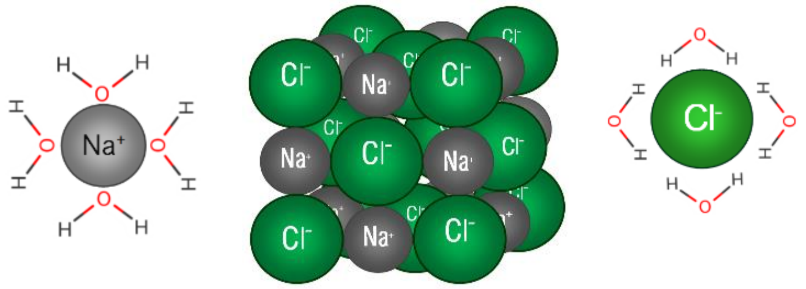
Enthalpy of Solution, $\Delta_{soln}H$



Introduction

You will probably have learned about an enthalpy change called the **Lattice Enthalpy, $\Delta_{LE}H$.** If you haven't already covered this, then you should read the primer called **Lattice Enthalpy and Born-Haber Cycles**, which is in *CramNow*.

Enthalpy of Solution, $\Delta_{soln}H$

This is the enthalpy change when 1 mole of ionic lattice is dissolved in a solvent to produce a very dilute solution (strictly, infinitely dilution!)

The **solvent** is typically water.

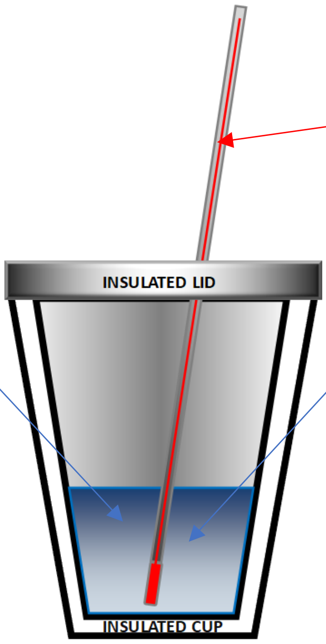
Note that the subscript (in this case ***soln***), should be placed **before the symbol**, H. You will often find this subscript placed after the H. IUPAC[*] states that that the subscript should be placed before H. To place it after the H would suggest that there is a change in the value of the named enthalpy change. This clearly not the case so we place it before H.

For a common example, such as that involving NaCl, this definition is represented by the chemical equation:

$$NaCl_{(s)} + aq \rightarrow Na^{+}_{(aq)} + Cl^{-}_{(aq)}$$

This enthalpy change is one that is very easy to find, by experiment. As an A level student, you will almost certainly carry out this experiment.

It simply involves dissolving a known mass of a given compound in a known volume of water. This must be done in an insulated cup (calorimeter). To improve accuracy, heat losses are further reduced by the use of an insulated lid. See below



Accurate thermometer. This typically will measure to an accuracy 0.1 °C

Known mass of **dry compound** added.

This allows you to calculate the number of moles that you are dissolving

Known **volume** (therefore known **mass**) of water.

This is needed so that you can work out how much **heat energy** was **released to** or **absorbed from** the water during the process of dissolving.

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[*] IUPAC stands for the *International Union of Pure and Applied Chemistry*. Amongst many other important functions, this organisation creates the many rules and conventions that we adhere to in the world of chemistry.

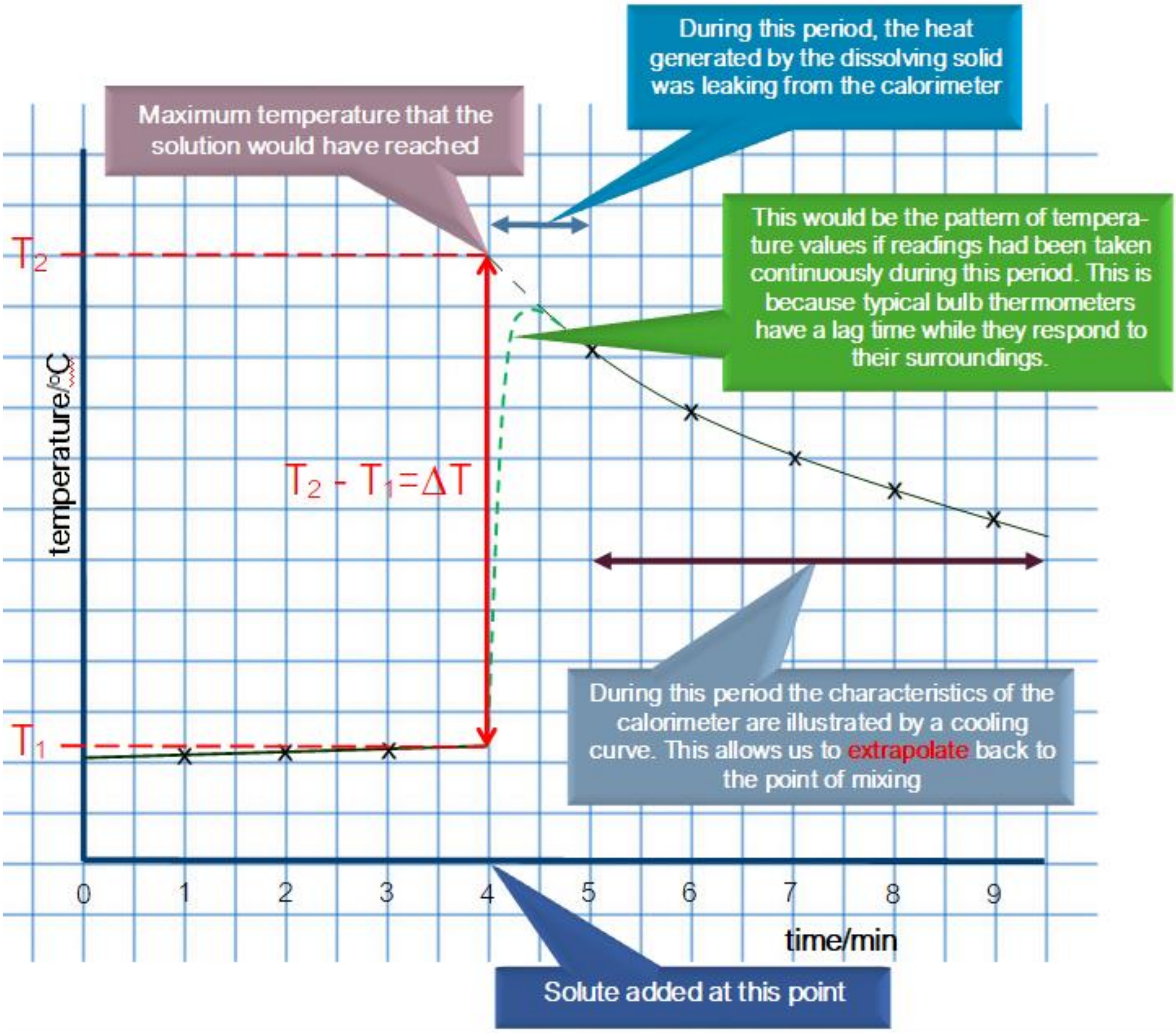
This experiment will create a temperature rise or fall in the water that is dissolving the compound. The water can be considered to be the ***surroundings*** in this context. It will be the water that **absorbs heat from** the process or **donates heat to** the process. The process (dissolving solid) is considered to be the ***system*** in this context. The fact that the system is insulated means that no heat energy can enter or leave the experiment. This means that this set-up is known as an *isolated system*. You have probably heard of a *closed system*. A *closed system* is a set-up that prevents loss or gain of matter but does allow heat into or out of itself.

So, from the experiment, you will have:

1. A **mass** of compound in **g**
2. A **volume** of water in **cm^3**
3. An initial **temperature** in **°C**
4. A final **temperature** in **°C**

Ideally, this is done by recording the temperature at fixed periods and then plotting a graph of ***temperature*** (y axis) against ***time*** (x axis). The cooling curve part of the graph is extrapolated back to the point of mixing to give the maximum temperature rise at the point of mixing. See diagram below.

Alternatively, a simple maximum temperature can be recorded but this is less accurate



Maximum temperature that the solution would have reached

During this period, the heat generated by the dissolving solid was leaking from the calorimeter

This would be the pattern of temperature values if readings had been taken continuously during this period. This is because typical bulb thermometers have a lag time while they respond to their surroundings.

During this period the characteristics of the calorimeter are illustrated by a cooling curve. This allows us to extrapolate back to the point of mixing

Solute added at this point

The mass can be converted into the number of moles, n

The heat change in the water (the surroundings) can be calculated using the simple equation that you should be familiar with:

$$\boxed{\text{Heat change in water} = q = m\,C\,\Delta T}$$

- q is measured in J

- m is the mass of **solvent** (you can also use the mass of solution which includes the mass of solute.) DO NOT simply use the mass of the solute. REALLY COMMON ERROR!

- C is the specific heat capacity of the water. Its value is 4.18 J $mol^{-1}K^{-1}$

- ΔT is the temperature change measured in °C (and therefore change measured in K)

Points to note:

If ΔT is positive, the water got warmer and the value of q must be **positive.**

To turn this into an enthalpy of solution, we need to work out whether the system (the dissolving solid) absorbed heat energy from the water (the surroundings) or released heat energy to the water (the surroundings).

REMEMBER, we are wanting to **say something about the system** (the process of dissolving).

Enthalpy changes are always about the system!

BUT, just like we always do, we took measurements in the **surroundings** (the water in which the process took place and the place where the thermometer is recording the temperature).

Heat that the surroundings absorbed was energy that the process released. The surroundings' gain was the system's loss. The negative sign in the equation below is there to account for this fact.

We can write an equation to convert q into $\Delta_{soln}H$.

$$\boxed{\Delta_{soln}H = \frac{-q}{n}}$$

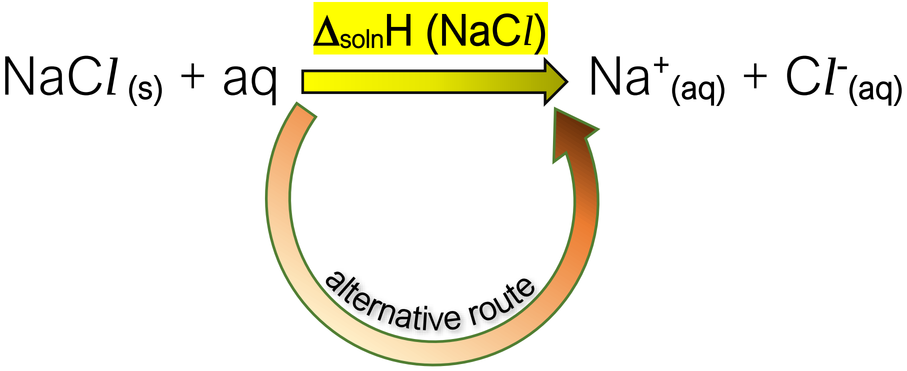
This makes sense. Exothermic processes have negative enthalpy changes.

Always apply some chemical common sense when you give answers to enthalpy change calculations like this. If the temperatures rise, there must have been an exothermic process occur and therefore, ΔH must be negative!

This goes back to the definition and convention for enthalpy changes. This states the *enthalpy change is the heat* ***absorbed*** *by the system* (*at constant pressure*. Don't worry about this pressure reference, right now).

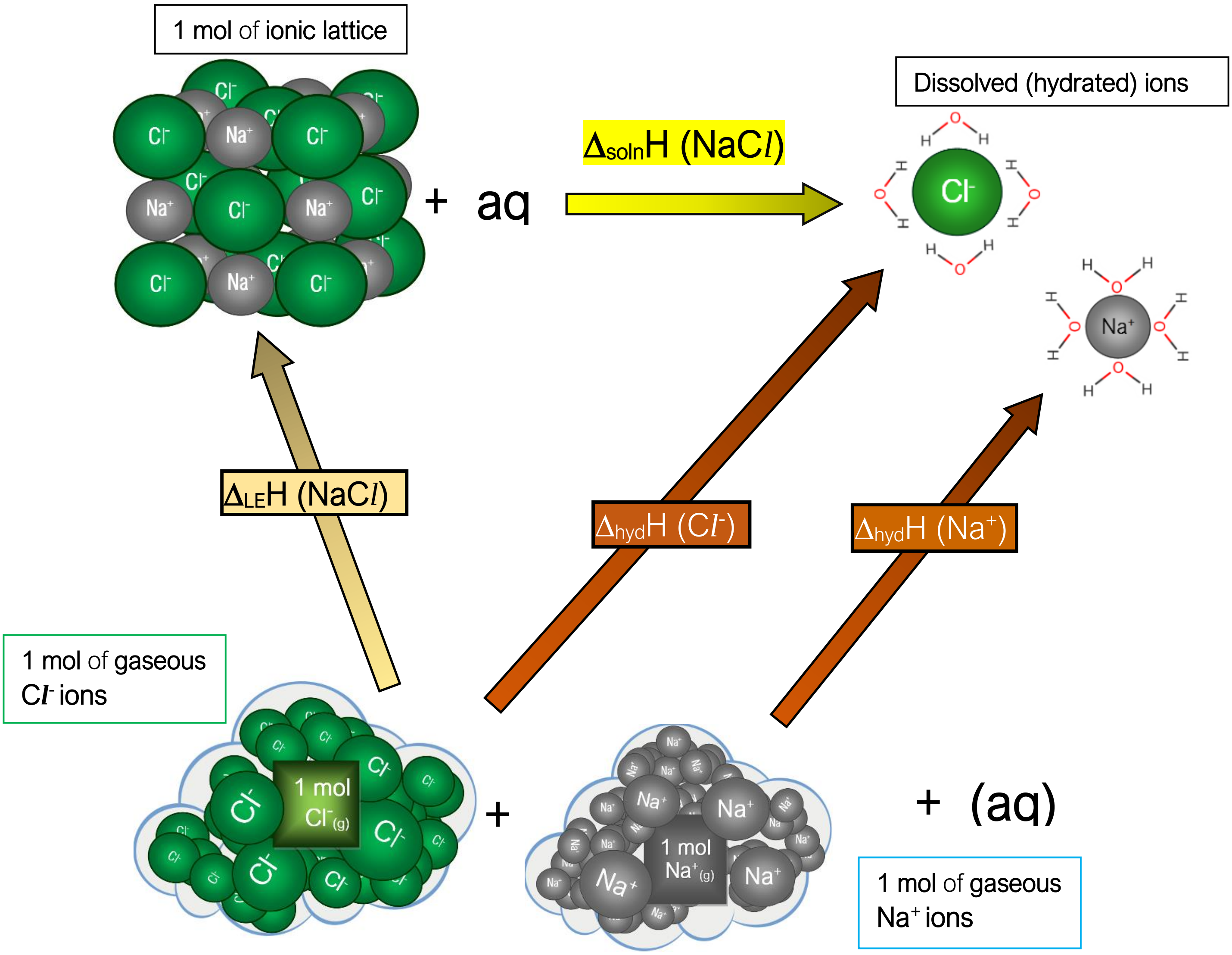
Developing A Hess Cycle for Enthalpy of Solution, $\Delta_{soln}H$

We will try to build an alternative route that can take us from the crystalline ionic lattice and water to the dilute solution of the compound.



$$NaCl_{(s)} + aq \xrightarrow{\Delta_{soln}H\ (NaCl)} Na^+_{(aq)} + Cl^-_{(aq)}$$

Here is a Hess Cycle illustrating the nature of the chemical species involved.



Applying Hess's Law, we can write the following:

$$\Delta_{soln}H\ (NaCl) = (-\ \Delta_{LE}H\ (NaCl)) + (+\Delta_{hyd}H\ (Na^+)) + (+\Delta_{hyd}H\ (Cl^-))$$

Rearranged slightly, we have:

$$\Delta_{soln}H\ (NaCl) = (\Delta_{hyd}H\ (Na^+)) + (\Delta_{hyd}H\ (Cl^-)) + (-\ \Delta_{LE}H\ (NaCl))$$

Inserting values:

$$\Delta_{soln}H\ (NaCl) = (-406) + (-378) + (-\ -787) = +3\ \text{kJ mol}^{-1}$$

In general, we can write:

$$\boxed{\Delta_{soln}H = [\Sigma\ \text{Enthalpies of Hydration of ions}] - [\ \text{Lattice Enthalpy}]}$$

Question 1

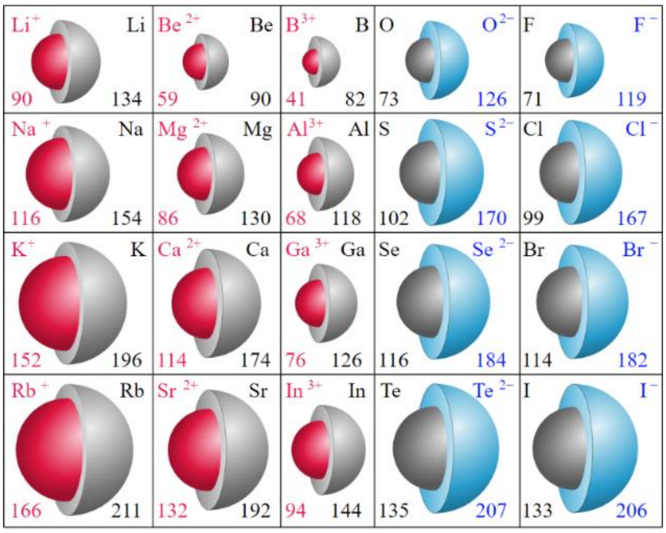
Using data from the table below, calculate $\Delta_{LE}H$ (KF).

solution $\Delta_{soln}H$	/kJmol^{-1}	hydration $\Delta_{hyd}H$	/kJmol^{-1}
LiCl	-37.0	Li^+	-520
NaF	+71	Na^+	-406
NaCl	+3.88	K^+	-322
NaBr	-1.0	Ag^+	-473
NaI	-7.5	Mg^{2+}	-1921
KF	-17.7	Ca^{2+}	-1650
KCl	+26	Al^{3+}	-4665
NaOH	-44.5		
KOH	-57.6	F^-	-506
NH_4NO_3	+25	Cl^-	-378
NH_4Cl	+17	Br^-	-336
		O^{2-}	-937

Atomic and Ionic Radii for a Range of Elements.

The **atoms** are coloured grey. Cations are red and anions are blue. Radii are measured in pm (10^{-12} m)

GROUP 1 GROUP 2 GROUP 3 GROUP 6 GROUP 7



This diagram and data were taken from Wikipedia.

Question 2

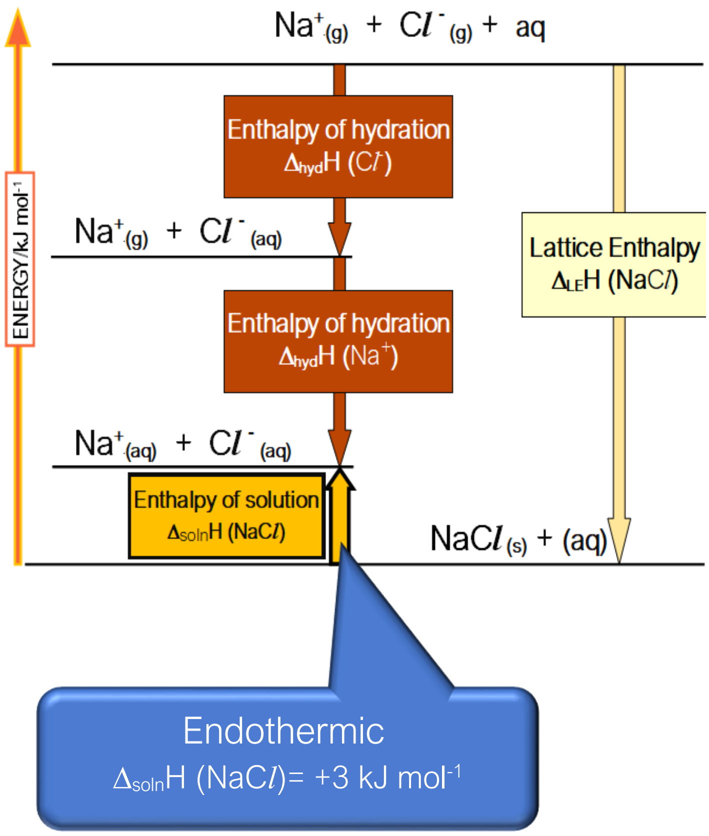
By inspecting the data in the tables above, what is the relationship between the size of ions and the hydration enthalpy? (see diagrams below for the answer)

Question 3

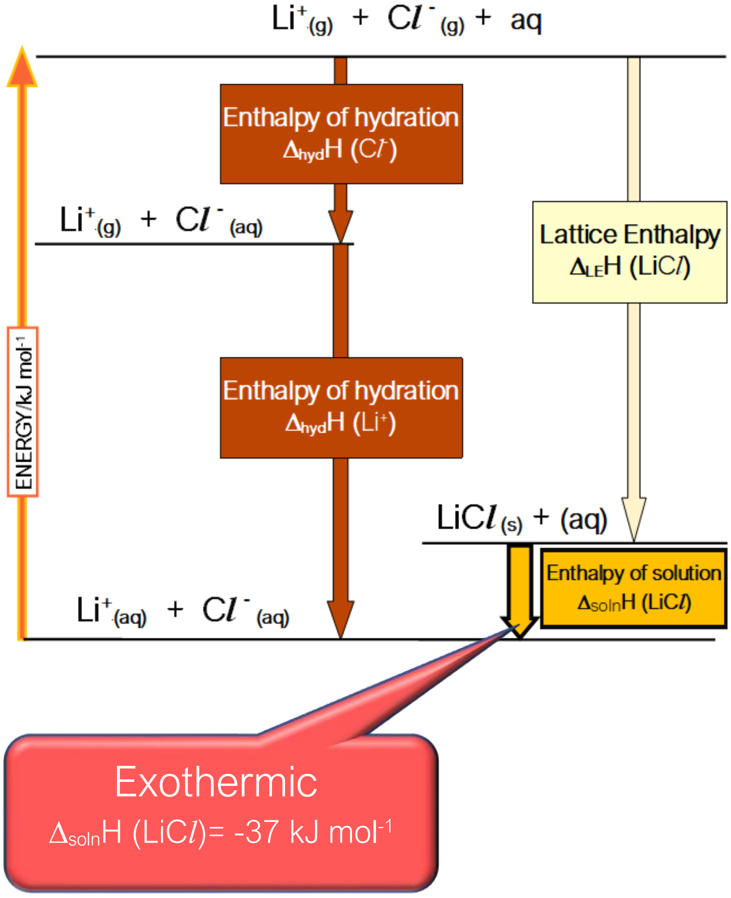
By inspecting the data in the tables above, what is the relationship between the size of the charge on ions and the hydration enthalpy? (see diagrams below for the answer)

Comparison of $\Delta_{soln}H$ for Sodium Chloride with Lithium Chloride

Hess Cycle for **NaC*l***



Hess Cycle for **LiC*l***



Points to note:

1. The Lattice Enthalpy $\Delta_{LE}H$ (LiC*l*) is more exothermic than $\Delta_{LE}H$ (NaC*l*).
2. BUT, the Hydration Enthalpy $\Delta_{hyd}H(Li^+)$ is significantly more exothermic than $\Delta_{hyd}H(Na^+)$ and by a greater magnitude that the difference in the Lattice Enthalpies.
3. These two factors, when considered together, help to explain why the Enthalpy of Solution of LiC*l* is exothermic and the Enthalpy of Solution of NaC*l* is endothermic.

****IMPORTANT NOTE! READ!****

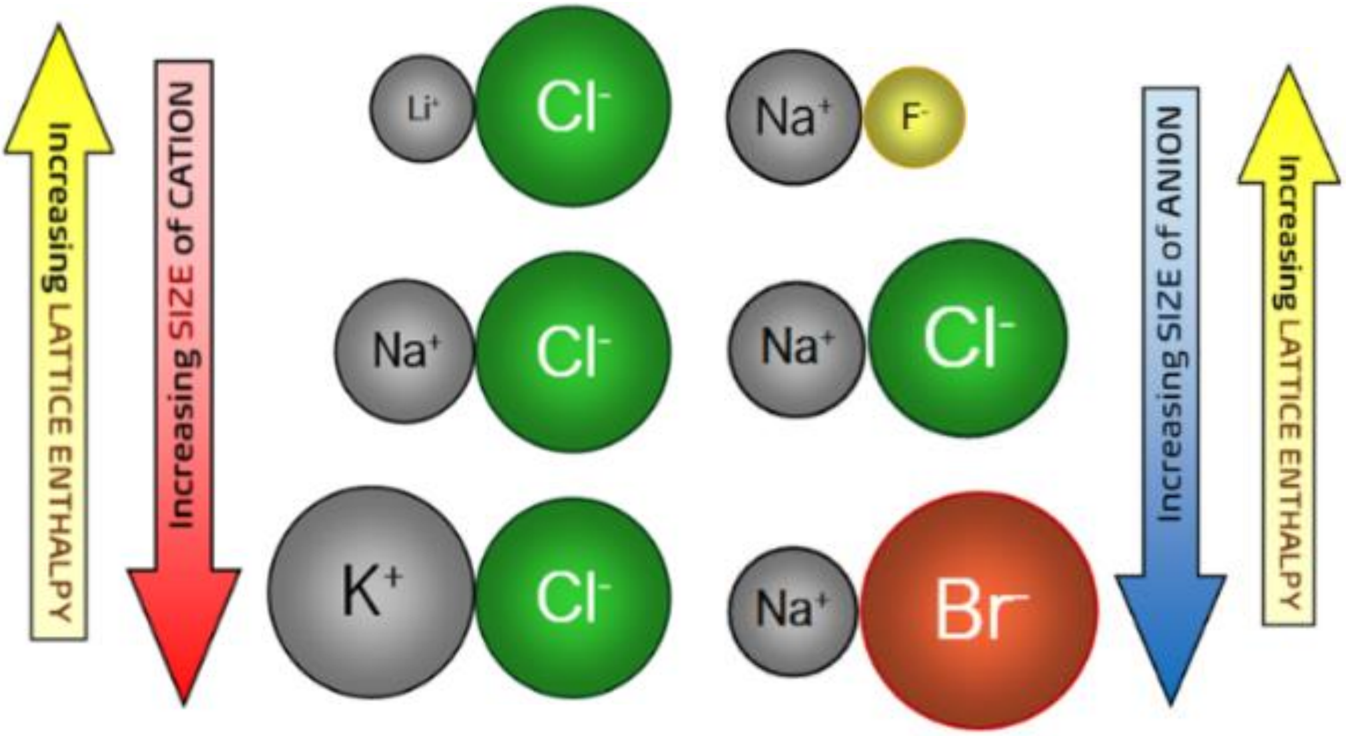
You will often see slightly different values for the same enthalpy change, depending upon your source! When you use data from different sources, it leads to slight differences in calculated values. Don't worry about a few kJ mol^{-1} difference over many hundreds or thousands of kJ mol^{-1}.

When selecting data over 25 years, I have tried to make them all agree with each other, but it is simply impossible. So, don't panic if you see different literature values to those presented here.

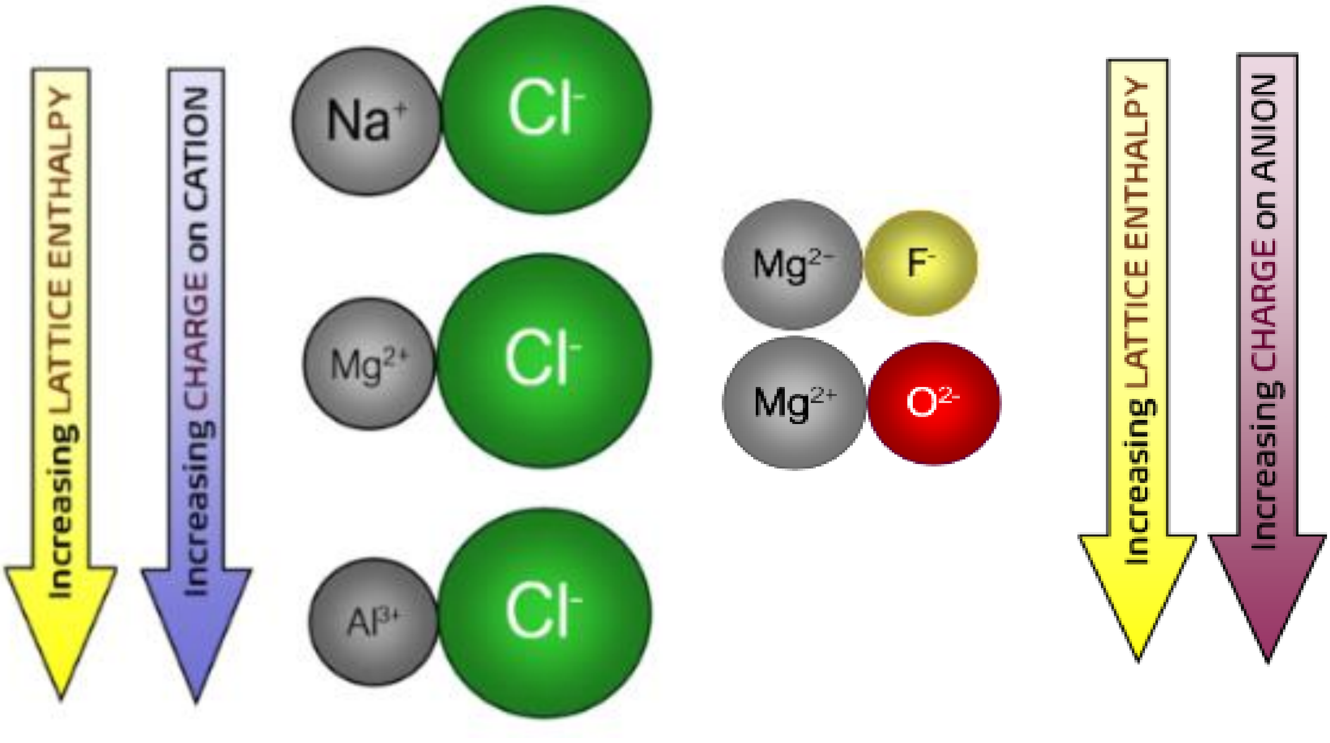
In an exam question, all the data will be internally consistent.

In summary:

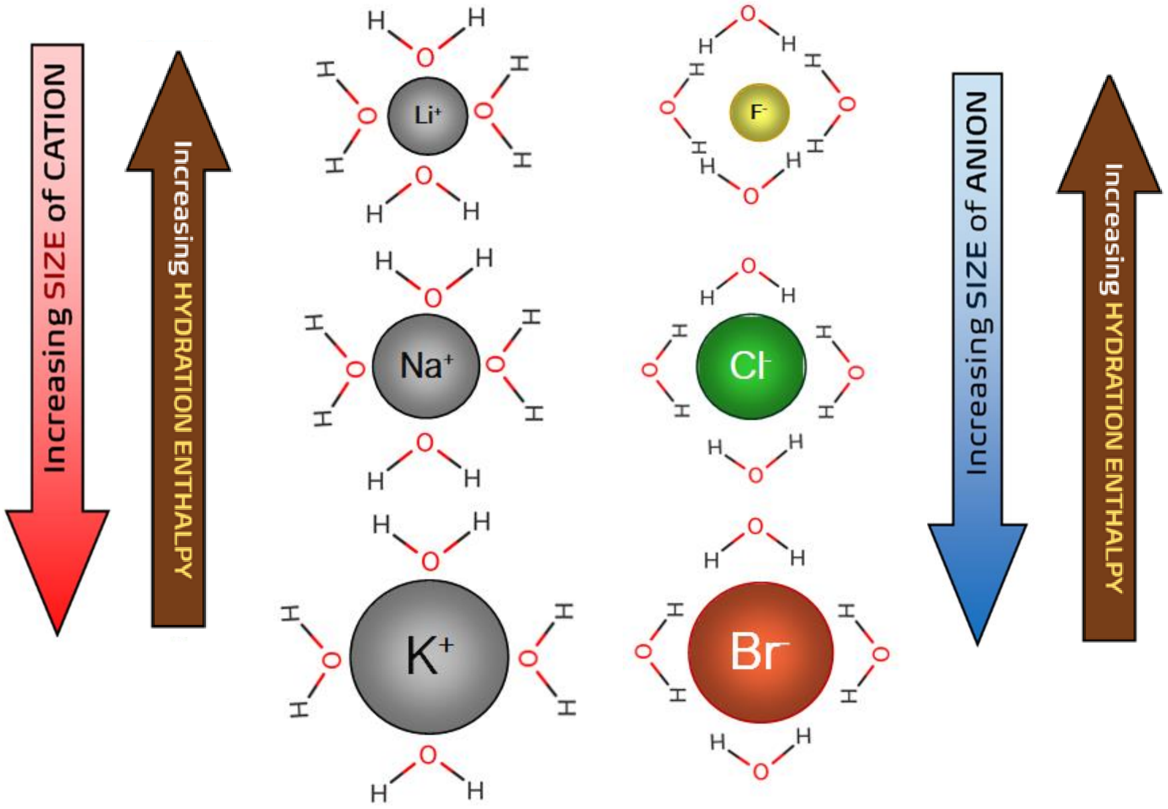
Effect of the **SIZE of IONS** on **LATTICE ENTHALPY, $\Delta_{LE}H$**



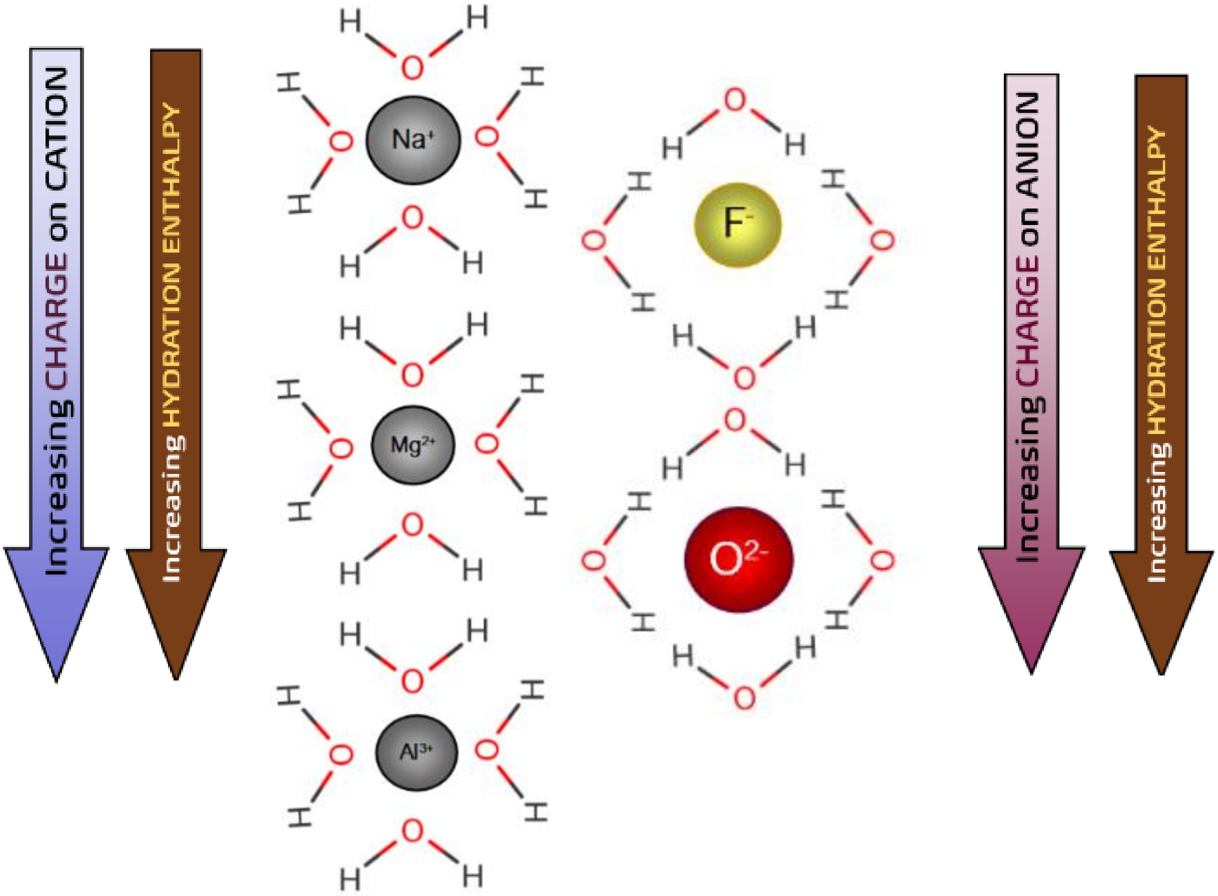
Effect of the the **SIZE of IONIC CHARGE** on the size of **LATTICE ENTHALPY, $\Delta_{LE}H$**



Effect of the **SIZE of IONS** on the size of **HYDRATION ENTHALPY**, $\Delta_{hyd}H$



Effect of the **SIZE of IONIC CHARGE** on the size of **HYDRATION ENTHALPY**, $\Delta_{hyd}H$



Question 4

Calculate the mass of ammonium nitrate $NH_4NO_{3(s)}$ that would need to dissolve in 40.0 cm^3 of water to give a temperature fall of 10.0 °C.

Assume that the calorimeter is a highly efficient thermal insulator with insignificant heat capacity.

Data: Lattice energy of $NH_4NO_{3\,(s)}$ –646
Enthalpy of hydration $NH_4{}^{+}{}_{(g)}$ –307
Enthalpy of hydration $NO^{3-}{}_{(g)}$ –314

ANSWER

Heat change in water = q = m C ΔT

q = 40.0g x 4.18 J °C^{-1} g^{-1} x -10.0°C = -1672 J

$\Delta_{soln}H = \frac{-q}{n}$

You need to obtain ***n*** so that you can calculate a mass of ammonium nitrate.
You have calculated ***q*** so you now need to find $\Delta_{soln}H$ ($NH_4NO_{3\,(s)}$)

$\Delta_{soln}H = [\Sigma$ **Enthalpies of Hydration of ions**$] - [$ **Lattice Enthalpy**$]$

$\Delta_{soln}H(NH_4NO_{3\,(s)}) = [(-307)+(-314)] - [-646] = 25$ kJ mol^{-1}
$-q/\Delta_{soln}H$ ($NH_4NO_{3\,(s)}$) = n = -1672 J / 25 kJ mol^{-1}= 0.06688 mol
mass = molar mass(NH_4NO_3) x n = 80.0 g mol^{-1} x 0.06688 mol= 5.35 g = answer