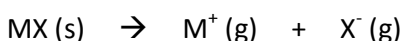


15.2 Born-Haber Cycle

Our calculations of enthalpies so far have involved covalent substances. Now we need to look at the enthalpy changes involved in the formation of giant ionic lattices.

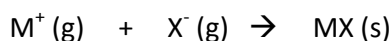
Lattice enthalpy is defined as either the:

*'the enthalpy change that occurs when one mole of a solid ionic crystal is broken into its ions in the gaseous state, at standard temperature and pressure. Because all the bonds in the ionic lattice are broken, it is an **endothermic** process, ΔH is positive.'* **The IB uses this definition.**



or

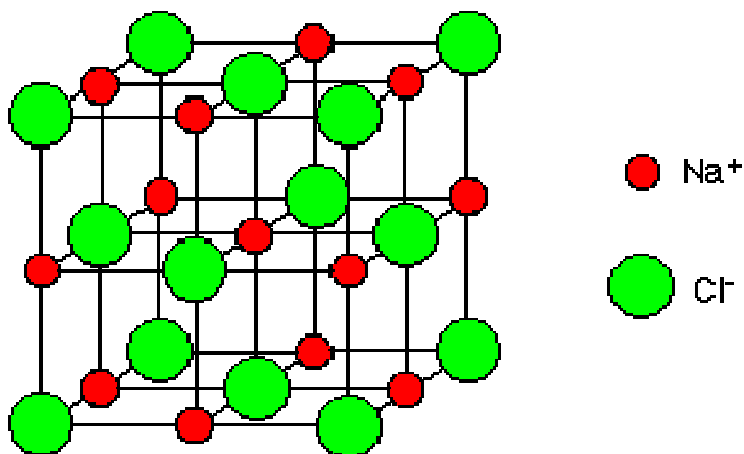
*'the enthalpy change that occurs when one mole of a solid ionic crystal is formed from its ions in the gaseous state, at standard temperature and pressure. Because all the bonds in the ionic lattice are made, it is an **exothermic** process, ΔH is negative.'*



[Remember that bond breaking is endothermic and bond making is exothermic]

Standard lattice enthalpy values for ionic solids are found in the IB Chemistry data booklet.

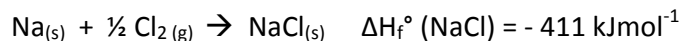
Sodium Chloride ionic lattice



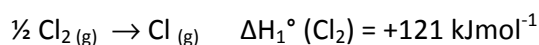
Born-Haber Cycles (named after Fritz Haber and Max Born) are simply energy / enthalpy cycles that show how ionic compounds are formed from their constituent elements. They are useful because they allow lattice enthalpies to be calculated theoretically using empirical data (observations and data collected from experiments).

Definitions involved in calculation of lattice enthalpy of NaCl

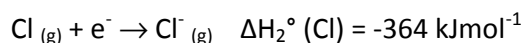
ΔH_f° standard enthalpy of formation of sodium chloride. The enthalpy change when one mole of a NaCl is formed from its elements under standard conditions. They are *exothermic* because new bonds are being made between the atoms of the elements sodium and chlorine.



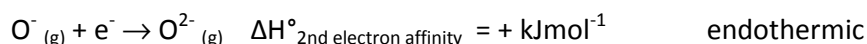
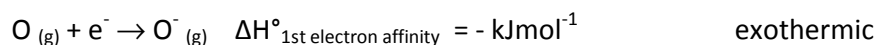
ΔH_1° standard enthalpy of atomization of chlorine. The energy required to change one mole of gaseous chlorine molecules into one mole of gaseous chlorine atoms. *Endothermic* because the bonds between the Cl-Cl atoms are being broken.



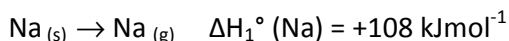
ΔH_2° standard enthalpy of first electron affinity of chlorine. The energy released when one mole of gaseous chlorine atoms gains one mole of electrons to form a -1 charged ion. *Exothermic* because the gaseous atom needs to release energy in order to slow down sufficiently to attract and an electron.



NOTE: Non-metal elements with -2 ions have two electron affinities. For example oxygen and sulfur form -2 ions and have a first and second electron affinity. The second electron affinity is endothermic and is defined as the energy absorbed when one mole of electrons is gained by a -1 ion. Energy is absorbed because the negative ion is gaining a negative electron. Because both the ion and the electron are negatively charged they repel each other so energy needs to be absorbed in order for the process to take place.



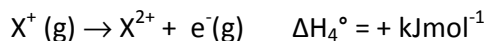
ΔH_1° standard enthalpy of atomization of sodium. The energy required to change one mole of solid sodium atoms into one mole of gaseous atoms. *Endothermic*, energy needs to be absorbed to change the state from a solid to a gas.



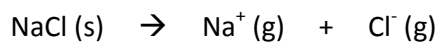
ΔH_4° first ionization energy of sodium. The enthalpy change when one mole of electrons is removed from a gaseous metal atom. *Endothermic*, energy needs to be absorbed to remove the electron.



The second ionisation energy is the energy absorbed when a second electron is released from a gaseous ion. *Endothermic*.



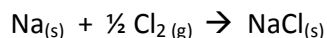
ΔH_5° lattice enthalpy of sodium chloride. The enthalpy change when one mole of ions in a solid ionic lattice is broken. *Endothermic*, because the ionic bonds between the sodium and chloride ions need to absorb energy in order to break them.



NOTE: The enthalpies of atomization and first ionization energy are always positive (endothermic). The enthalpy of first electron affinity is negative (exothermic).

Born-Haber Cycle for NaCl

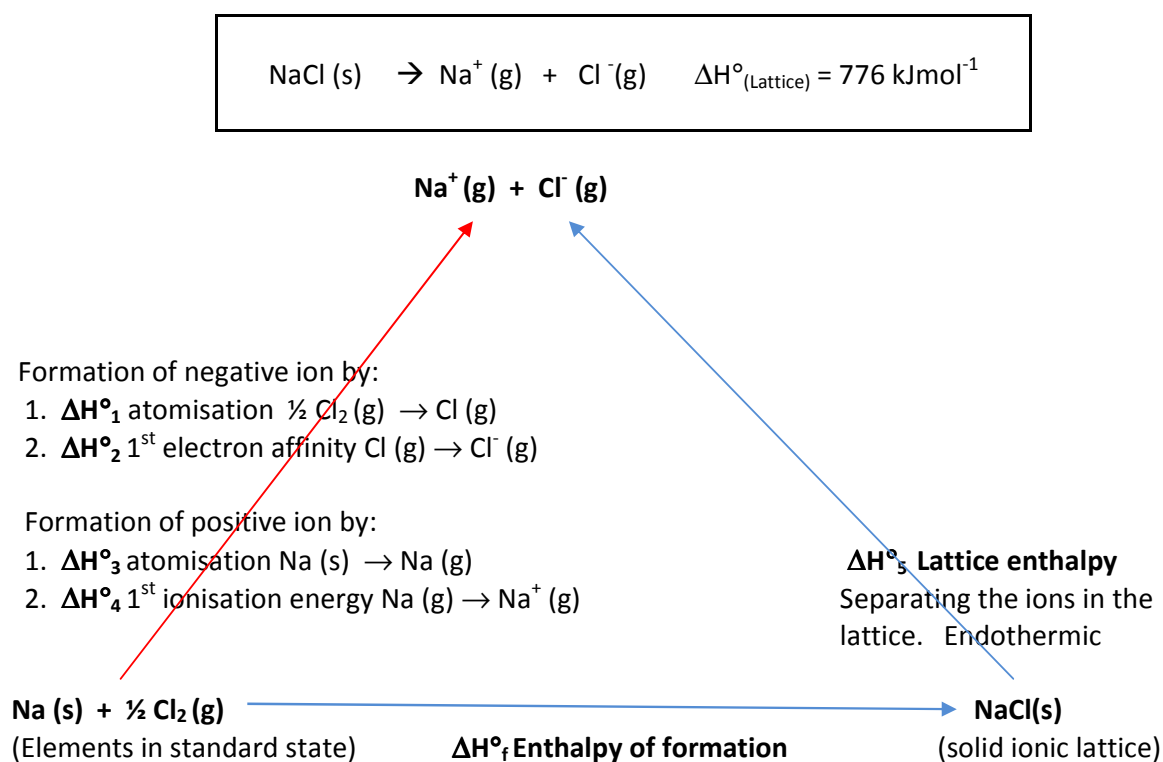
The formation of the ionic compound starts with the elements in their standard states, and ends with them as ions in a giant ionic lattice.



Before the elements can form an ionic lattice they need to be atomized (turned into gaseous atoms) and then ionized (turned into ions). The process involved are atomization, ionization energy and electron affinity.

A Born-Haber cycle combines all of the steps above, using the principles of Hess's Law to determine the overall lattice enthalpy

The Born-Haber cycle for NaCl (s)



By Hess's law:

$$\Delta H_f^\ominus + \Delta H_{5(\text{Lattice})}^\ominus = \Delta H_1^\ominus + \Delta H_2^\ominus + \Delta H_3^\ominus + \Delta H_4^\ominus$$

therefore

$$\Delta H_{5(\text{Lattice})}^\ominus = (\Delta H_1^\ominus + \Delta H_2^\ominus + \Delta H_3^\ominus + \Delta H_4^\ominus) - \Delta H_f^\ominus \text{ (kJmol}^{-1}\text{)}$$

For a born Haber Cycle for NaCl go to <http://onsager.bd.psu.edu/~jircitano/BH.html>

Exercise

Using the values for the enthalpies of atomisation, first ionization, first electron affinity and formation given above calculate the lattice enthalpy for sodium chloride.

Answer

$$\Delta H_f^\ominus + \Delta H_{(\text{LE NaCl})}^\ominus = \Delta H_{\text{atm}(\text{Na})}^\ominus + \Delta H_{1\text{stIE}(\text{Na})}^\ominus + \Delta H_{\text{atm}(\text{Cl}_2)}^\ominus + \Delta H_{\text{EA}(\text{Cl}_2)}^\ominus$$

$$\begin{aligned}\Delta H_{5^\ominus(\text{LE NaCl})} &= (\Delta H_{\text{atm}(\text{Na})}^\ominus + \Delta H_{1\text{stIE}(\text{Na})}^\ominus + \Delta H_{\text{atm}(\text{Cl}_2)}^\ominus + \Delta H_{\text{EA}(\text{Cl}_2)}^\ominus) - \Delta H_f^\ominus \\ &= (+108) + (+500) + (+121) + (-364) - (-411) \\ &= 365 - -411 \\ &= 776 \text{ kJmol}^{-1} \text{ endothermic (decimal rule for SF)}\end{aligned}$$

15.2.2 Factors affecting the size of the lattice enthalpy

Recall that lattice enthalpy is defined as the enthalpy change that occurs when one mole of a solid ionic crystal is broken into its ions in the gaseous state, at standard temperature and pressure. It's magnitude (size) depends on the size (radius) and charge on the positive and negative ions and can be represented using the following relationship.

$$\text{Lattice Enthalpy} \propto \frac{(\text{charge on positive ion}) \times (\text{charge on negative ion})}{\text{Sum of the ionic radii}}$$

As the lattice enthalpy increases the ionic lattice becomes more stable. This is because the electrostatic attraction between the positive and negative ions becomes stronger, so more energy is needed to break apart the ions.

Consider the following data:

Ionic compound	Lattice Enthalpy (kJ mol ⁻¹)	Cation/Anion/ Size	Explanation
LiCl	826	Cation (+ ion) size increasing Li ⁺ → Na ⁺ → K ⁺	As the ionic radius of the ions increases the lattice enthalpy decreases because the positive and negative ions are further away from one another, decreasing the electrostatic attraction between them, making it easier to separate the ions.
NaCl	771		
KCl	701		
NaCl	771	Anion (- ion) size increasing Cl ⁻ → Br ⁻ → I ⁻	
NaBr	733		
NaI	684		
NaCl	771	Charge on cation increasing Na ⁺ → Mg ²⁺	When the charge on the ions increases the lattice enthalpy increases because there is a greater electrostatic attraction between the positive and negative ions of the lattice and therefore more energy is required to separate them.
MgCl ₂	2493		
MgCl ₂	2493	Charge on anion increasing Cl ⁻ → O ²⁻	
MgO	3889		

(Ionic radii data can be found in table 8 of the IB Chemistry data booklet)

When the charge increases the lattice enthalpy increases →

When the radius increases the lattice enthalpy decreases →

NOTE: Remember positive ions (cations) are smaller than their atoms and negative ions (anions) are larger than their atoms and ionic radius increase down a group of the periodic table and decreases across a period.

Therefore the **lattice enthalpy** will be **greatest** from a **small sized ion** with a **large charge**. The charge on the ion causes the lattice energy to increase more than the size of the ion (ionic radius).

Why is the lattice enthalpy affected in this way? According to coulombs law a theoretical mathematical model used to explain lattice enthalpies the size of the force of attraction F of one ion for another is given by the formula:

$$F = k \frac{q_1 q_2}{r^2}$$

where q_1 and q_2 are the charges on the ion and r^2 is the distance between them.

This formula shows that increasing the charge on either ion will increase the force between them. Decreasing the size of one or both ions will decrease the distance between them and thus increase the attractive force.

Factors affecting the magnitude of lattice energy

Effect of ionic size

compound	lattice energy /kJ mol ⁻¹	ions	effect of size
NaCl	-776		ionic size increases: • greater distance between centres of ions • attraction between ions decreases • lattice energy becomes less negative.
NaBr	-742		
NaI	-705		

Effect of ionic charge

With increased charge on cation, two factors increase the magnitude of lattice energy:	$\text{Na}^+ \longrightarrow \text{Mg}^{2+}$ increased charge \longrightarrow greater attraction decreasing size \longrightarrow greater attraction
With increased charge on anion, two competing factors:	$\text{Cl}^- \longrightarrow \text{O}^{2-}$ increased charge \longrightarrow greater attraction increased size \longrightarrow less attraction

NOTE: This example has the lattice enthalpy as exothermic, the IB uses the endothermic process. When the ionic radius of the negative ion increases the lattice enthalpy becomes less positive.

5.2.4 Using lattice enthalpy to predict ionic or covalent character

Born-Haber cycles can be used to deduce how ionic a substance is. The table below shows lattice enthalpies calculated from Born-Haber cycles using both empirical data (from experiments) and from theoretical mathematical models (using coulombs law).

Compound	Lattice enthalpy (kJ mol^{-1})		% difference (error) $\frac{\text{Experimental} - \text{theoretical}}{\text{experimental}} \times 100$
	Experimental Born-Haber	Theoretical	
AgCl	905	770	$(770-905) \div 905 \times 100 = 14.9\%$
NaCl	771	766	$(766-771) \div 771 \times 100 = 0.649\%$

Sodium chloride has a much smaller % difference between its experimental and theoretical values than the silver chloride.

The larger difference for AgCl means that it is not as close to the theoretical mathematical model suggesting that it is probably less ionic in nature and has other bonding present.

Evidence for the existence of covalent bonding is provided by electronegativity values. The difference in the electronegativity between the silver and chlorine is small ($\text{Ag}(3.0) - \text{Cl}(1.9) = 1.1$) suggesting that silver chloride is covalent in nature. Remember according to Pauling's electronegativity values differences greater than 1.8 tend to occur between elements that are more ionic in nature and a small electronegativity difference (0-1.8) are more likely to indicate a covalent bond.

Further evidence of this covalent nature can be found by examining melting points. The melting point of the silver chloride (455°C) is considerably lower than that of sodium chloride (801°C), suggesting that silver chloride is more covalent in nature. Remember a low melting point indicates a substance is molecular covalent and a high melting point an ionic lattice.

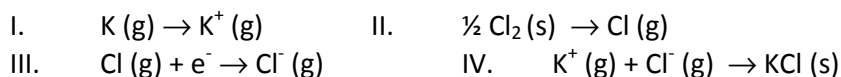
Questions

1. Draw and label a Born-Haber cycle for the formation of calcium oxide.
2. Calculate the lattice enthalpy of calcium oxide from the following data.
 - enthalpy of atomisation of $\text{Ca}(s)$: 178 kJmol^{-1}
 - first ionization energy of $\text{Ca}(g)$: 590 kJmol^{-1}
 - second ionization energy of $\text{Ca}(g)$: 1150 kJmol^{-1}
 - enthalpy of atomization of $\text{O}_2(g)$: 249 kJmol^{-1}
 - first electron affinity of $\text{O}(g)$: -141 kJmol^{-1}
 - second electron affinity of $\text{O}(g)$: 844 kJmol^{-1}
 - enthalpy of formation of $\text{CaO}(s)$: -635 kJmol^{-1}

3. The lattice enthalpy of calcium bromide is the energy change for the reaction
- A) $\text{Ca(g)} + 2\text{Br(g)} \rightarrow \text{CaBr}_2\text{(g)}$
 B) $\text{CaBr}_2\text{(s)} \rightarrow \text{Ca(g)} + 2\text{Br(g)}$
 C) $\text{Ca(s)} + \text{Br}_2\text{(l)} \rightarrow \text{CaBr}_2\text{(s)}$
 D) $\text{CaBr}_2\text{(s)} \rightarrow \text{Ca(g)} + \text{Br}_2\text{(g)}$
 E) $\text{CaBr}_2\text{(s)} \rightarrow \text{Ca}^{2+}\text{(g)} + 2\text{Br}^-\text{(g)}$
4. The standard enthalpy of formation of KCl(s) is -437 kJmol^{-1} . In a Born-Haber cycle for the formation of KCl(s) , which enthalpy change(s) are exothermic?
- A) the lattice enthalpy and the electron affinity of chlorine
 B) the electron affinity of chlorine
 C) the formation of Cl(g) from $\text{Cl}_2\text{(g)}$
 D) the enthalpy of atomization of K(s) and the first ionization energy of K(g)
 E) lattice enthalpy
5. Calculate the lattice enthalpy of silver chloride from the following data.
- enthalpy of atomisation of Ag(s) : 284 kJmol^{-1}
 first ionization energy of Ag(g) : 731 kJmol^{-1}
 enthalpy of atomisation of $\text{Cl}_2\text{(g)}$: 122 kJmol^{-1}
 first electron affinity of Cl(g) : -349 kJmol^{-1}
 enthalpy of formation of AgCl(s) : -127 kJmol^{-1}
- A) 1037 kJmol^{-1}
 B) 661 kJmol^{-1}
 C) 915 kJmol^{-1}
 D) 1613 kJmol^{-1}
 E) 1359 kJmol^{-1}
6. Calculate the first electron affinity of iodine from the following data.
- enthalpy of atomisation of Ag(s) : 284 kJmol^{-1}
 first ionization energy of Ag(g) : 731 kJmol^{-1}
 enthalpy of atomisation of $\text{I}_2\text{(g)}$: 107 kJmol^{-1}
 Lattice enthalpy of AgI(s) : 889 kJmol^{-1}
 enthalpy of formation of AgI(s) : -62 kJmol^{-1}
- A) -295 kJmol^{-1}
 B) 889 kJmol^{-1}
 C) 295 kJmol^{-1}
 D) -161 kJmol^{-1}
 E) 765 kJmol^{-1}

7. Calculate the lattice enthalpy of magnesium chloride from the following data.
- enthalpy of atomisation of Mg(s): 148 kJmol^{-1}
 - first ionization energy of Mg(g): 736 kJmol^{-1}
 - second ionization energy of Mg(g): 1450 kJmol^{-1}
 - enthalpy of atomisation of Cl₂(g): 122 kJmol^{-1}
 - electron affinity of Cl(g): -349 kJmol^{-1}
 - enthalpy of formation of MgCl₂(s): -641 kJmol^{-1}
- A) 2521 kJmol^{-1}
 B) 1239 kJmol^{-1}
 C) 2748 kJmol^{-1}
 D) 3917 kJmol^{-1}
 E) 2635 kJmol^{-1}
8. State with a reason whether the following steps in the Born Haber cycle of potassium chloride are exothermic or endothermic.
- a) $\frac{1}{2} \text{Cl}_2(\text{g}) \rightarrow \text{Cl}(\text{g})$
 b) $\text{Cl}(\text{g}) \rightarrow \text{Cl}^-(\text{g})$
 c) $\text{K}(\text{s}) \rightarrow \text{K}(\text{g})$
 d) $\text{K}(\text{g}) \rightarrow \text{K}^+(\text{g})$
 e) $\text{K}^+(\text{g}) + \text{Cl}^-(\text{g}) \rightarrow \text{KCl}(\text{s})$
9. Define the following terms and then using MgO as an example write equations to represent each term. State whether the process is exothermic or endothermic. Include states.
- a) standard enthalpy of formation
 b) standard lattice enthalpy
 c) standard enthalpy of atomization for a metal and non metal
 d) standard enthalpy of 1st ionization
 e) standard enthalpy of 2nd ionization
 f) standard 1st electron affinity
 g) standard 2nd electron affinity
10. Which one of the following quantities is not involved in the Born-Haber cycle?
- A. ionization energy
 B. lattice enthalpy
 C. electronegativity
 D. enthalpy of formation

11. The Born-Haber cycle for the formation of potassium chloride includes the steps below:



Which of these steps are exothermic?

- A. I and II B. III and IV
C. I, II and III only D. I, II and IV only

12. The lattice energy is dependent on two main factors, the size of the ions and the charge on the ions. Which combination of these would produce the greatest lattice enthalpy?

13. Which one of the following solids would you expect to have the greatest lattice enthalpy?

- A. RbCl B. CaS C. BaI_2 D. LiF

14. Which of the following has the largest lattice enthalpy?

- A) $\text{MgCl}_2 \text{(s)}$
B) KCl (s)
C) LiCl (s)
D) NaCl (s)
E) AgCl (s)

15. Explain why the melting points of the group 1 metal chlorides decreases down the group.

16. Of what use are theoretical values produced using mathematical models for helping chemists understand the nature of ionic and covalent bonds?

17. Consider the following theoretical and experimental lattice enthalpies and then deduce the order of increasing covalent character.

Compound	Lattice enthalpy (kJ mol^{-1})	
	Experimental	Theoretical
KF	801	795
CaO	3513	3477
LiO	744	728

18. Describe and explain the trend in ionic radius across the 3rd period and down groups 1 and 7.

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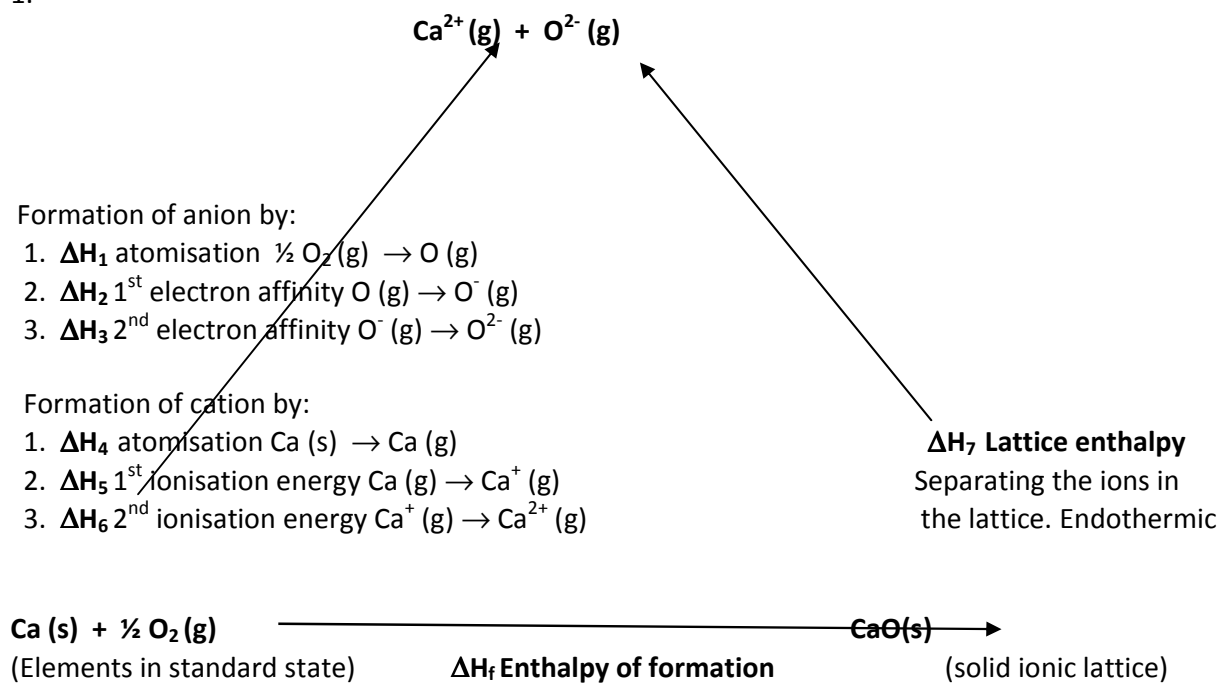
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15.2 Lattice Enthalpy

ANSWERS

1.



$$\Delta H_f^\ominus + \Delta H_{7(\text{Lattice})}^\ominus = \Delta H_1^\ominus + \Delta H_2^\ominus + \Delta H_3^\ominus + \Delta H_4^\ominus + \Delta H_5^\ominus + \Delta H_6^\ominus$$

15.2 Lattice Enthalpy

ANSWERS

2.

$$\Delta H_f^\ominus + \Delta H_{7(\text{Lattice})}^\ominus = \Delta H_1^\ominus + \Delta H_2^\ominus + \Delta H_3^\ominus + \Delta H_4^\ominus + \Delta H_5^\ominus + \Delta H_6^\ominus$$

$$\begin{aligned}\Delta H_{7(\text{LE CaO})}^\ominus &= \Delta H_1^\ominus + \Delta H_2^\ominus + \Delta H_3^\ominus + \Delta H_4^\ominus + \Delta H_5^\ominus + \Delta H_6^\ominus - \Delta H_f^\ominus \\ &= 178 + 590 + 1150 + 249 + (-141) + 844 - (-635) \\ &= 2870 - (-635) \\ &= 3505 \text{ kJmol}^{-1}\end{aligned}$$

3. E The lattice enthalpy is defined as the enthalpy change that occurs when one mole of a solid ionic crystal is broken into its ions in the gaseous state, at standard temperature and pressure.

4. B The first electron affinity and enthalpy of formation are the only processes that are exothermic.

5. C

$$\begin{aligned}\Delta H_{(\text{LE AgCl})}^\ominus &= \Delta H_{\text{atmAg}}^\ominus + \Delta H_{1\text{st IE}}^\ominus + \Delta H_{\text{atmCl}_2}^\ominus + \Delta H_{1\text{st EA}}^\ominus - \Delta H_f^\ominus \\ &= 284 + 731 + 122 + (-349) - (-127) \\ &= 788 - (-127) \\ &= 915 \text{ kJmol}^{-1}\end{aligned}$$

6. A

$$\begin{aligned}\Delta H_{(\text{LE AgI})}^\ominus &= \Delta H_{\text{atmAg}}^\ominus + \Delta H_{1\text{st IE}}^\ominus + \Delta H_{\text{atmI}_2}^\ominus + \Delta H_{1\text{st EA}}^\ominus - \Delta H_f^\ominus \\ \Delta H_{1\text{st EA}}^\ominus &= \Delta H_{(\text{LE AgI})}^\ominus - \Delta H_{\text{atmAg}}^\ominus - \Delta H_{1\text{st IE}}^\ominus - \Delta H_{\text{atmI}_2}^\ominus + \Delta H_f^\ominus \\ &= 889 - 284 - 731 - 107 + (-62) \\ &= -295 \text{ kJmol}^{-1}\end{aligned}$$

7. A

$$\begin{aligned}\Delta H_{(\text{LE MgCl}_2)}^\ominus &= \Delta H_{\text{atmMg}}^\ominus + \Delta H_{1\text{st IE}}^\ominus + \Delta H_{2\text{nd IE}}^\ominus + \Delta H_{\text{atmCl}_2}^\ominus + \Delta H_{1\text{st EA}}^\ominus - \Delta H_f^\ominus \\ &= 148 + 736 + 1450 + \mathbf{2(122)} + \mathbf{2(-349)} - (-641) \\ &= 1880 - (-641) \\ &= 2521 \text{ kJmol}^{-1}\end{aligned}$$

Because there are 2 moles of Cl in MgCl_2 , the standard enthalpy of atomisation and first electron affinity values need to be multiplied by 2. This is because these definitions are based on one mole, not two.

8. a) atomization - endothermic energy needs to be absorbed to break the bonds between chlorine molecules.

- b) electron affinity - exothermic energy is the gaseous atom needs to release energy in order to slow down and be able to attract and an electron.
- c) atomization – endothermic energy needs to be absorbed to change state from solid to gas.
- d) first ionization energy - endothermic energy needs to be absorbed to remove an electron
- e) exothermic – reverse of lattice enthalpy - energy needs to be released to bring ions together
9. See page 2
10. C Electronegativity. Born Haber cycles are for ionic compounds.
11. B
 I 1st ionization energy - endothermic
 II atomization – endothermic
 III electron affinity – exothermic
 IV reverse of the lattice enthalpy – exothermic
 The first electron affinity (III) and reverse of the lattice enthalpy (IV) are the only processes that are exothermic.
12. The lattice enthalpy will be greatest from a small sized ion with a large charge
 (The charge on the ion causes the lattice energy to increase more than the size of the ion)
13. B Both Ca and S are have the largest charge (+2)
14. A magnesium chloride, due to +2 ion for magnesium
15. LiCl, NaCl, KCl;
 Electrostatic attraction between the positive and negative ions in the ionic lattice decreases;
 So less energy needs to be absorbed to break the bond;
16. Shows that ionic compounds have different amounts of covalent character.
17. KF (difference = 0.749%), CaO (difference = 1.025 %), LiO (difference = 2.15 %)
18. Ionic radius increases down groups 1 and 7;
 because the number of shells increases ;

 Ionic radius decreases across the 3rd period;
 For the metal ions even though the number of protons is increasing for each additional electron lost the remaining electrons have a greater share of the positive charge which increases the attractive force between the positive protons and the negative electrons causing the electron shells to be attracted more strongly to the atom;
 Likewise for the non-metal ions even though the number of protons is increasing the extra electrons gained increases the amount of electron-electron repulsion in the outer shell, increasing the ionic radius.