Assignment: Enthalpy of Solution of Ionic Compounds

2018-2019

A factor that determine the solubilities of salts is whether the enthalpy change of solution, $\Delta H_{sol,}$, of the salt is positive or negative. The enthalpy change is the energy associated with the process:

$$M^{+z}X^{-z}_{(s)} \longrightarrow M^{+z}_{(aq)} + X^{-z}_{(aq)}$$

The enthalpy change of solution, ΔH_{sol} is the enthalpy change when one mole of solute dissolves in an infinite volume of water, (so that further dilution has no additional effect).

The following relationship was deduced from the lab performed in the class:

$$\mathbf{\Delta H_{solution} = \Delta H_{hydration} - \Delta H_{lattice}}$$

The enthalpy of solution is a small difference between two much larger quantities, hence it can change from positive to negative, with only relatively small variations in either lattice enthalpy or hydration enthalpy.

If ΔH_{sol} is positive, the salt is likely to be insoluble or of very low solubility. I
If ΔH_{sol} is approximately zero or negative, then the salt is likely to be soluble or very soluble.

This has some bearing on the solubility of ionic compounds, because most spontaneous changes have negative ΔH^0 values. The following generalization can be made:

'The more negative the enthalpy of solution, the more soluble the substance.'

Assignment

1. Refer to the following **Table I**, which shows hydration enthalpies and ionic radii for a number of anions and cations to answer the following questions:

Table I

Cation	**Ionic Radius (nm)**	**ΔH^0_{hyd} (kJ mol^{-1})**
Group I		
Li^{+1}	0.060	- 159
Na^{+1}	0.095	- 406
K^{+1}	0.133	- 322
Rb^{+1}	0.148	- 301
Cs^{+1}	0.169	- 276
Group II		
(Be^{+2})	0.013	- 2450
Mg^{+2}	0.065	- 1920
Ca^{+2}	0.099	- 1650
Sr^{+2}	0.113	- 1480
Ba^{+2}	0.135	- 1380

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a) From Table determine two pairs of ions of different charge in which the ionic radius is almost the same. What is the effect on hydration enthalpy of varying the charge?
b) What explanation can you give for your answer to (a)?
c) For ions of the same charge, what is the effect on hydration enthalpy of increasing radius?
d) What explanation can you give for your answer to (c)?
e) What similar trends and explanations may be deduced for anions?

Conclusions:
Enthalpy changes of hydration are more negative:
i. If the ion is small
ii. If the ion has two or three units of charge on it. (ΔH_{hyd} (Al^{+3}) = – 4750 kJ mol^{-1})

Lattice energies are determined by the magnitude of:
i. The charge on the ion
ii. The inter-ionic distance
(iii. The type of lattice: the way the ions pack together in the lattice, i.e. the lattice type).

2. The energy evolved when one mole of gaseous calcium ions is hydrated according to the equation:

$$Ca^{+2}_{(g)} + aq \dashrightarrow Ca^{+2}_{(aq)}$$

is greater than the corresponding value for barium ions, Ba^{+2}. Justify.

3. In order to calculate a value for the enthalpy change for the reaction:

$$LiCl_{(s)} + aq \dashrightarrow Li^{+1}_{(aq)} + Cl^{-1}_{(aq)}$$

which of the following is (are) necessary?
a) Ionisation energy of Li b) Electron affinity of Cl c) Lattice energy of LiCl

4. Aluminium oxide and iron (III) oxide have the same type of crystal structure, but the lattice enthalpy of aluminium oxide is considerably greater than that of iron (III) oxide. Explain why the lattice enthalpies should differ in this way.

5. Draw a Born - Haber cycle to show how the lattice enthalpy of a metal oxide M_2O_3 could be determined, clearly indicating the enthalpy terms involved in each stage of the cycle.

6. Which compound in each of the following pairs of ionic substances has the most exothermic latttice energy? Justify your answers.
a) LiF, CsF b) $BaCl_2$, BaO c) Na_2SO_4, $CaSO_4$ d) KF, K_2O

7. Rationalise the following lattice energy values:

Compound	**Lattice Energy (kJ mol^{-1})**
CaSe	- 2862
Na_2Se	- 2130
CaTe	- 2721
Na_2Te	- 2095

8. The lattice energies of the oxides and chlorides of iron (II) and iron (III) are:

- 2631, - 3865, - 5359, - 14 774 (kJ mol^{-1})

Match the appropriate formula to each lattice energy. Explain.

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9. Some energy data are tabulated below:

Process	**Δ H⁰ (298 K) kJ mol^{-1}**
$Na_{(s)}$ ---> $Na_{(g)}$	+108
½ $Cl_{2(g)}$ ---> $Cl_{(g)}$	+121
$Na_{(g)}$ ---> $Na^{+1}_{(g)}$ + e^-	+496
$Cl_{(g)}$ + e^- ---> $Cl^{-1}_{(g)}$	- 349
$Ca_{(g)}$ ---> $Ca^{+2}_{(g)}$ + 2 e^-	+1736
$Ca^{+2}_{(g)}$ ---> $Ca^{+3}_{(g)}$ + e^-	+4941
$Ca^{+2}_{(g)}$ + 2 $Cl^{-1}_{(g)}$ ---> $CaCl_{2\,(s)}$	-2220
$Ca^{+3}_{(g)}$ + 3 $Cl^{-1}_{(g)}$ ---> $CaCl_{3(s)}$	- 4800
$NaCl_{(s)}$ ---> $Na^{+1}_{(g)}$ + $Cl^{-1}_{(g)}$	+787
$NaCl_{(s)}$ + aq ---> $Na^{+1}_{(aq)}$ + $Cl^{-1}_{(aq)}$	+4

Use the above tabulated information to answer the following questions:

a) Calculate the standard molar enthalpy change for the process:

$$Na_{(s)} + \tfrac{1}{2}\, Cl_{2(g)} \longrightarrow Na^{+1}_{(g)} + Cl^{-1}_{(g)}$$

b) Explain why $CaCl_{3(s)}$ does not exist but $CaCl_{2(s)}$ does.

c) Comment on the difference between the values of the enthalpy change of lattice breaking of $NaCl_{(s)}$ and the enthalpy of solution of $NaCl_{(s)}$ in water and define a term which is useful in this context.

d) Discuss the process occurring at the molecular level when solid NaCl dissolves in water.

e) Calculate the standard enthalpy of formation of sodium chloride.

f) State and discuss the general principles which govern the extent to which compounds are soluble in water.

10. Use the following data to estimate Δ H^o_f for barium chloride:

$$Ba_{(s)} + Cl_{2(g)} \longrightarrow BaCl_{2(s)}$$

Property	**(kJ mol^{-1})**
Lattice energy	- 2056
First ionisation energy of Ba	503
Second ionisation energy of Ba	965
Electron affinity of Cl	- 349
Bond energy of $Cl_{2(g)}$	239
Enthalpy of sublimation of Ba	178

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