

# Energetics HL

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IB CHEMISTRY HL

25 <b>Mn</b> Manganese 54.938045	16 <b>S</b> Sulfur 32.065	<b>J</b>	6 <b>C</b> Carbon 12.0107	2 <b>He</b> Helium 4.002602	25 <b>Mn</b> Manganese 54.938045
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## 15.1 Energy cycles

### Understandings:

- Representative equations (e.g  $M^+_{(g)} \rightarrow M^+_{(aq)}$ ) can be used for enthalpy/energy of hydration, ionization, atomization, electron affinity, lattice, covalent bond and solution.
- Enthalpy of solution, hydration enthalpy and lattice enthalpy are related in an energy cycle.

### Applications and skills:

- Construction of Born-Haber cycles for group 1 and 2 oxides and chlorides.
- Construction of energy cycles from hydration, lattice and solution enthalpy. For example, dissolution of solid NaOH or  $NH_4Cl$  in water.
- Calculation of enthalpy changes from Born-Haber or dissolution energy cycles.
- Relate size and charge of ions to lattice and hydration enthalpies.
- Perform lab experiments which could include single replacement reactions in aqueous solutions.

### Guidance:

- Polarizing effect of some ions producing covalent character in some largely ionic substances will not be assessed.
- The following enthalpy/energy terms should be covered: ionization, atomization, electron affinity, lattice, covalent bond, hydration and solution.
- Value for lattice enthalpies (section 18), enthalpies of aqueous solutions (section 19) and enthalpies of hydration (section 20).

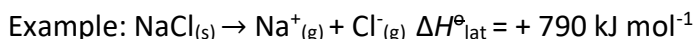
## Syllabus checklist

<b>Objective</b>	<b>I am confident with this</b>	<b>I need to review this</b>	<b>I need help with this</b>
Construct a Born-Haber cycle group 1 and 2 oxides and chlorides			
Calculate the lattice enthalpy and enthalpy of formation from a Born-Haber cycle			
Explain the factors that affect the value of the lattice enthalpy			
Construct energy cycles for the enthalpy change of solution			
Calculate the enthalpy change of solution from an energy cycle			
Explain the factors that affect the value of the hydration enthalpy			

## Lattice enthalpy ( $\Delta H^\circ_{\text{lat}}$ )

Lattice enthalpy can be defined in two ways:

- 1) The enthalpy change when one mole of solid ionic compound is separated into its gaseous ions under standard conditions (endothermic).



- 2) The enthalpy change when one mole of solid ionic compound is formed from its gaseous ions under standard conditions (exothermic).

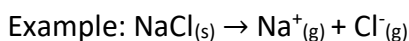


- The IB uses the **first** definition.

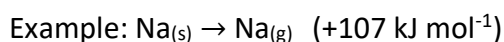
**$\Delta H^\circ_{\text{lat}}$  is endothermic and has a positive  $\Delta H$ .**

## Some important definitions:

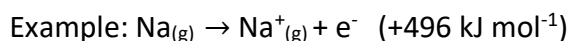
- **Lattice enthalpy ( $\Delta H^\circ_{\text{lat}}$ )** - the enthalpy change when one mole of a solid ionic compound is separated into gaseous ions under standard conditions (endothermic).



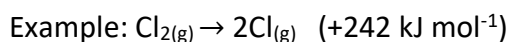
- **Enthalpy of atomisation ( $\Delta H^\circ_{\text{atom}}$ )** – the enthalpy change when one mole of gaseous atoms is formed from an element in its standard state (endothermic).



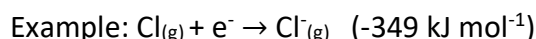
- **First ionisation energy ( $\Delta H^\circ_{\text{i}}$ )** – the minimum energy required to remove one mole of electrons from one mole of gaseous atoms (endothermic)



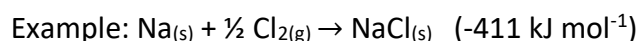
- **Bond dissociation enthalpy ( $E$ )** – the enthalpy change when one mole of bonds is broken in the gaseous state (endothermic).



- **First electron affinity ( $\Delta H^\circ_{\text{e}}$ )** – the enthalpy change when one mole of electrons are added to one mole of gaseous atoms (exothermic).

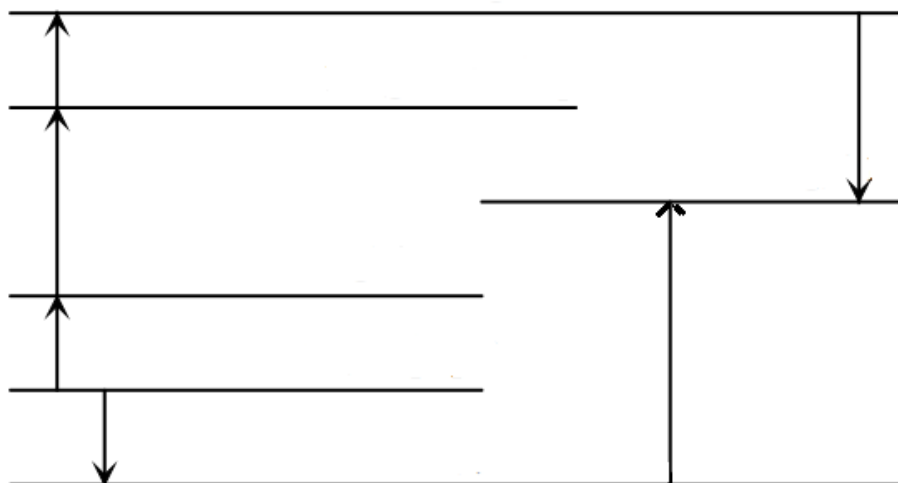


- **Standard enthalpy change of formation ( $\Delta H^\circ_{\text{f}}$ )** - The enthalpy change when one mole of a compound is formed from its elements in their standard states under standard conditions.



**Exercises:**

- 1) Using the values given above, construct a Born-Haber cycle using the template below, and calculate the  $\Delta H^\ominus_{\text{lat}}$  for NaCl.



- 2) Using the values given in the table below, construct a Born-Haber cycle and calculate the  $\Delta H^\ominus_{\text{lat}}$  for  $\text{CaF}_2$

$\Delta H_{\text{at}} \text{Ca}_{(s)}$ (enthalpy of atomization)	+179 kJ mol <sup>-1</sup>
$E \text{F}_{2(g)}$ (bond dissociation enthalpy)	+158 kJ mol <sup>-1</sup>
$\Delta H^\ominus_{\text{i}} \text{Ca}_{(g)}$ (1 <sup>st</sup> ionisation energy)	+590 kJ mol <sup>-1</sup>
$\Delta H^\ominus_{\text{i}} \text{Ca}^+_{(g)}$ (2 <sup>nd</sup> ionisation energy)	+1150 kJ mol <sup>-1</sup>
$\Delta H^\ominus_{\text{e}} \text{F}_{(g)}$ (first electron affinity)	-348 kJ mol <sup>-1</sup>
$\Delta H_{\text{f}} \text{CaF}_{2(s)}$ (enthalpy of formation)	-1220 kJ mol <sup>-1</sup>

### Factors that affect lattice enthalpy

- The charge on the ion; an ion with a higher charge will have a stronger force of attraction, therefore a higher lattice enthalpy.

Example: MgO has a higher lattice enthalpy than NaCl.

- The ionic radius of the ions; an increase in ionic radius decreases the attraction between the ions.

Example: NaCl has a higher lattice enthalpy than KBr.

### Exercises:

1. Which combination of ionic radius and ionic charge would result in the highest lattice enthalpy for an ionic compound?

	Ionic radius	Ionic charge
A.	small	high
B.	large	high
C.	small	low
D.	large	low

2. Which is a correct definition of lattice enthalpy?

- A. It is the enthalpy change that occurs when an electron is removed from 1 mol of gaseous atoms.
- B. It is the enthalpy change that occurs when 1 mol of a compound is formed from its elements.
- C. It is the enthalpy change that occurs when 1 mol of solid crystal changes into a liquid.
- D. It is the enthalpy change that occurs when 1 mol of solid crystal is broken into its gaseous ions.

3. Which ionic compound has the greatest lattice enthalpy?

- A. MgO
- B. CaO
- C. NaF
- D. KF

4. Which is the correct order of increasing magnitude of lattice enthalpy (lowest first)?

A.  $\text{NaCl} < \text{KCl} < \text{MgS} < \text{MgO}$

B.  $\text{MgO} < \text{MgS} < \text{KCl} < \text{NaCl}$

C.  $\text{KCl} < \text{NaCl} < \text{MgS} < \text{MgO}$

D.  $\text{MgO} < \text{NaCl} < \text{KCl} < \text{MgS}$

5. Which ionic compound has the most endothermic lattice enthalpy?

A.  $\text{NaCl}$

B.  $\text{KCl}$

C.  $\text{NaF}$

D.  $\text{KF}$

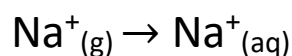
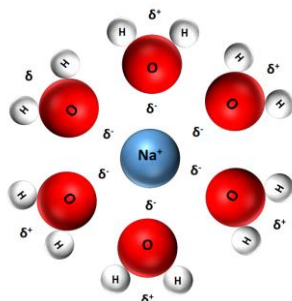
## Enthalpies of solution and hydration

### Enthalpy of solution $\Delta H^{\ominus}_{\text{sol}}$

- The enthalpy change of solution ( $\Delta H^{\ominus}_{\text{sol}}$ ) is the enthalpy change when one mole of an ionic substance dissolves in water to give a solution of infinite dilution.
- A solution of infinite dilution is one where there is a sufficiently large excess of water that adding any more does not cause any further heat to be absorbed or evolved.

### Enthalpy of hydration $\Delta H^{\ominus}_{\text{hyd}}$

- The enthalpy of hydration ( $\Delta H^{\ominus}_{\text{hyd}}$ ) is the enthalpy change when one mole of gaseous ions dissolve in water to give a solution of infinite dilution.
- When a gaseous ion is hydrated, ion-dipole forces occur between the gaseous ion and the dipoles of the water molecule.
- The formation of ion-dipole forces releases energy so  $\Delta H_{\text{hyd}}$  values are always negative.
- The higher the charge on the ion and the smaller the ionic radius, the more exothermic the value of the  $\Delta H_{\text{hyd}}$ .

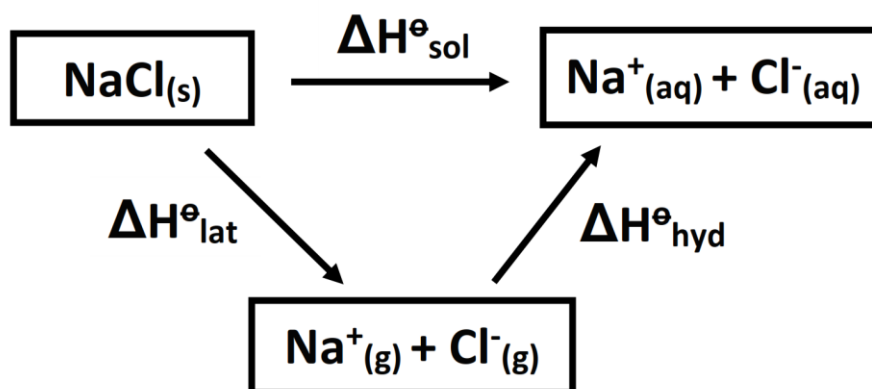


### Dissolving

- The solid ionic compound is broken down into its gaseous ions ( $\Delta H^{\ominus}_{\text{lat}}$ ).
- The gaseous ions are hydrated by water molecules ( $\Delta H^{\ominus}_{\text{hyd}}$ ).



Energy cycle for the dissolving process



$$\Delta H^{\ominus}_{\text{sol}} = \Delta H^{\ominus}_{\text{lat}} + \Delta H^{\ominus}_{\text{hyd}}$$

Exercises:

1. Construct an enthalpy cycle and calculate the enthalpy change of solution ( $\Delta H^{\ominus}_{\text{sol}}$ ) for calcium fluoride ( $\text{CaF}_2$ ).

$\Delta H^{\ominus}_{\text{hyd}} \text{Ca}^{2+}$ ( $\text{kJ mol}^{-1}$ )	-1616
$\Delta H^{\ominus}_{\text{hyd}} \text{F}^-$ ( $\text{kJ mol}^{-1}$ )	-504
$\Delta H^{\ominus}_{\text{lat}} (\text{CaF}_2)$ ( $\text{kJ mol}^{-1}$ )	+2651

2. Construct an enthalpy cycle and calculate the lattice enthalpy ( $\Delta H^{\ominus}_{\text{lat}}$ ) for NaOH

$\Delta H^{\ominus}_{\text{hyd}} \text{Na}^+$ ( $\text{kJ mol}^{-1}$ )	-424
$\Delta H^{\ominus}_{\text{hyd}} \text{OH}^-$ ( $\text{kJ mol}^{-1}$ )	-519
$\Delta H^{\ominus}_{\text{sol}} (\text{NaOH})$ ( $\text{kJ mol}^{-1}$ )	-44.5

### Factors that affect $\Delta H^\ominus_{\text{hyd}}$

- The size of the hydration enthalpy is determined by the attraction between the ions and the water molecules.
- The size of the ion; the smaller the ion, the stronger the attraction and the higher the  $\Delta H^\ominus_{\text{hyd}}$
- The charge on the ion; the greater the charge on the ion, the stronger the attraction and the higher the  $\Delta H^\ominus_{\text{hyd}}$

### Exercises:

1) Explain why the enthalpy change of hydration ( $\Delta H^\ominus_{\text{hyd}}$ ) of  $\text{Na}^+$  is greater than  $\text{K}^+$

2) Explain why the enthalpy change of hydration ( $\Delta H^\ominus_{\text{hyd}}$ ) of  $\text{Mg}^{2+}$  is greater than  $\text{Li}^+$

## 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 ( $\Delta H$ ), change in entropy ( $\Delta S$ ), and absolute temperature ( $T$ ).
- 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 ( $\Delta S$ ) from given standard entropy values ( $S^\ominus$ ).
- Application of  $\Delta G = \Delta H - T\Delta S$
- Relation of  $\Delta G$  to position of equilibrium.

### Guidance:

- Examine various reaction conditions that affect  $\Delta G$ .
- $\Delta G$  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.

### Syllabus checklist

Objective	I am confident with this	I need to review this	I need help with this
Predict, by looking at the state symbols of reactants and products, whether a reaction has an increase or decrease in entropy.			
Calculate changes in entropy using standard entropy values			
Calculate the $\Delta G$ for a reaction using the equation using the equation $\Delta G = \Delta H - T\Delta S$			
Explain the effect of $\Delta H$ , $\Delta S$ and $T$ on the spontaneity of a chemical reaction			

## Spontaneity

- A spontaneous process is a process that occurs without adding energy (other than the energy required to overcome the energy barrier).

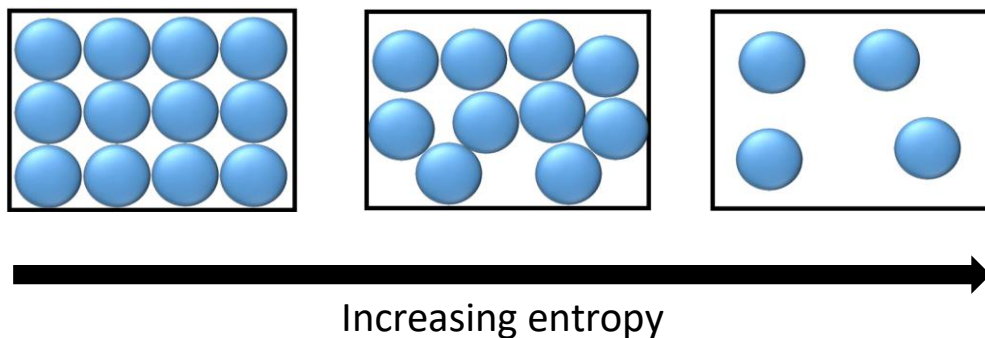


- Spontaneous processes can be either fast or slow.



## Entropy ( $S$ )

- Entropy ( $S$ ) refers to the distribution of available energy among the particles in a system.
- The more ways the energy can be distributed, the greater the entropy.
- Gases have a higher entropy than liquids which have a higher entropy than solids.
- Entropy increases as temperature increases.



### Factors that increase entropy (positive entropy change, + $\Delta S$ )

Dissolving	$\text{NaCl}_{(s)} \rightarrow \text{Na}^+_{(aq)} \text{Cl}^-_{(aq)}$
Increase in mol of gas	$\text{CaCO}_{3(s)} \rightarrow \text{CaO}_{(s)} + \text{CO}_{2(g)}$ $\text{C}_3\text{H}_{8(g)} + 5\text{O}_{2(g)} \rightarrow 3\text{CO}_{2(g)} + 4\text{H}_2\text{O}_{(g)}$ $\text{CH}_{4(g)} + \text{H}_2\text{O}_{(g)} \rightarrow 3\text{H}_{2(g)} + \text{CO}_{(g)}$

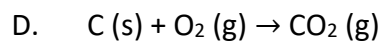
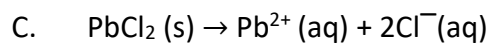
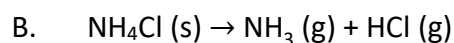
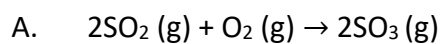
### Factors that decrease entropy (negative entropy change, - $\Delta S$ )

Crystallisation	$\text{Na}^+_{(aq)} \text{Cl}^-_{(aq)} \rightarrow \text{NaCl}_{(s)}$
Decrease in mol of gas	$\text{N}_{2(g)} + 3\text{H}_{2(g)} \rightleftharpoons 2\text{NH}_{3(g)}$ $\text{C}_2\text{H}_{4(g)} + \text{H}_2(g) \rightarrow \text{C}_2\text{H}_6(g)$ $2\text{Mg}_{(s)} + \text{O}_{2(g)} \rightarrow 2\text{MgO}_{(s)}$

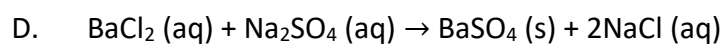
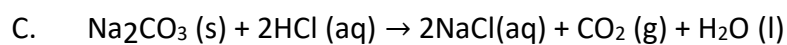
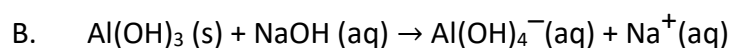
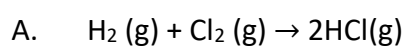
### Exercises:

- What is the correct order of decreasing entropy for a pure substance?
  - gas > liquid > solid
  - solid > liquid > gas
  - solid > gas > liquid
  - liquid > solid > gas
- Which change will **not** increase the entropy of a system?
  - Increasing the temperature
  - Changing the state from liquid to gas
  - Mixing different types of particles
  - A reaction where four moles of gaseous reactants changes to two moles of gaseous products
- Which reaction has the greatest increase in entropy?
  - $\text{SO}_2(g) + 2\text{H}_2\text{S}(g) \rightarrow 2\text{H}_2\text{O}(l) + 3\text{S}(s)$
  - $\text{CaO}(s) + \text{CO}_2(g) \rightarrow \text{CaCO}_3(s)$
  - $\text{CaC}_2(s) + 2\text{H}_2\text{O}(l) \rightarrow \text{Ca}(\text{OH})_2(s) + \text{C}_2\text{H}_2(g)$
  - $\text{N}_2(g) + \text{O}_2(g) \rightarrow 2\text{NO}(g)$

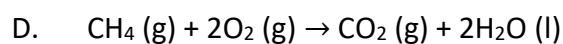
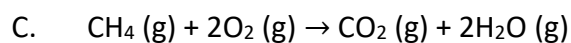
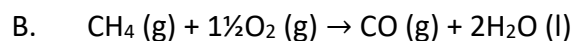
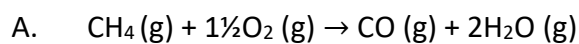
4. Which reaction has the most negative change in entropy?



5. Which reaction has the largest increase in entropy?



6. Which reaction has the greatest positive entropy change?



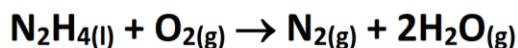
## Standard entropy change ( $\Delta S^\circ$ )

- The standard entropy change of reaction can be calculated using this equation:

$$\Delta S^\circ_{\text{reaction}} = \sum S^\circ_{\text{products}} - \sum S^\circ_{\text{reactants}}$$

- A perfectly ordered crystal at zero kelvin has an entropy of zero.
- Absolute entropy values are positive.

**Example:** Calculate the entropy change for this reaction:

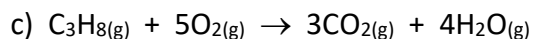
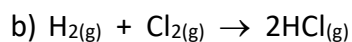
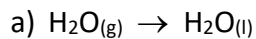


	$S^\circ$ ( $\text{J K}^{-1} \text{mol}^{-1}$ )
$\text{N}_2\text{H}_4(\text{l})$	121
$\text{O}_2(\text{g})$	205
$\text{N}_2(\text{g})$	192
$\text{H}_2\text{O}(\text{g})$	188

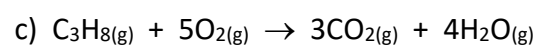
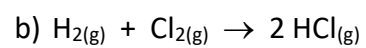
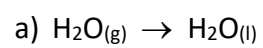
**Exercise:** Use the data in the table to answer the questions.

Substance	$S^\circ$ ( $\text{J K}^{-1} \text{mol}^{-1}$ )	Substance	$S^\circ$ ( $\text{J K}^{-1} \text{mol}^{-1}$ )
$\text{H}_2\text{O}(\text{g})$	189	$\text{CO}_2(\text{g})$	214
$\text{H}_2\text{O}(\text{l})$	70	$\text{C}_3\text{H}_8(\text{g})$	270
$\text{H}_2(\text{g})$	131	$\text{O}_2(\text{g})$	205
$\text{Cl}_2(\text{g})$	223		
$\text{HCl}(\text{g})$	187		

1) Predict the sign of  $\Delta S^\circ$  for the following reactions and explain your reasoning.



2) Calculate  $\Delta S^\circ$  for the above reactions.





### Gibbs free energy

- The energy associated with a chemical reaction that can be used to do work.
- $\Delta G$  must be negative for a spontaneous process.

$$\Delta G = \Delta H - T\Delta S$$

$\Delta G$  – Gibbs free energy change ( $\text{kJ mol}^{-1}$ )

$\Delta H$  – change in enthalpy ( $\text{kJ mol}^{-1}$ )

T – temperature in kelvin, K

$\Delta S$  – change in entropy ( $\text{J K}^{-1} \text{mol}^{-1}$ )

**Example:** Calculate  $\Delta G$  for this reaction at 500 K, using the data in the table. State and explain if the reaction is spontaneous at that temperature.



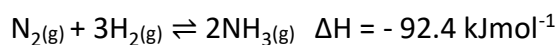
Compound	$\Delta H_f^\ominus$ ( $\text{kJ mol}^{-1}$ )	$S^\ominus$ ( $\text{JK}^{-1}\text{mol}^{-1}$ )
$\text{CaCO}_{3(s)}$	-1207	92.9
$\text{CaO}_{(s)}$	-635	39.7
$\text{CO}_{2(g)}$	-394	214

Calculate the temperature at which the reaction will be spontaneous:

### Exercises:

1. A reaction has a standard enthalpy change,  $\Delta H^\ominus$ , of +10.00 kJ mol<sup>-1</sup> at 298 K. The standard entropy change,  $\Delta S^\ominus$ , for the same reaction is +10.00 J K<sup>-1</sup> mol<sup>-1</sup>. What is the value of  $\Delta G^\ominus$  for the reaction in kJ mol<sup>-1</sup>?

2. Consider the following reaction:



- (i) The absolute entropy values,  $S$ , at 298 K for  $\text{N}_{2(\text{g})}$ ,  $\text{H}_{2(\text{g})}$  and  $\text{NH}_{3(\text{g})}$  are 192, 131 and 193 J K<sup>-1</sup> mol<sup>-1</sup> respectively. Calculate  $\Delta S^\ominus$  for the reaction and explain the sign of  $\Delta S^\ominus$ .
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
- (ii) Calculate  $\Delta G^\ominus$  for the reaction at 298 K. State and explain whether the reaction is spontaneous.

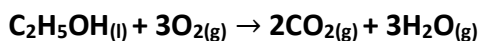
### Standard change in Gibbs free energy ( $\Delta G^\ominus$ )

- The standard change in Gibbs free energy ( $\Delta G^\ominus$ ) is the change in Gibbs free energy measured under standard conditions (298 K and 100 kPa).

$$\Delta G^\ominus = \sum \Delta G_f^\ominus \text{ products} - \sum \Delta G_f^\ominus \text{ reactants}$$

- $\Delta G_f^\ominus$  - standard Gibbs free energy of formation is the change in Gibbs free energy when one mole of a compound is formed from its elements in their standard states under standard conditions (100 kPa and 298 K).

**Example:** Calculate the  $\Delta G^\ominus$  for the following reaction. State and explain if the reaction is spontaneous at 298 K.



Compound	$\Delta G_f^\ominus / \text{kJ mol}^{-1}$
$\text{C}_2\text{H}_5\text{OH}_{(l)}$	-175
$\text{CO}_{2(g)}$	-394
$\text{H}_2\text{O}_{(g)}$	-229
$\text{O}_{2(g)}$	0

## The effect of $\Delta H$ , $\Delta S$ and T on the spontaneity of a chemical reaction

### Exothermic reactions

$\Delta H$	$\Delta S$	T	$\Delta G$	spontaneity
negative < 0	positive > 0	any temperature		

- $\Delta H$  is negative and  $\Delta S$  is positive, therefore  $\Delta G$  will be negative at any temperature.
- An exothermic reaction with an increase in entropy will be spontaneous at any temperature.

$\Delta H$	$\Delta S$	T	$\Delta G$	spontaneity
negative < 0	negative < 0	high		

$\Delta H$	$\Delta S$	T	$\Delta G$	spontaneity
negative < 0	negative < 0	low		

- $\Delta G$  will be negative only at low temperatures; at high T, ( $T\Delta S$ ) makes  $\Delta G$  positive.

### Endothermic reactions

$\Delta H$	$\Delta S$	T	$\Delta G$	spontaneity
positive > 0	negative < 0	any temperature		

- $\Delta H$  is positive and  $\Delta S$  is negative, therefore  $\Delta G$  will be positive at any temperature.
- An endothermic reaction with a decrease in entropy will be non-spontaneous at any temperature.

$\Delta H$	$\Delta S$	T	$\Delta G$	spontaneity
positive > 0	positive > 0	high		

$\Delta H$	$\Delta S$	T	$\Delta G$	spontaneity
positive > 0	positive > 0	low		

- $\Delta G$  will be negative only at high temperatures ( $T\Delta S > \Delta H$ ); at low temperatures  $\Delta H > T\Delta S$  ( $+\Delta G$ ).

## Summary

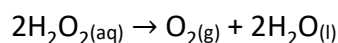
$\Delta S$		
$\Delta H < 0$ $\Delta S > 0$	$\Delta H > 0$ $\Delta S > 0$	
Spontaneous at any temperature	Spontaneous at <b>high</b> temperatures	
		$\Delta H$
$\Delta H < 0$ $\Delta S < 0$	$\Delta H > 0$ $\Delta S < 0$	
Spontaneous at <b>low</b> temperatures	Non-spontaneous at any temperature	

## Exercises:

- Some words used in chemistry can have a specific meaning which is different to their meaning in everyday English. State what the term *spontaneous* means when used in a chemistry context.
- Under what circumstances is a reaction spontaneous at all temperatures?

	$\Delta H^\ominus$	$\Delta S^\ominus$
A.	+	+
B.	+	-
C.	-	-
D.	-	+

- When hydrogen peroxide decomposes, the temperature of the reaction mixture increases.



What are the signs of  $\Delta H$ ,  $\Delta S$  and  $\Delta G$  for this reaction?

	$\Delta H$	$\Delta S$	$\Delta G$
A.	-	-	-
B.	-	+	-
C.	+	+	-
D.	-	+	+

4.  $\Delta G^\ominus$  calculations predict that a reaction is always spontaneous for which of the following combinations of  $\Delta H^\ominus$  and  $\Delta S^\ominus$ ?

A.  $+\Delta H^\ominus$  and  $+\Delta S^\ominus$

B.  $+\Delta H^\ominus$  and  $-\Delta S^\ominus$

C.  $-\Delta H^\ominus$  and  $-\Delta S^\ominus$

D.  $-\Delta H^\ominus$  and  $+\Delta S^\ominus$

5. What are the signs of  $\Delta H^\ominus$  and  $\Delta S^\ominus$  for a reaction that is non-spontaneous at low temperature but spontaneous at high temperature?

	$\Delta H^\ominus$	$\Delta S^\ominus$
A.	-	-
B.	+	-
C.	-	+
D.	+	+