15.1 Energy cycles

$\Delta H_i^\ominus$

The first ionization energy is the minimum energy required to remove one mole of electrons from one mole of gaseous atoms.

The reaction beween sodium and chlorine

The first ionization energy ($\Delta H_i^\ominus$) corresponds to the energy needed to form the positive ion.

$$Na(g) \rightarrow Na^+(g) + e^-(g) \qquad \Delta H_i^\ominus = +496 \text{ kJ mol}^{-1}$$

The first electron affinity is the enthalpy change when one mole of gaseous electrons is added to one mole of gaseous atoms.

$\Delta H_e^\ominus$

This process was discussed in Chapters 2 and 3, where we saw that sodium, which is on the left of the Periodic Table, has a relatively low ionization energy. The first **electron affinity** ($\Delta H_e^\ominus$) is the enthalpy change when one mole of gaseous atoms attracts one mole of electrons. Values are tabulated in section 7 of the IB data booklet. For chlorine:

$$Cl(g) + e^-(g) \rightarrow Cl^-(g) \qquad \Delta H_e^\ominus = -349 \text{ kJ mol}^{-1}$$

As the electron is attracted to the positively charged nucleus of the Cl atom, the process is exothermic.

Add the equations for first ionization energy and first electron affinity:

$$Na(g) + Cl(g) \rightarrow Na^+(g) + Cl^-(g) \qquad \Delta H^\ominus = -349 + 496 = +147 \text{ kJ mol}^{-1}$$

Still unfavourable

$$Na^+(g) + Cl^-(g) \rightarrow NaCl(s) \qquad \Delta H^\ominus = -790 \text{ kJ mol}^{-1}$$

The lattice enthalpy is the enthalpy change that occurs when one mole of a solid ionic compound is separated into gaseous ions under standard conditions.

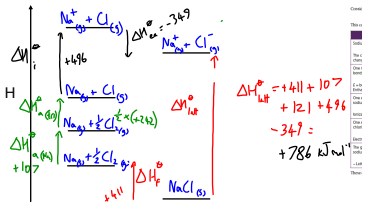
It is this step of the process which explains the readiness of sodium and chlorine to form an ionic compound.

This value is called the lattice enthalpy. It is given +790 in the data booklet so therefore is refering to the endothermic process of breaking up the lattice.

$$NaCl(s) \rightarrow Na^+(g) + Cl^-(g) \qquad \Delta H_{lat}^\ominus = +790 \text{ kJ mol}^{-1}$$

Experimental lattice enthalpies and the Born–Haber cycle

If we cannot calculate this lattic enthalpy value directly in the lab then we can use Hess's Law to work it out via another route. This is called a Born-Haber cycle.



$\Delta H_{lat}^\ominus = +411 + 107 + 121 + 496 - 349 = +786 \text{ kJ mol}^{-1}$

Worked example

(a) Write an equation to represent the lattice energy of magnesium oxide, MgO.
(b) Write an equation to represent the second electron affinity of oxygen and comment on the relative values of the first and second values given in section 8 of the IB data booklet.
(c) Use the following data, and further information from sections 8 and 11 of the IB data booklet to construct a Born–Haber cycle for magnesium oxide.
(d) Calculate the lattice energy of magnesium oxide.

Mg^{2+} O^{2-}

Additional data:

- enthalpy change of atomization for Mg(s) = +148 kJ mol^{-1}
- second ionization energy of magnesium = +1 451 kJ mol^{-1}
- enthalpy change of formation of MgO(s) = −602 kJ mol^{-1}

H: $Mg^{2+}_{(g)} + O^{2-}_{(g)}$; $MgO_{(s)}$

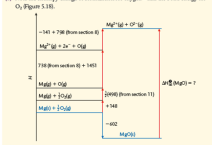
Solution

(a) $MgO(s) \rightarrow Mg^{2+}(g) + O_2(g)$
(b) $O^-(g) + e^-(g) \rightarrow O^{2-}(g)$

The first electron affinity corresponds to the attraction of an outer electron into the outer energy level of an oxygen atom. This is an exothermic process.

The second electron affinity corresponds to a negatively charged oxide ion accepting an additional outer electron into an outer energy level despite the mutual repulsion between the negatively charged species. This is an endothermic process.

(c) Note the enthalpy change of atomization for oxygen = half the bond energy for O_2 (Figure 5.18).



(d) From the diagram we have

$\Delta H_{lat}^\ominus(MgO) = +602 + 148 + 1/2(498) + (738 + 1451) + (-53 - 142)$ kJ mol^{-1}

$\Delta H_{lat}^\ominus(MgO) = +3799$ kJ mol^{-1}

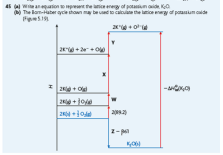
Overview

42 Identify the process which has the sign of its associated enthalpy change different from the rest.
A $Cl(g) + e^- \rightarrow Cl^-(g)$
B $K(g) \rightarrow K^+(g) + e^-$
C $K(g) \rightarrow K^+(g) + Cl^-(g)$
D $Cl_2(g) \rightarrow 2Cl(g)$

43 Which equation represents the electron affinity of potassium?
A $K(g) \rightarrow K^+(g) + e^-$
B $K(g) \rightarrow K^-(g) + e^-$
C $K(g) + e^- \rightarrow K^-(g)$
D $K^+(g) + e^- \rightarrow K(g)$

44 Identify the process which corresponds to the standard enthalpy change of atomization of bromine.
A $Br_2(g) \rightarrow 2Br(g)$
B $Br_2(l) \rightarrow 2Br(g)$
C $Br_2(g) \rightarrow Br_2(l)$
D $Br_2(l) \rightarrow Br_2(g)$

45 **(a)** Write an equation to represent the lattice energy of potassium oxide, K_2O.
(b) The Born–Haber cycle shown may be used to calculate the lattice energy of potassium oxide (Figure 5.19).

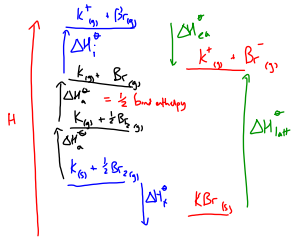


42 A 43 C 44 D

45 (a) $K_2O(s) \rightarrow 2K^+(g) + O^{2-}(g)$

(b) $W = \Delta H_{atom}^\ominus(O)$, the enthalpy of atomization of oxygen (which also corresponds to $\frac{1}{2}$ E(O=O), the O=O bond enthalpy)
$X = 2(\Delta H^\ominus(K))$, 2 × the first ionization energy of potassium
$Y = \Delta H_{ea}^\ominus(O) + \Delta H_{ea}^\ominus(O)$, the sum of the first and second electron affinities of oxygen
$Z = \Delta H_f^\ominus(K_2O(s))$, the standard enthalpy of formation of $K_2O(s)$

(c) $\Delta H_{lat}^\ominus(K_2O) = 2(61 + 2(89.2) + 2(419)) + \frac{1}{2}(498) + (-141) + (-753)$
$= +2238$ kJ mol^{-1}



Theoretical lattice enthalpies can be calculated from the ionic model

The energy needed to separate the ions depends on the product of the ionic charges and the sum of the ionic radii.

* An increase in the ionic radius of one of the ions decreases the attraction between the ions.
* An increase in the ionic charge increases the ionic attraction between the ions.

Enthalpy of solution

Size:

	F^-	Cl^-	Br^-	I^-
Li^+	1049	864	820	764
Na^+	930	790	754	705
K^+	829	720	691	650
Rb^+	795	695	668	632
Cs^+	759	670	647	613

Charge:

	$\Delta H^{\ominus}_{lattice}$ (kJ mol^{-1})		$\Delta H^{\ominus}_{lattice}$ (kJ mol^{-1})	Explanation of difference
NaCl	1049	$MgCl_2$	2540	$MgCl_2$ has more than double the lattice enthalpy of NaCl as Mg^{2+} has double the charge of Na^+ and a smaller ionic radius.
CaF_2	2651	CaO	3401	CaO has higher lattice enthalpy than CaF_2 as O^{2-} has double the charge of F^-. The value is less than double as O^{2-} has a larger ionic radius than F^-

Problems:

Compound	Ionic radius of $M^{+/}$ 10^{-12} m	$\Delta H^{\ominus}_{lat}$/kJ mol^{-1} (Born–Haber)
NaI	102	705
AgI	115	892

These calculations use the "Ionic model" so assume perfect ionic bonding however there may be a degree of covalency in reality eg AgI

Exercises

46 Which one of the following compounds would be expected to have the highest lattice enthalpy?

A Na_2O **B** MgO **C** CaO **D** KCl

47 Theoretical lattice enthalpies can be calculated on the ionic model. The values for the sodium halides are tabulated below.

Halide	$\Delta H^{\ominus}_{lat}$/ kJ mol^{-1}
NaF	+910
NaCl	+769
NaBr	+732
NaI	+682

Explain the trend in lattice enthalpies of sodium halides.

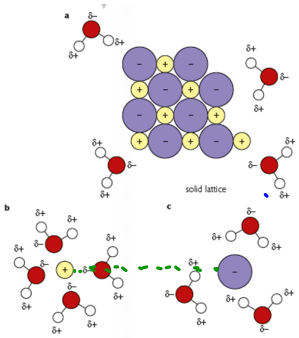
48 The theoretical lattice enthalpies, based on the ionic model, of sodium chloride and magnesium oxide are shown below.

Compound	$\Delta H^{\ominus}_{lat}$ / kJ mol^{-1}
NaCl	+769
MgO	+3795

Explain why magnesium oxide has the higher lattice enthalpy compared to sodium chloride.

Enthalpies of solution

The enthalpy change of solution is the enthalpy change when one mole of a solute is dissolved in a solvent to infinite dilution under standard conditions of temperature (298 K) and pressure (1.0×10^5 Pa).



Why infinite dilution ? As the concentration of the solution affects the interaction between the solute and solvent particles, we must refer to a solution in which there are no dissolved solute particles interfering. Therefore we refer to an infinitely dilute solution.

$$NH_4Cl(s) \xrightarrow{H_2O} NH_4^+(aq) + Cl^-(aq) \qquad \Delta H^\ominus_{sol} = +14.78\ kJ\ mol^{-1}$$

Once the ions are surrounded by a lattice of water molecules we say they are hydrated .

The strength of these interactions is given by their hydration enthalpies .

The hydration enthalpy of an ion depends on the attraction between the ions and the polar water molecules

The enthalpy change of hydration of an ion is the enthalpy change that occurs when one mole of gaseous ions is dissolved to form an infinitely dilute solution of one mole of aqueous ions under standard conditions of temperature and pressure.

$M^{n+}(g) \rightarrow M^{n+}(aq)$ $\quad Na^+_{(g)} \rightarrow Na^+_{(aq)}$ $\quad \Delta H^\ominus_{hyd}(M^{n+})$

$X^{m-}(g) \rightarrow X^{m-}(aq)$ $\quad Cl^-_{(g)} \rightarrow Cl^-_{(aq)}$ $\quad \Delta H^\ominus_{hyd}(X^{m-})$

As there is a force of attraction between the ions and the polar water molecules, it is an exothermic process and the enthalpy changes are negative.

Consider the following hydration energies of the Group 1 cations and Group 17 anions.

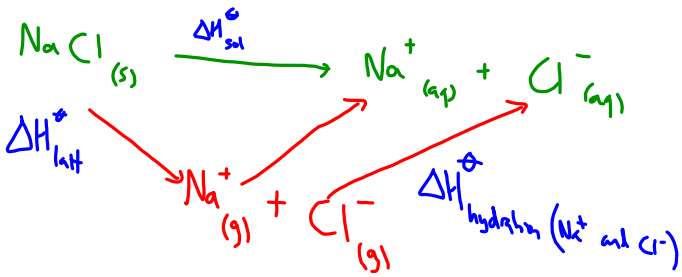
Cations	$\Delta H^\ominus_{hyd}$ / kJ mol^{-1}	Anions	$\Delta H^\ominus_{hyd}$ / kJ mol^{-1}
Li^+	–538	F^-	–504
Na^+	–424	Cl^-	–359
K^+	–340	Br^-	–328
Rb^+	–315	I^-	–287

The values become less exothermic as the groups are descended and the ionic radius increases. The electrostatic attraction between the ions and the water molecule decreases with increasing distance.

The enthalpy change of solution is related to the lattice enthalpy and the hydration enthalpies of the constituent ions

The solution of a substance can be understood by imagining that the solid is first sublimed into gaseous ions, which are then plunged into water.

$$\Delta H^\ominus_{sol}(NaCl) = \Delta H^\ominus_{lattice}(NaCl) + \Delta H^\ominus_{hyd}(Na^+) + \Delta H^\ominus_{hyd}(Cl^-)$$
$$= +790 - 424 - 359\ kJ\ mol^{-1}$$
$$= +7\ kJ\ mol^{-1}$$



15.2 Entropy and spontaneity

Understandings:

- Entropy (S) refers to the distribution of available energy among the particles. The more ways the energy can be distributed the higher the entropy.
- Gibbs free energy (G) relates the energy that can be obtained from a chemical reaction to the change in enthalpy (ΔH), change in entropy (ΔS), and absolute temperature.

  Guidance

  ΔG is a convenient way to take into account both the direct entropy change resulting from the transformation of the chemicals, and the indirect entropy change of the surroundings as a result of the gain/loss of heat energy. Examine various reaction conditions that affect ΔG.
- Entropy of gas > liquid > solid under same conditions.

Applications and skills:

- Prediction of whether a change will result in an increase or decrease in entropy by considering the states of the reactants and products.
- Calculation of entropy changes (ΔS) from given values ($S^{\ominus}$).
- Application of $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$ in predicting spontaneity and calculation of various conditions of enthalpy and temperature that will affect this.

  Guidance

  Thermodynamic data are given in section 12 of the data booklet.
- Relation of ΔG to position of equilibrium.

25. Si se somete al hidrocarburo $C_{10}H_{18}$ a combustión completa:

a) Formule y ajuste la reacción que se produce.

b) Calcule el número de moles de O_2 que se consumen en la combustión completa de 276 g de hidrocarburo.

c) Determine el volumen de aire, a 25 °C y 1 atm, necesario para la combustión completa de dicha cantidad de hidrocarburo (O_2 al 20 % en el aire).

(C. Madrid, 2001)

$R = 0.082$ atm L K^{-1} mol^{-1}

b. 29 mol O_2 → $PV = nRT$

c. 708.64 L O_2

$x \times \frac{20}{100} = 708.64$

33. Para determinar la riqueza de una partida de cinc se tomaron 50,0 g de una muestra homogénea y se trataron con ácido clorhídrico del 37 % en peso y densidad 1,18 g/mL, consumiéndose 126 mL de ácido. La reacción de cinc con ácido clorhídrico produce cloruro de cinc e hidrógeno. Calcule:

a) La molaridad de la disolución de ácido clorhídrico. = 11,96 M

b) El porcentaje de cinc en la muestra. = 98,51 %

(Castilla y León, 2006)

H = 1

Zn = 65.4

Cl = 35.5

Moles of HCl used:

moles = C × V = 11.96 × 0.126 L

$1.18 \frac{g}{mL} \cdot \frac{37}{100} \cdot \frac{1000\ mL}{1\ L} \cdot \frac{1\ mol}{36.5\ g} = 11.96$ mol dm^{-3}

b.

$Zn + 2HCl \rightarrow ZnCl_2 + H_2$

$x \rightarrow 1.5$ mol

$= 0.75$ mol $= 40$ g Zn

$\frac{40}{50} \times 100 = -\%$

32. Se mezclan 20 g de Zn puro con 200 mL de HCl 6 M. Como la relación es 1:2 en Zn:HCl, es evidente el desprendimiento de hidrógeno, ¿qué habrá quedado sin reaccionar: y, por tanto, el Zn es el reactivo limitante. cinc o ácido?, ¿qué volumen de hidrógeno, medido a 27 °C y 760 mm Hg, se habrá desprendido? = 7,52 L

19. Se dispone de ácido clorhídrico comercial del 36 % en peso y densidad 1,18 g/mL.

a) ¿Qué cantidad de este ácido necesitaremos para preparar 1 L de disolución de concentración 2 M? = 172 mL disolución H_2SO_4

b) ¿Cuáles serán la fracción molar y la molalidad de esta disolucion? = 2 mol HCl

(La Rioja, 2005)

3. **En una bomba calorimétrica se queman totalmente 100 g de un combustible, originando un aumento en la temperatura de 1 litro de agua de 30 °C. Calcula el calor desprendido en la reacción de combustión.**

Datos: c_e (H_2O) = 4180 J · kg^{-1} · K^{-1}.

Print pages:
7, 8, 9, 11, 12, 13,

$Q = m \cdot c \cdot \Delta T$

La variación de calor se obtiene de la expresión:

$$\Delta Q = m \cdot c_e \cdot \Delta T$$

donde sustituyendo la masa, el calor específico y el incremento de la temperatura, queda:

$\Delta T = (T_f - T_i) = 30\,°C$, que equivale a una diferencia de 30 K

Se obtiene que el calor desprendido es:

$$\Delta Q = 0{,}1\ \text{kg} \cdot 4180\ \text{J/(kg} \cdot \text{K)} \cdot 30\ \text{K} = 12\,540\ \text{J}$$