

CHAPTER 20: Lattice Energy

20.1 Introduction to Lattice Energy

20.2 Born-Haber Cycles

20.3 Ion Polarisation

20.4 Enthalpy Changes in Solutions

Learning outcomes:

- (a) explain and use the term lattice energy (ΔH negative, i.e. gaseous ions to solid lattice).
- (b) explain, in qualitative terms, the effect of ionic charge and of ionic radius on the numerical magnitude of a lattice energy.
- (c) apply Hess' Law to construct simple energy cycles, and carry out calculations involving such cycles and relevant energy terms, with particular reference to:
 - (i) the formation of a simple ionic solid and of its aqueous solution.
 - (ii) Born-Haber cycles (including ionisation energy and electron affinity).
- (d) interpret and explain qualitatively the trend in the thermal stability of the nitrates and carbonates in terms of the charge density of the cation and the polarisability of the large anion.
- (e) interpret and explain qualitatively the variation in solubility of Group II sulfates in terms of relative magnitudes of the enthalpy change of hydration and the corresponding lattice energy.

20.1 Introduction to Lattice Energy

What is lattice energy?

- 1) In a solid ionic crystal lattice, the ions are bonded by strong ionic bonds between them. These forces are only completely broken when the ions are in gaseous state.
- 2) *Lattice energy (or lattice enthalpy)* is the enthalpy change when one mole of solid ionic lattice is formed from its scattered gaseous ions.
- 3) Lattice energy is **always negative**. This is because energy is always released when bonds are formed.
- 4) Use sodium chloride, NaCl as an example. It can be described as the enthalpy change when one mole of sodium chloride is formed from its scattered gaseous sodium and chloride ions. The value is -787 kJ mol^{-1} .
- 5) Lattice energy is a good indication of the strength ionic bonds. The higher the magnitude of lattice energy, the stronger the ionic bond formed. This is because more energy is released when strong bonds are formed.

Factors affecting lattice energy

- 1) There are two factors which govern the magnitude of lattice energy:
 - i. **Charge on the ions.**
 - ii. **Radius of the ions.**
- 2)
 - i. The higher the charge on the ion, the higher the lattice energy.
 - ii. This is because ions of higher charge have stronger attraction towards each other. Hence more energy is released when bonds are formed between them.

iii. For example, magnesium oxide, MgO has a higher lattice energy than sodium chloride. This is because Mg^{2+} and O^{2-} have higher charge than Na^{+} and Cl^{-} ions.

3) i. The larger the ionic radius, the lower the lattice energy.

ii. This is because the attraction between ions gets weaker as the distance between them increases. Hence less energy is released when bonds are formed between them.

iii. For example, the lattice energy of sodium halides gets lower from sodium fluoride to sodium iodide. This is because as the size of the halide ion increases, the distance between sodium and halide ions increases.

Electron affinity

- 1) The *first electron affinity*, ΔH_{eal} is the energy released when one mole of electrons is added to each atom in one mole of the atoms of the element to form one mole of gaseous 1- ions.

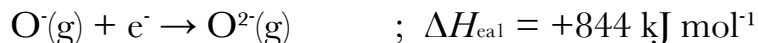
For example:



- 2) The use of electron affinities are almost always confined to Group 6 and 7 elements.
- 3) Generally, first electron affinities are **exothermic**, this is because there is an attraction between the positive nucleus and the incoming electron. Energy is released when this attraction is set up.
- 4) Electron affinity is **a measure of the attraction between the incoming electron and the nucleus** - the stronger the attraction, the more energy is released.
- 5) The factors that govern the magnitude of electron affinity is the same as the ones for ionisation energy - **nuclear charge, distance between nucleus and incoming electron and shielding effect of electrons**.
- 6) Going down a Group, the magnitude of first electron affinity **decreases**. This is because the distance between incoming electron and the nucleus increases, therefore the attractive force between them is less. The increasing nuclear charge is offset by the increasing shielding effect by inner electrons.
- 7) Take Group 7 as an example, the elements follow the pattern described, except for fluorine. This is because fluorine is a **very small atom with high electron density**. A repulsion between electrons is created hence the attraction between nucleus and incoming electrons is less. In Group 6, oxygen and the rest follow the exact same trend.
- 8) Group 6 elements have a **lower** electron affinity compared to their corresponding Group 7 elements. This is because the nuclear charge of Group 6 elements is lower, less attraction is set up between the nucleus and outer electrons, therefore less energy is released.

- 9) The *second electron affinity*, $\Delta H_{\text{ea}2}$ is the energy released when one mole of electrons is added to each gaseous 1- ions of to form one mole of gaseous 2- ions.

For example:



- 10) Second electron affinities are usually **endothermic**, this is because energy is required to add electrons into an already negative region due to the repulsion between electrons.

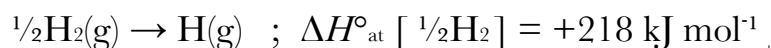
Recall some enthalpy changes

- 1) *Standard enthalpy change of formation*, $\Delta H^\circ_{\text{f}}$ is the enthalpy change when one mole of a compound is formed from its elements under standard condition.

The reactants and products must be in their standard states.



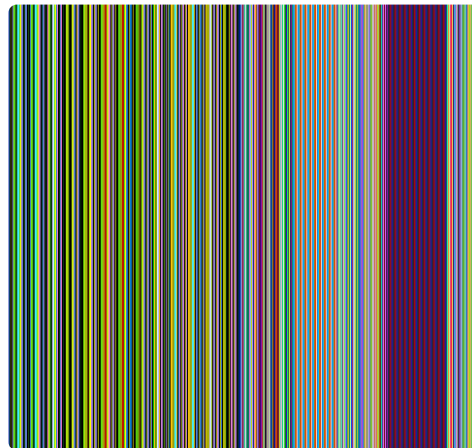
- 2) *Standard enthalpy change of atomisation*, $\Delta H^\circ_{\text{at}}$ is the enthalpy change when one mole of gases atoms is formed from its element under standard conditions.



20.2 Born-Haber Cycles

What are Born-Haber cycles?

- 1) Lattice energy cannot be determined experimentally, however, it can be calculated using a special type of Hess' cycle, this is called the **Born-Haber cycle**.
- 2) It assumes that the final product is the solid ionic compound. To make this compound, we start with its elements in their standard states, and convert them to ions in gaseous state. These ions are then converted to the solid lattice. Lattice energy can be obtained by considering the energetics of the entire process.



3) A typical Born-Haber cycle looks like this, take sodium chloride, NaCl as an example:

Here, the final product is NaCl(s). To make this, we begin with Na(s) + 1/2Cl₂(g). This is then converted step-by-step into Na⁺(g) + Cl⁻(g). This is done using atomisation energy, ionisation energy and electron affinity.

The energy released when the gaseous ions join to form the lattice is the lattice energy.

By Hess' Law,

$$-411 = +107 + 496 + 122 - 349 + \text{LE}$$

$$\text{LE} = -411 - 107 - 496 - 122 + 349$$

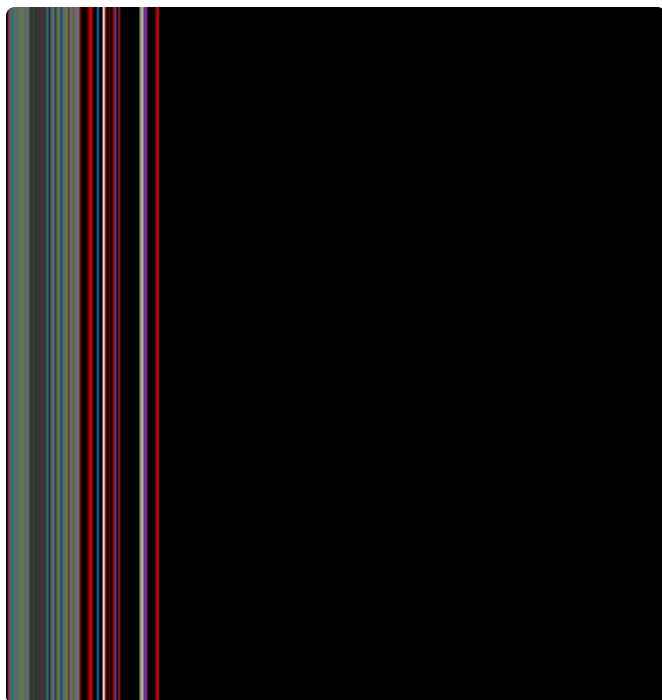
$$\text{LE} = -787 \text{ kJ mol}^{-1}$$

- -411 is the enthalpy change of formation.
- +107 is the enthalpy change of atomisation of Na.
- +496 is the first ionisation energy of Na.
- +122 is the enthalpy change of atomisation of 1/2Cl₂.
- -349 is the first electron affinity of Cl.

Note:

1) Each level should only indicate one type of enthalpy change.

4) Another example, Born-Haber cycle of magnesium chloride, MgCl_2 .



The thing to note here is the multiplication of atomisation enthalpy and electron affinity of Cl by 2 and also the use of second ionisation energy for Mg.

20.3 Ion Polarisation

Polarising power and polarisability

- 1) Not all ionic compounds are fully ionic, the same goes to covalent compounds. Pure ionic and covalent bondings are extremes.
- 2) In an ionic compound, the positive charge on the cation may attract the negative electron cloud of the anion towards it. This results in distortion of the electron cloud of the anion.
- 3) The factors which affect ion polarisation are:
 - i. the charge density of the cation.
 - ii. the size of the anion.
- 4) A cation is said to have a high charge density if it has a high charge spread over a small volume. For example, Mg^{2+} has a higher charge density than Ba^{2+} .

- 5) i. The higher the charge density of the cation, the higher the polarising power. **(Easier to polarise)**
 ii. The larger the size of the anion, the higher the polarisability. **(Easier to be polarised)**
- 6) Ion polarisation causes ionic bonds to have a certain degree of covalent character, making them impure.

Ion polarisation and thermal stability

Refer to Chapter 11: Group II, section 11.4.

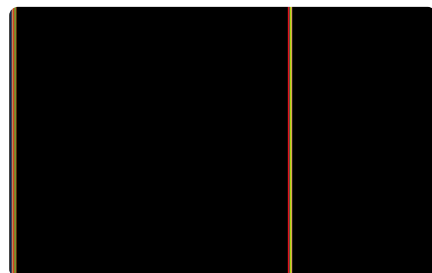
20.4 Enthalpy Changes in Solutions

Recall enthalpy change of solution and hydration

- 1) *Standard enthalpy change of solution*, $\Delta H^\circ_{\text{sol}}$ is the enthalpy change when one mole of ionic compounds is dissolved in water to form an infinitely dilute solution under standard conditions.

$$\text{MgCl}_2(\text{s}) + \text{aq} \rightarrow \text{MgCl}_2(\text{aq}) \quad ; \Delta H = \Delta H^\circ_{\text{sol}}$$
- 2) Standard enthalpy change of solution can be exothermic or endothermic, that is, some substance dissolve exothermically while others dissolve endothermically. So, why is there a difference?
- 3) *Standard enthalpy change of hydration*, $\Delta H^\circ_{\text{hyd}}$ is the enthalpy change when one mole of gases ions dissolves in water to form hydrated ions of infinite dilution under standard conditions.

$$\text{Ca}^{2+}(\text{g}) + \text{aq} \rightarrow \text{Ca}^{2+}(\text{aq}) \quad ; \Delta H = \Delta H^\circ_{\text{hyd}}$$
- 4) Standard enthalpy change of hydration is **always exothermic**, this is because when an ion dissolves in water, bonds are formed between the ions and water molecules. This bond is called the **ion-dipole bond**.

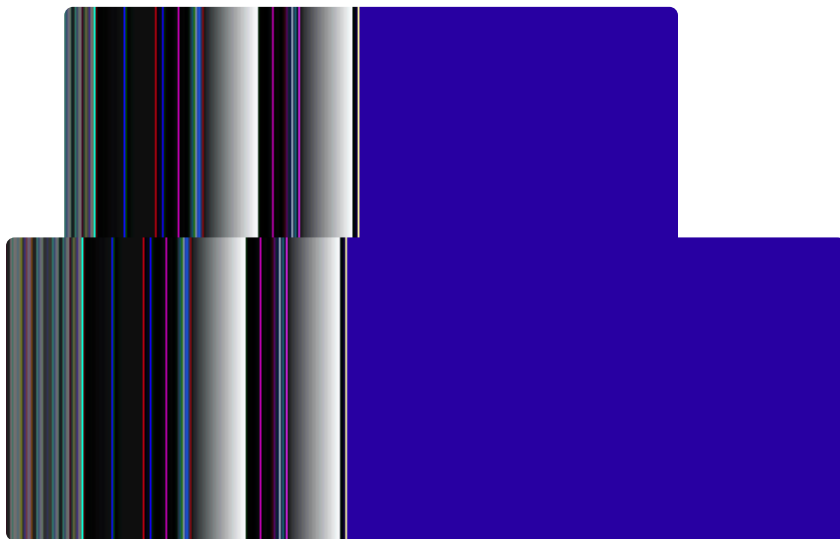


- 5) Factors affecting the magnitude of hydration enthalpy are:
- the size of the ion.
 - the charge on the ion.
- 6) i. The larger the size of the ion, the lower the hydration enthalpy. For example, hydration enthalpy of the Group II ions decreases down the Group.
- The higher the charge of the ion, the higher the hydration enthalpy. For example, Group II ions have higher hydration enthalpy compared to their corresponding Group I ions.

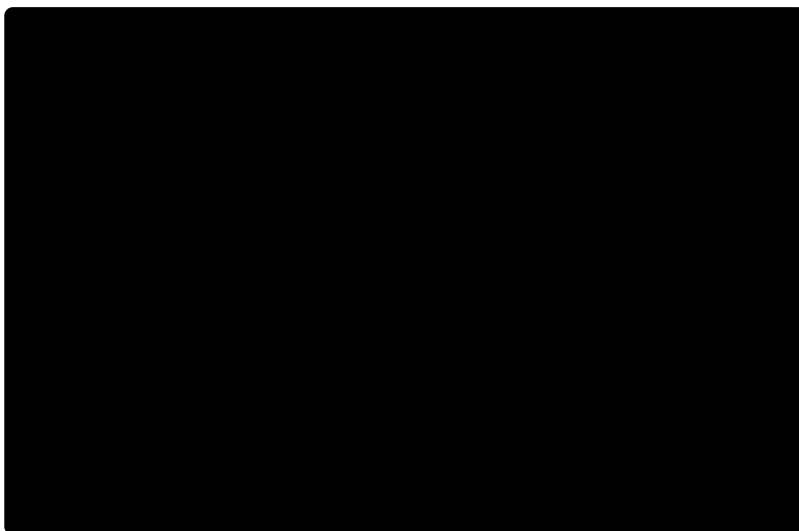
The process of dissolving

- 1) i. The process of dissolving is imagined as if the **solid ionic lattice is first broken down to form gaseous ions**. Lattice energy is absorbed.
- These **gaseous ions are then dissolved in water**, this is how they exist in the final solution. The energy involved here is hydration enthalpy.
 - The energy involved in the entire process(from solid ionic lattice to hydrated ions) is the solution enthalpy.

- 2) Therefore, take sodium chloride, NaCl as an example:



3) An example:



Solubility of Group II sulfates

- 1) The solubility of Group II sulfates **decreases** down the Group.
- 2) The solubility is governed by the sign of the enthalpy change of solution, $\Delta H^\circ_{\text{sol}}$. If $\Delta H^\circ_{\text{sol}} > 0$, the sulfate is relatively insoluble. If $\Delta H^\circ_{\text{sol}} < 0$, the sulfate is relatively soluble.
- 3) The sign of $\Delta H^\circ_{\text{sol}}$ is governed by the relative magnitude of $\Delta H^\circ_{\text{hyd}}$ and $\Delta H^\circ_{\text{latt}}$.
- 4) i. Going down the Group, if $\Delta H^\circ_{\text{hyd}}$ **decreases faster than** $\Delta H^\circ_{\text{latt}}$, the sulfates become more insoluble down the Group.
ii. Going down the Group, if $\Delta H^\circ_{\text{latt}}$ **decreases faster than** $\Delta H^\circ_{\text{hyd}}$, the sulfates become more soluble down the Group.
- 5) In the case of Group II sulfates, the former is true.
- 6) i. Hydration enthalpy decreases faster down the Group because the size of the cations increases dramatically down the Group, the anion is a constant.
ii. Lattice energy decreases slower down the Group because the sulfate ion is much larger than the Group II ions. As a result, the sulfate ion contributes to a greater part in the magnitude of lattice energy. That is, the increase in size of the cations is relatively insignificant.