION ENTHALPIES (/kJ mole^{-1})**				
$H^+(g)$	-1075	$F^-(g)$	-457		F^-	Cl^-	Br^-	I^-
$Li^+(g)$	-499	$Cl^-(g)$	-381	Li^+	+1031	+848	+803	+759
$Na^+(g)$	-390	$Br^-(g)$	-351	Na^+	+918	+780	+742	+705
$K^+(g)$	-305	$I^-(g)$	-307	K^+	+817	+711	+679	+651
$Mg^{2+}(g)$	-1891	$OH^-(g)$	-460	Mg^{2+}	+2957	+2526	+2440	+2327
$Ca^{2+}(g)$	-1562			Ca^{2+}	+2630	+2258	+2176	+2074
$Sr^{2+}(g)$	-1337			Sr^{2+}	+2492	+2156	+2075	+1963

Example 1 Using the data table, calculate the heat of solution of potassium bromide, KBr(s)

Applying the general energy cycle seen in fig.2 to potassium bromide and inserting the relevant data using the data table produces the cycle:



Exam Hint: *Take care to show the correct states of matter for each species in the cycle.*

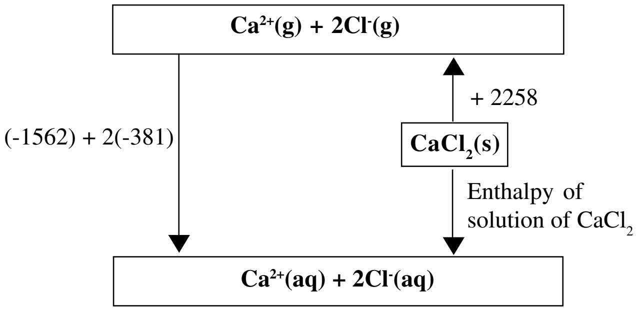
Applying Hess's Law, gives:

$$\Delta H^\circ_{soln}[KBr(s)] = (+679) + (-305) + (-351)$$
$$= \mathbf{+\ 23\ kJ\ mole^{-1}}$$

Exam Hint: *Make sure you include units with your final answer.*

Example 2 Using the data table, calculate the heat of solution of calcium chloride, $CaCl_2(s)$

Again, applying the general energy cycle and inserting the relevant data using the data table, produces the cycle shown:



Applying Hess's Law, gives:

$$\Delta H^\circ_{soln}[CaCl_2(s)] = (+2258) + (-1562) + 2(-381)$$
$$= \mathbf{-66\ kJ\ mole^{-1}}$$

Exam Hint*: Make sure you allow for the number of moles of ions being hydrated. In this example 2 x (-381) is needed because calcium chloride contains 2 moles of chloride ions per mole.*

Relating Enthalpies of Solution to Trends in Solubility

Sulphate	Solubility (/mol dm^{-3}) at 25°C	Hydroxide	Solubility (/mol dm^{-3}) at 25°C
$MgSO_4$	1.83	$Mg(OH)_2$	2.00×10^{-4}
$CaSO_4$	4.66×10^{-2}	$Ca(OH)_2$	1.53×10^{-2}
$SrSO_4$	7.11×10^{-4}	$Sr(OH)_2$	3.37×10^{-2}
$BaSO_4$	9.43×10^{-6}	$Ba(OH)_2$	0.150

These data show that the solubilities of the group II sulphates *decease* down the group whereas the solubilities of the corresponding hydroxides *increase*. This suggests that the enthalpy of solution becomes *more endothermic* for the sulphates causing them to become less likely to dissolve. However, the enthalpy of solution must become *more exothermic* for the hydroxides causing them to become more likely to dissolve. Why do these opposite trends occur?

Remember, enthalpies of solution are calculated from two basic factors:

ΔH°_{soln} = **ENDOTHERMIC** Lattice Dissociation Energy **+** **EXOTHERMIC** Hydration Enthalpies.

In order to account for the different trends in solubility for the group II sulphates and hydroxides it is necessary to look at the *relative* trends in lattice energies and hydration energies down the group.

Ion	ΔH°_{hydn}(/kJ mole^{-1})	Sulphate	Lattice Energy (/kJ mole^{-1})	Hydroxide	Lattice Energy (/kJ mole^{-1})
$Mg^{2+}(g)$	-1891	$MgSO_4$	+2999	$Mg(OH)_2$	+3087
$Ca^{2+}(g)$	-1562	$CaSO_4$	+2710	$Ca(OH)_2$	+2628
$Sr^{2+}(g)$	-1337	$SrSO_4$	+2550	$Sr(OH)_2$	+2333
$Ba^{2+}(g)$	-1128	$BaSO_4$	+2427	$Ba(OH)_2$	+2053

Using these data, the enthalpy of solution can be estimated for each compound.

ΔH°_{soln} for $MgSO_4 = +2999 - 1891 + (\Delta H^\circ_{hydn}[SO_4^{2-}]) = +108$ + a constant

ΔH°_{soln} for $CaSO_4 = +2710 - 1562 + (\Delta H^\circ_{hydn}[SO_4^{2-}]) = +1148$ + a constant

ΔH°_{soln} for $SrSO_4 = +2550 - 1337 + (\Delta H^\circ_{hydn}[SO_4^{2-}]) = +1213$ + a constant

ΔH°_{soln} for $BaSO_4 = +2427 - 1128 + (\Delta H^\circ_{hydn}[SO_4^{2-}]) = +1299$ + a constant

ΔH°_{soln} for $Mg(OH)_2 = +3087 - 1891 + (2\Delta H^\circ_{hydn}[OH^-]) = +1196$ + a constant

ΔH°_{soln} for $Ca(OH)_2 = +2628 - 1562 + (2\Delta H^\circ_{hydn}[OH^-]) = +1066$ + a constant

ΔH°_{soln} for $Sr(OH)_2 = +2333 - 1337 + (2\Delta H^\circ_{hydn}[OH^-]) = +996$ + a constant

ΔH°_{soln} for $Ba(OH)_2 = +2053 - 1128 + (2\Delta H^\circ_{hydn}[OH^-]) = +925$ + a constant

These calculations show that the enthalpies of solution of the sulphates become more endothermic, resulting in a decrease in solubility. However, those of the hydroxides become more exothermic, resulting in an increase in solubility.

In both cases the endothermic lattice energy contribution decreases (becomes more exothermic) as the cation size increases but, because of the smaller size of the hydroxide ion, the decrease is more rapid for the hydroxides than for the sulphates. This more than compensates for the corresponding decrease (becoming less exothermic) in the hydration energies as the cations increase in size. Overall, the endothermic contributions by the lattice energies become less significant in the enthalpy of solution calculations for the hydroxides than for the sulphates.

Practice Questions

1. Using the data tables and an appropriate energy cycle, calculate a value for the molar enthalpy of a solution of magnesium iodide, $MgI_2(s)$.

2. Using the data tables and an appropriate energy cycle, calculate a value for the molar enthalpy of a solution of lithium chloride, LiCl(s).

3. (a) Write equations, including state symbols, for which the enthalpy change is

   (i) the enthalpy of hydration of an ion M^+

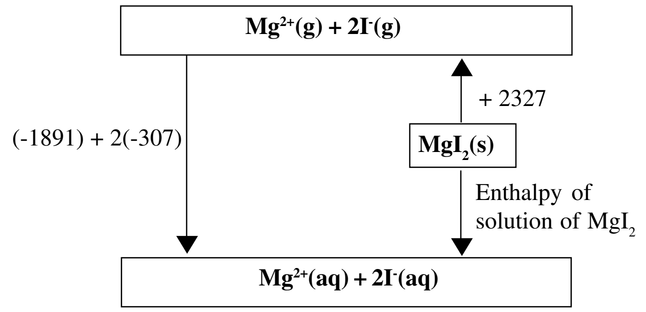
   (ii) the enthalpy of solution of a salt MX

   (b) The standard enthalpy change for
   $NaF(s) \rightarrow Na^+(g) + F^-(g)$ is + 918 kJmol^{-1}.
   Name this standard enthalpy change.

   The enthalpy of solution of sodium fluoride is +71 kJ mol^{-1}. The enthalpy of hydration of a fluoride ion is -457 kJ mol^{-1}. Use these data, an appropriate energy cycle and the enthalpy value given in part (b) to calculate the enthalpy of hydration of a sodium ion.

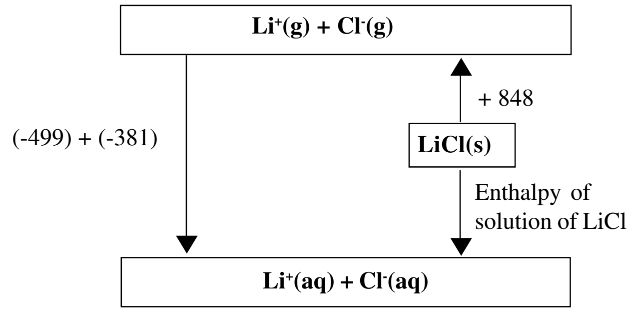
Answers

1.



Enthalpy of solution of MgI_2
= +2327 - 1891 – 614
= -178 kJ mole^{-1}

2.

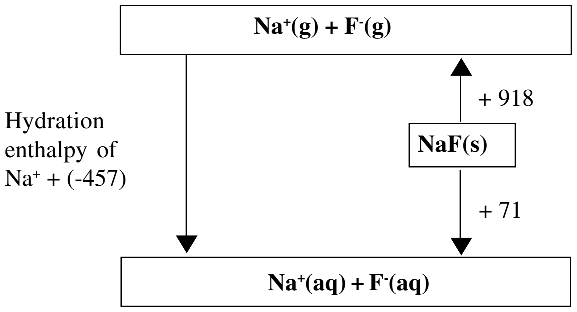


Enthalpy of solution of LiCl
= +848 - 499 – 381
= - 32 kJ mole^{-1}

3. (a) (i) $M^+(g) + aq \rightarrow M^+(aq)$
(ii) $MX(s) + aq \rightarrow M^+(aq) + X^-(aq)$

(-499) + (-381)

(b) The lattice dissociation energy



$+17 = +918 + \Delta H^{\circ}_{hydn}[Na^+] - 457$

$\Delta H^{\circ}_{hydn}[Na^+] = +71 - 918 + 457$
$= -390$ kJ mole^{-1}

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