Standard Enthalpy Change of Hydration / $\Delta H^{\ominus}_{hyd}$

Definition: The Standard enthalpy change of hydration ($\Delta H^{\ominus}_{hyd}$) of an ion is defined as the enthalpy change when one mole of the gaseous ions is dissolved in a large quantity of water under standard conditions.

$$Na^{+}_{(g)} + aq \longrightarrow Na^{+}_{(aq)} \qquad \Delta H^{\ominus}_{hyd} = -406\ kJ\ mol^{-1}$$

$$Cl^{-}_{(g)} + aq \longrightarrow Cl^{-}_{(aq)} \qquad \Delta H^{\ominus}_{hyd} = -366\ kJ\ mol^{-1}$$

What is the enthalpy change of hydration of NaCl?

$$Na^{+}_{(g)} + Cl^{-}_{(g)} + aq \longrightarrow Na^{+}_{(aq)} + Cl^{-}_{(aq)} \qquad \Delta H^{\ominus}_{hyd} = -772\ kJ\ mol^{-1}$$

$\Delta H^{\ominus}_{hyd}$ Is always negative.

Standard Enthalpy Change of Solution / $\Delta H^{\ominus}_{sol}$

Definition: The standard enthalpy change of solution ($\Delta H^{\ominus}_{sol}$) is defined as the enthalpy change when one mole of a substance dissolves in such a large volume of solvent that addition of more solvent produces no further change under standard conditions.

$$NH_{3\,(g)} + aq \longrightarrow NH_{3\,(aq)} \qquad \Delta H^{\ominus}_{sol} = -35.2\ kJ\ mol^{-1}$$

$$HCl_{(g)} + aq \longrightarrow H^{+}_{(aq)} + Cl^{-}_{(aq)} \qquad \Delta H^{\ominus}_{sol} = -72.4\ kJ\ mol^{-1}$$

$$NaCl_{(s)} + aq \longrightarrow Na^{+}_{(aq)} + Cl^{-}_{(aq)} \qquad \Delta H^{\ominus}_{sol} = +4.0\ kJ\ mol$$

$\Delta H^{\ominus}_{sol}$ Can be positive or negative

If $\Delta H^{\ominus}_{sol}$ is very positive-insoluble in water

If $\Delta H^{\ominus}_{sol}$ is very negative-soluble in water

Standard Enthalpy Change of Atomisation

Definition: The standard enthalpy change of atomization ($\Delta H^{\ominus}_{at}$) is defined as the enthalpy change when an element (or a compound) is converted into one mole of free gaseous atoms under standard condition.

$C_{(s)} \longrightarrow C_{(g)}$ $\Delta H^{\ominus}_{at} = +715\ kJ\ mol^{-1}$

$Na_{(s)} \longrightarrow Na_{(g)}$ $\Delta H^{\ominus}_{at} = +109\ kJ\ mol^{-1}$

$\frac{1}{2}O_{2(g)} \longrightarrow O_{(g)}$ $\Delta H^{\ominus}_{at} = +248\ kJ\ mol^{-1}$

$\Delta H^{\ominus}_{at}$ Is always +ve

Lattice Energy

The lattice energy of an ionic crystal is the heat energy evolved when one mole of crystalline solid is formed from its separate gaseous ions under standard conditions.

$Na^{+}_{(g)} + Cl^{-}_{(g)} \longrightarrow NaCl_{(s)}$ $\Delta H^{\ominus} = -781\ kJ\ mol^{-1}$

$Na^{+}_{(g)} + F^{-}_{(g)} \longrightarrow NaF_{(s)}$ $\Delta H^{\ominus} = -919\ kJ\ mol^{-1}$

All lattice energy are negative because heat energy is evolved when the ions forms electrovalent bonds.

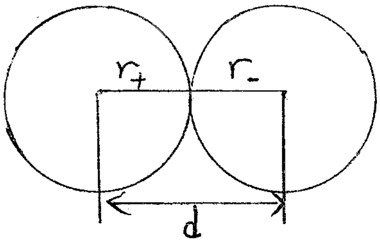
The higher the lattice energy (the more exothermic), the stronger the bond

Factors affecting lattice energy:

-ionic charge

-ionic radius

-crystal structure



$$\text{lattice energy} \propto \frac{q_+ \cdot q_-}{(r_+ + r_-)}$$

q_+ and q_- are charge on ions
$(r_+ + r_-)$ is the internuclear distance, d.

The bigger the ionic charge, the bigger the lattice energy

The smaller the ionic radius the bigger the lattice energy

Compound	Lattice energy kJ/mol		% difference
	theoretical	Expsimental	
NaCl	−776	−786	1.3
NaBr	−733	−744	1.5
NaI	−684	−697	1.9
AgCl	−768	−890	15.9
AgBr	−759	−877	15.5
AgI	−736	−867	17.8

NaCl, NaBr and NaI are considered fully ionic with no covalent character

AgCl, AgBr and AgI are not fully ionic. They form ionic crystal with considerable percentage of covalent character

Electronegativity: Na-0.9, Ag-1.75, Cl-3.0, Br-2.8, I-2.5

Electronegativity difference between Ag ion and halide ions are lower compared to Na ion and halide ions. Electrons are incompletely transferred in Ag halides.

Electron Affinity

Electron affinity is the enthalpy change measured in kJ mol , when one mole of electron is added to one mole of atoms or ions in the gaseous state.

The first electron affinity of an element is the enthalpy change when an electron is added to each atom in a mole of gaseous atoms to form singly charged negative ions:

$$X_{(g)} + e^- \longrightarrow X^-_{(g)} \qquad \Delta H^\ominus = -x\ kJ\ mol^{-1}$$

The second electron affinity is the enthalpy change when one electron is added to each 1− gaseous ion in one mole, to form one mole of gaseous 2−ions.

$$X^-_{(g)} + e^- \longrightarrow X^{2-}_{(g)} \qquad \Delta H^\ominus = +y\ kJ\ mol^{-1}$$

Born-Haber Cycle

Lattice energy cannot be measured directly from experiments. It can be obtained indirectly using Hess Law and Born-Haber cycle.

A relationship between the standard enthalpy change of formation of the ionic solid and five stages of enthalpy changes.

$$\begin{tikzcd}
Na_{(s)} \arrow[d, "\Delta H_1^\ominus"'] & + \frac{1}{2}Cl_{2(g)} \arrow[d, "\Delta H_2^\ominus"] \arrow[r, "\Delta H_f^\ominus"] & NaCl_{(s)} \arrow[ddd, dash, "\Delta H_5^\ominus"'] \\
Na_{(g)} \arrow[d, "\Delta H_3^\ominus"'] & Cl_{(g)} \arrow[d, "\Delta H_4^\ominus"] & \\
Na^+_{(g)} & + \ Cl^-_{(g)} & \\
\underbrace{(\text{free ions})} \arrow[rr, dash] & & {}
\end{tikzcd}$$

$\Delta H_1^\ominus$ = enthalpy change of atomisation of Na

$\Delta H_2^\ominus$ = enthalpy change of atomisation of Cl_2

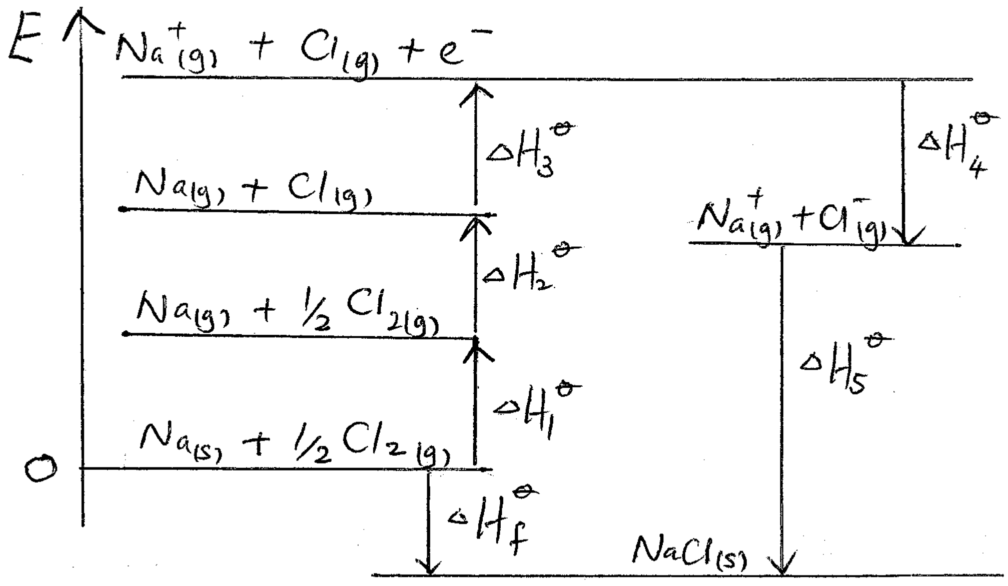
$\Delta H_3^\ominus$ = first ionisation energy of Na

$\Delta H_4^\ominus$ = electron affinity of chlorine

$\Delta H_5^\ominus$ = lattice energy of NaCl

Apply Hess' Law

$$\Delta H_f^\ominus = \Delta H_1^\ominus + \Delta H_2^\ominus + \Delta H_3^\ominus + \Delta H_4^\ominus + \Delta H_5^\ominus$$



Apply Hess' Law

$$\Delta H_f^\ominus = \Delta H_1^\ominus + \Delta H_2^\ominus + \Delta H_3^\ominus + \Delta H_4^\ominus + \Delta H_5^\ominus$$

Note:

ΔH +ve – arrows pointing upwards
ΔH −ve – arrows pointing downwards

<u>Ionic crystal dissolves in water</u>

the following process occurs:

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

The dissolution of an ion solid in water can be viewed as:

- The crystal lattice breaks down to form isolated gaseous ions
- The hydration of the gaseous ions

$Na^+Cl^-_{(s)} \longrightarrow Na^+_{(g)} + Cl^-_{(g)}$	$-\Delta H_{latt}$
$Na^+_{(g)} + Cl^-_{(g)} + aq \longrightarrow Na^+_{(aq)} + Cl^-_{(aq)}$	ΔH_{hyd}
$Na^+Cl^-_{(s)} + aq \longrightarrow Na^+_{(aq)} + Cl^-_{(aq)}$	ΔH_{sol}

$$\boxed{\Delta H_{sol} = \Delta H_{hyd} - \Delta H_{latt}}$$

The dissolution process can also be represented by the following enthalpy cycle:

$$\begin{tikzcd}
Na^+Cl^-_{(s)} \arrow[rr, "\Delta H^\ominus_{sol}"] \arrow[dr, "-\Delta H^\ominus_{latt}"'] & & Na^+_{(aq)} + Cl^-_{(aq)} \\
& Na^+_{(g)} + Cl^-_{(aq)} \arrow[ur, "\Delta H^\ominus_{hyd}"'] &
\end{tikzcd}$$

Apply Hess' Law,

$$\Delta H^\ominus_{sol} = -\Delta H^\ominus_{latt} + \Delta H^\ominus_{hyd}$$

Example 1

To determine the enthalpy change of solution, ΔH_{sol} of LiCl.

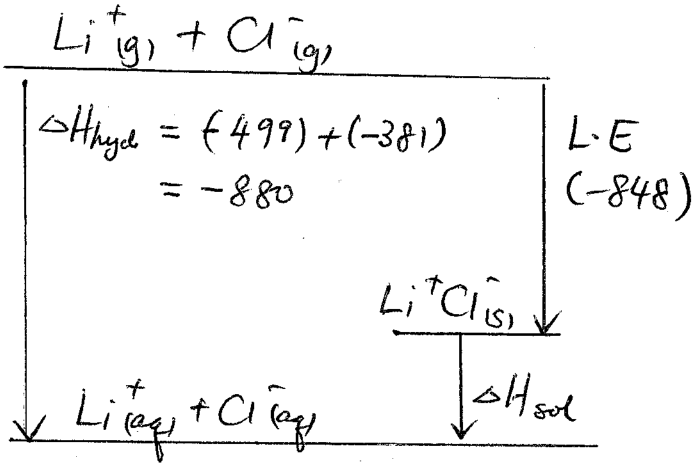
given : lattice energy LiCl = -848 kJ mol^{-1}

enthalpy change of hydration :

$Li^+ = -499$ kJ mol^{-1}

$Cl^- = -381$ kJ mol^{-1}

Energy cycle for LiCl



Apply Hess' Laws,

$$\Delta H_{sol} = -880 - (-848)$$
$$= -32 \text{ kJ mol}^{-1}$$

Example 2

To determine the enthalpy change of solution, ΔH_{sol} of NaCl.

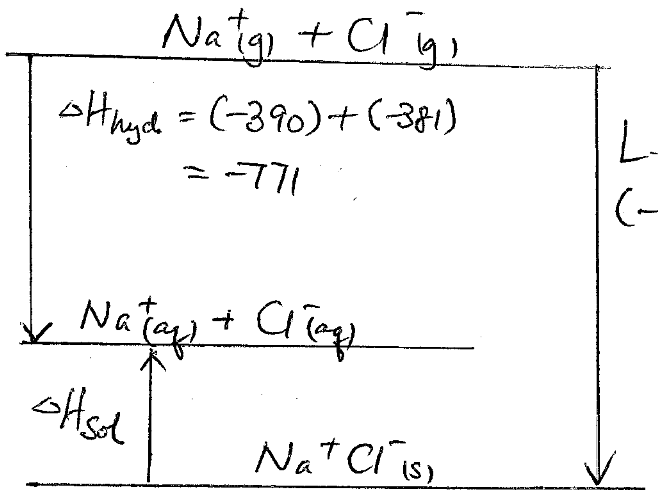
given: Lattice energy NaCl $= -776\ kJ\ mol^{-1}$

enthalpy change of hydration:

$Na^+ = -390\ kJ\ mol^{-1}$

$Cl^- = -381\ kJ\ mol^{-1}$

Energy cycle for NaCl



Apply Hess' Law,

$$\Delta H_{sol} = -771 - (-776)$$
$$= +5\ kJ\ mol^{-1}$$