Energetics HL (answers)

IB CHEMISTRY HL

25	16		6	2	25
Mn	**S**	**J**	**C**	**He**	**M**n
Manganese	Sulfur		Carbon	Helium	Manganese
54.938045	32.065		12.0107	4.002602	54.938045

15.1 Energy cycles

Understandings:

- Representative equations (eg $M^+_{(g)}$ ➜ $M^+_{(aq)}$) 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).

Lattice enthalpy (ΔH$^{e}_{lat}$)

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).
   Example: $NaCl_{(s)} \rightarrow Na^{+}_{(g)} + Cl^{-}_{(g)}$ $\Delta H^{o}_{lat} = +790 kJ\ mol^{-1}$
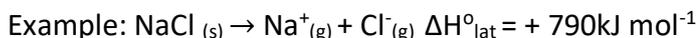
2) The enthalpy change when one mole of solid ionic compound is formed from its gaseous ions under standard conditions (exothermic).
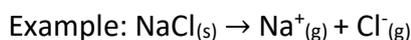   Example: $Na^{+}_{(g)} + Cl^{-}_{(g)} \rightarrow NaCl_{(s)}$ $\Delta H^{e}_{lat} = -790 kJ\ mol^{-1}$

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

ΔH$^{e}_{lat}$ is endothermic and has a positive ΔH.

Some important definitions:
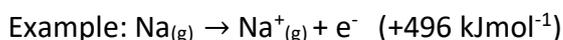
- **Lattice enthalpy (ΔH$^{\ominus}_{lat}$)** - the enthalpy change when one mole of a solid ionic compound is separated into gaseous ions under standard conditions (endothermic).

  Example: $NaCl_{(s)} \rightarrow Na^{+}_{(g)} + Cl^{-}_{(g)}$

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

 Example: $Na_{(s)} \rightarrow Na_{(g)}$ (+107 $kJmol^{-1}$)

- **First ionisation energy (ΔH$^{\ominus}_{i}$)** – the minimum energy required to remove one mole of electrons from one mole of gaseous atoms (endothermic)

  Example: $Na_{(g)} \rightarrow Na^{+}_{(g)} + e^{-}$ (+496 $kJmol^{-1}$)

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

  Example: $Cl_{2(g)} \rightarrow 2Cl_{(g)}$ (+242 $kJmol^{-1}$)

- **First electron affinity (ΔH$^{\ominus}_{e}$)** – the enthalpy change when one mole of electrons are added to one mole of gaseous atoms (exothermic).
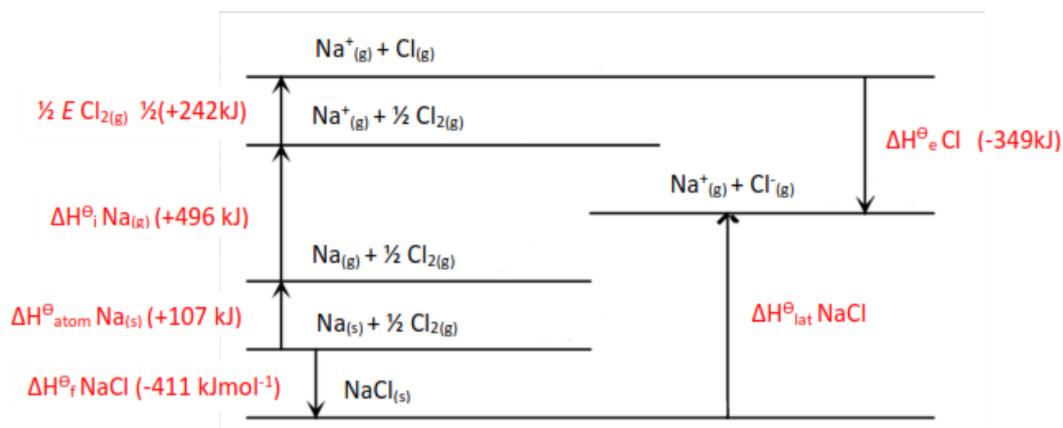
  Example: $Cl_{(g)} + e^{-} \rightarrow Cl^{-}_{(g)}$ (-349 $kJmol^{-1}$)
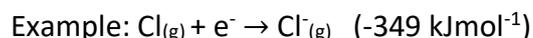
- **Standard enthalpy change of formation (ΔH$^{\ominus}_{f}$)** - The enthalpy change when one mole of a compound is formed from it elements in their standard states under standard conditions.

  Example: $Na_{(s)} + ½ Cl_{2(g)} \rightarrow NaCl_{(s)}$ (-411 $kJmol^{-1}$)
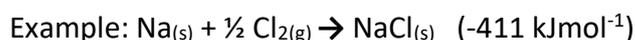
Exercises:

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

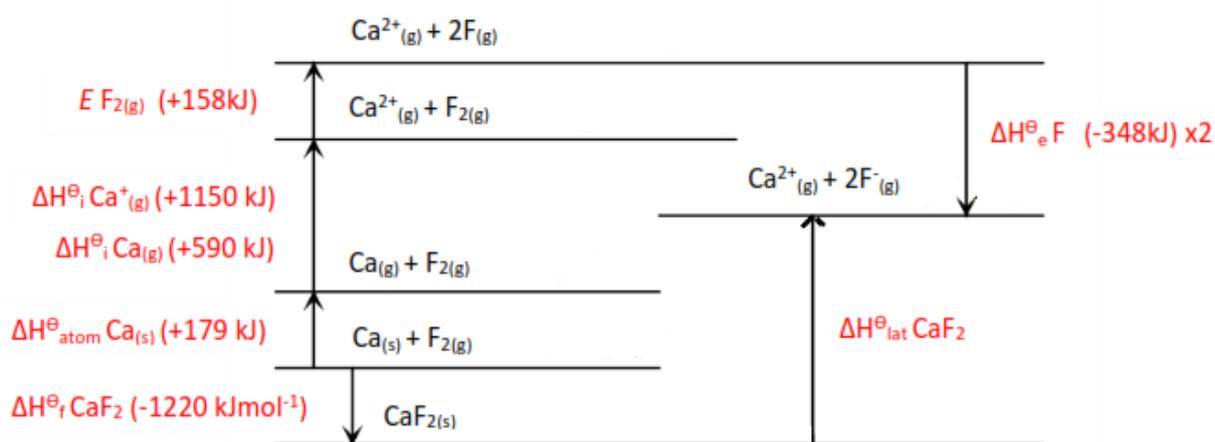$Na^+_{(g)} + Cl_{(g)}$

½ E $Cl_{2(g)}$ ½(+242kJ) $Na^+_{(g)} + ½ Cl_{2(g)}$

$\Delta H^\ominus_e$ Cl (-349kJ)

$Na^+_{(g)} + Cl^-_{(g)}$

$\Delta H^\ominus_i$ $Na_{(g)}$ (+496 kJ)

$Na_{(g)} + ½ Cl_{2(g)}$

$\Delta H^\ominus_{atom}$ $Na_{(s)}$ (+107 kJ) $Na_{(s)} + ½ Cl_{2(g)}$

$\Delta H^\ominus_{lat}$ NaCl

$\Delta H^\ominus_f$ NaCl (-411 kJmol^{-1}) $NaCl_{(s)}$

$\Delta H^\ominus_{lat} = (\Delta H^\ominus_{atom} Na_{(s)}) + (\Delta H^\ominus_i Na_{(g)}) + (½ E Cl_{2(g)}) + (\Delta H^\ominus_e Cl) - (\Delta H^\ominus_f NaCl)$

$\Delta H^\ominus_{lat} = (+107) + (+496) + (+121) + (-349) - (-411)$

$\Delta H^\ominus_{lat} = +786$ kJmol^{-1}

2) Using the values given in the table below, construct a Born-Haber cycle and calculate the $\Delta H^\ominus_{lat}$ for CaF_2

$Ca^{2+}_{(g)} + 2F_{(g)}$

E $F_{2(g)}$ (+158kJ) $Ca^{2+}_{(g)} + F_{2(g)}$

$\Delta H^\ominus_e$ F (-348kJ) x2

$Ca^{2+}_{(g)} + 2F^-_{(g)}$

$\Delta H^\ominus_i$ $Ca^+_{(g)}$ (+1150 kJ)
$\Delta H^\ominus_i$ $Ca_{(g)}$ (+590 kJ) $Ca_{(g)} + F_{2(g)}$

$\Delta H^\ominus_{atom}$ $Ca_{(s)}$ (+179 kJ) $Ca_{(s)} + F_{2(g)}$

$\Delta H^\ominus_{lat}$ CaF_2

$\Delta H^\ominus_f$ CaF_2 (-1220 kJmol^{-1}) $CaF_{2(s)}$

$\Delta H^\ominus_{lat} = (\Delta H^\ominus_{atom} Ca_{(s)}) + (\Delta H^\ominus_i Ca_{(g)}) + (\Delta H^\ominus_i Ca^+_{(g)}) + (E F_{2(g)}) + 2(\Delta H^\ominus_e F_2) - (\Delta H^\ominus_f CaF_2)$

$\Delta H^\ominus_{lat} = (+179) + (+590) + (+1150) + (+158) + 2(-348) - (-1220)$

$\Delta H^\ominus_{lat} = +2601$ kJmol^{-1}

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? A

	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? D

   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

   A. MgO

   B. CaO

   C. NaF

   D. KF

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

    A.   NaCl < KCl < MgS < MgO

    B.   MgO < MgS < KCl < NaCl

    C.   KCl < NaCl < MgS < MgO

    D.   MgO < NaCl < KCl < MgS

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

    A.   NaCl

    B.   KCl

    C.   NaF

    D.   KF

Enthalpies of solution and hydration

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

- The enthalpy change of solution ($\Delta H^{\ominus}_{sol}$) 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 $\Delta H^{\ominus}_{hyd}$

- The enthalpy of hydration ($\Delta H^{\ominus}_{hyd}$) 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 ΔH_{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 ΔH_{hyd} .

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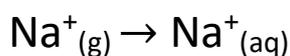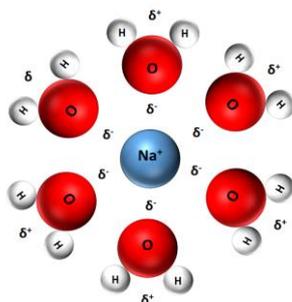
Dissolving
- The solid ionic compound is broken down into its gaseous ions ($\Delta H^{\ominus}_{lat}$).
- The gaseous ions are hydrated by water molecules ($\Delta H^{\ominus}_{hyd}$).

Energy cycle for the dissolving process
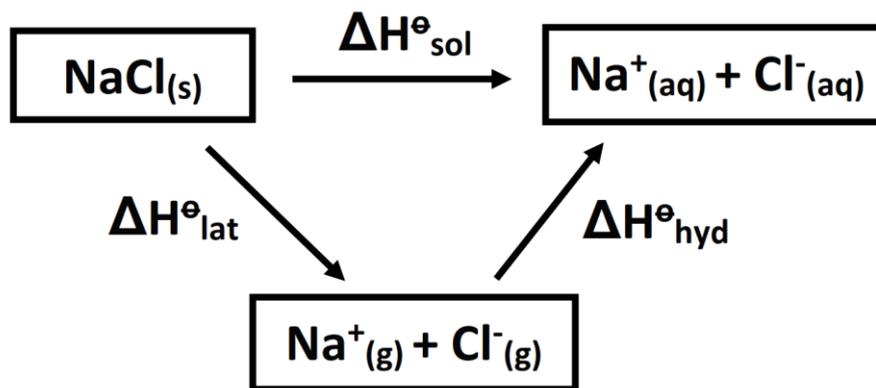
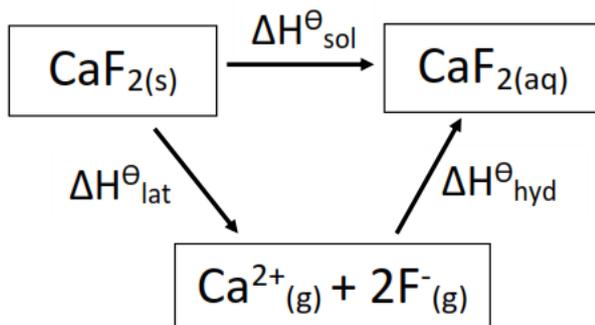$$\Delta H^{\ominus}_{sol} = \Delta H^{\ominus}_{lat} + \Delta H^{\ominus}_{hyd}$$

Exercises:

1. Construct an enthalpy cycle and calculate the enthalpy change of solution ($\Delta H^{\ominus}_{sol}$) for calcium fluoride (CaF_2).

$\Delta H^{\ominus}_{hyd}$ Ca^{2+} (kJ mol^{-1})	-1616
$\Delta H^{\ominus}_{hyd}$ F$^-$ (kJ mol^{-1})	-504
$\Delta H^{\ominus}_{lat}$ (CaF_2) (kJ mol^{-1})	+2651

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

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

1) Enthalpy cycle for CaF_2
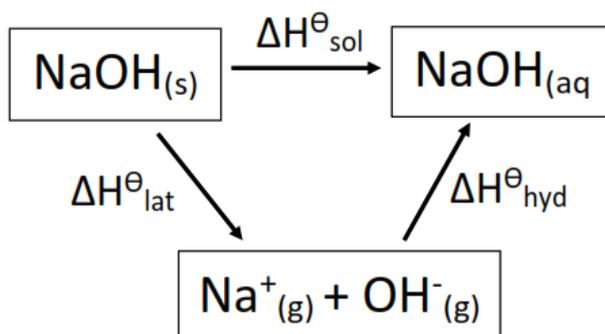

$\Delta H^{\ominus}_{sol} = \Delta H^{\ominus}_{lat} + \Delta H^{\ominus}_{hyd}$

$\Delta H^{\ominus}_{sol} = +2651 + (-1616 + 2 \times -504)$

$\Delta H^{\ominus}_{sol} = +27\ kJmol^{-1}$

2) Enthalpy cycle for NaOH

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

$\Delta H^{\ominus}_{lat}\ (NaOH) = -44.5 - (-424 + -519)$

$\Delta H^{\ominus}_{lat}\ (NaOH) = +898\ kJmol^{-1}$

Factors that affect $\Delta H^{\ominus}_{hyd}$

- 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 $\Delta H^{\ominus}_{hyd}$

- The charge on the ion; the greater the charge on the ion, the stronger the attraction and the higher the $\Delta H^{\ominus}_{hyd}$

Exercises:

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

Na$^+$ has a smaller ionic radius than K$^+$, therefore a greater $\Delta H^{\ominus}_{hyd}$ (stronger electrostatic attraction between the Na$^+$ ion and the negative dipole of the water molecule).

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

Mg^{2+} has a higher charge on the ion, therefore a greater $\Delta H^{\ominus}_{hyd}$ (same reason as above).

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 (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 (ΔS) from given standard entropy values ($S^{\ominus}$).
*   Application of $\Delta G = \Delta H - T\Delta S$
*   Relation of ΔG to position of equilibrium.

Guidance:
*   Examine various reaction conditions that affect ΔG
* 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.

Spontaneity

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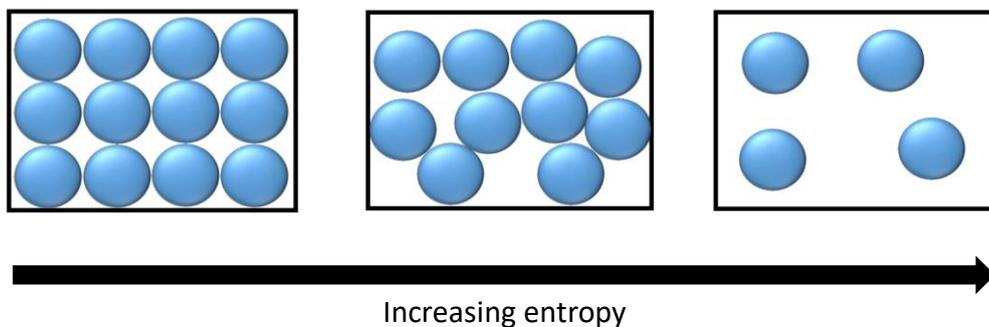

- Spontaneous processes can be either fast or slow.

Entropy
- 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.

Increasing entropy

Factors that increase entropy (positive entropy change, +Δ*S*)

Dissolving	$NaCl_{(s)} \rightarrow Na^+_{(aq)} \, Cl^-_{(aq)}$
Increase in mol of gas	$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$ $C_3H_{8(g)} + 5O_{2(g)} \rightarrow 3CO_{2(g)} + 4H_2O_{(g)}$ $CH_{4\,(g)} + H_2O_{(g)} \rightarrow 3H_{2(g)} + CO_{(g)}$

Factors that decrease entropy (negative entropy change, -Δ*S*)

Crystallisation	$Na^+_{(aq)} \, Cl^-_{(aq)} \rightarrow NaCl_{(s)}$
Decrease in mol of gas	$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ $C_2H_{4(g)} + H_{2(g)} \rightarrow C_2H_{6(g)}$ $2Mg_{(s)} + O_{2(g)} \rightarrow 2MgO_{(s)}$

Exercises:

1. What is the correct order of decreasing entropy for a pure substance?

    A. gas > liquid > solid

    B. solid > liquid > gas

    C. solid > gas > liquid

    D. liquid > solid > gas

    A – gases have the highest entropy, followed by liquids and then solids which have the lowest entropy.

2. Which change will **not** increase the entropy of a system?

    A. Increasing the temperature

    B. Changing the state from liquid to gas

    C. Mixing different types of particles

    D. A reaction where four moles of gaseous reactants changes to two moles of gaseous products

    D – there is a decrease in the number of moles of gas in the products, therefore a decrease in entropy.

3. Which reaction has the greatest increase in entropy?

   A. SO_2 (g) + $2H_2S$ (g) → $2H_2O$ (l) + 3S (s)

   B. CaO (s) + CO_2 (g) → $CaCO_3$ (s)

   C. CaC_2 (s) + 2 H_2O (l) → $Ca(OH)_2$ (s) + C_2H_2 (g)

   D. N_2 (g) + O_2 (g) → 2NO (g)

   C – in this reaction, one mole of solid and one mole of liquid react to form one mole of solid and one mole of gas. Gases have a higher entropy than solids therefore entropy increases.

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

   A. $2SO_2$ (g) + O_2 (g) → $2SO_3$ (g)

   B. NH_4Cl (s) → NH_3 (g) + HCl (g)

   C. $PbCl_2$ (s) → Pb^{2+} (aq) + $2Cl^-$ (aq)

   D. C (s) + O_2 (g) → CO_2 (g)

   A – there is a decrease in the number of moles of in the products, therefore the entropy change will be the most negative.

5. Which reaction has the largest increase in entropy?

   A. H_2 (g) + Cl_2 (g) → 2HCl(g)

   B. $Al(OH)_3$ (s) + NaOH (aq) → $Al(OH)_4^-$(aq) + Na^+(aq)

   C. Na_2CO_3 (s) + 2HCl (aq) → 2NaCl(aq) + CO_2 (g) + H_2O (l)

   D. $BaCl_2$ (aq) + Na_2SO_4 (aq) → $BaSO_4$ (s) + 2NaCl (aq)

   C – solid and aqueous reactants become gases and liquids. Gases and liquids have higher entropy than solids, therefore entropy increases.

6. Which reaction has the greatest positive entropy change?

   A. CH_4 (g) + $1½O_2$ (g) → CO (g) + $2H_2O$ (g)

   B. CH_4 (g) + $1½O_2$ (g) → CO (g) + $2H_2O$ (l)

   C. CH_4 (g) + $2O_2$ (g) → CO_2 (g) + $2H_2O$ (g)

   D. CH_4 (g) + $2O_2$ (g) → CO_2 (g) + $2H_2O$ (l)

   A – 2 ½ moles of gas in the reactants form 3 moles of gas in the products which is an
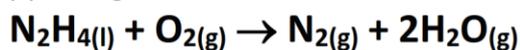
increase in entropy.

Standard entropy change ($\Delta S^{\ominus}$)

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

$$\Delta S^{\ominus}_{reaction} = \sum S^{\ominus}_{products} - \sum S^{\ominus}_{reactants}$$

- 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:

$$N_2H_{4(l)} + O_{2(g)} \rightarrow N_{2(g)} + 2H_2O_{(g)}$$

	$S^{\ominus}$ (J K^{-1} mol^{-1})
$N_2H_{4(l)}$	121
$O_{2(g)}$	205
$N_{2(g)}$	192
$H_2O_{(g)}$	188

$\Delta S^{\ominus}$ = (192 + 2 × 188) − (205 + 121) = 242 J K^{-1} mol^{-1}

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

Substance	$S^{\ominus}$ (J K^{-1}mol^{-1})	Substance	$S^{\ominus}$ (J K^{-1}mol^{-1})
$H_2O_{(g)}$	189	$CO_{2(g)}$	214
$H_2O_{(l)}$	70	$C_3H_{8(g)}$	270
$H_{2(g)}$	131	$O_{2(g)}$	205
$Cl_{2(g)}$	223		
$HCl_{(g)}$	187		

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

a) $H_2O_{(g)} \rightarrow H_2O_{(l)}$ negative $\Delta S^{\ominus}$ - gases have higher entropy than liquids.

b) $H_{2(g)} + Cl_{2(g)} \rightarrow 2HCl_{(g)}$ small change in entropy – same number of moles of gas in reactants and products.

c) $C_3H_{8(g)} + 5O_{2(g)} \rightarrow 3CO_{2(g)} + 4H_2O_{(g)}$ positive $\Delta S^{\ominus}$ - six moles of gas in reactants, seven moles of gas in products.

2) Calculate $\Delta S^{\ominus}$ for the above reactions.

   a) $H_2O_{(g)} \rightarrow H_2O_{(l)}$ $\Delta S^{\ominus} = -119$ J K^{-1} mol^{-1}

   b) $H_{2(g)} + Cl_{2(g)} \rightarrow 2HCl_{(g)}$ $\Delta S^{\ominus} = +20$ J K^{-1} mol^{-1}

   c) $C_3H_{8(g)} + 5O_{2(g)} \rightarrow 3CO_{2(g)} + 4H_2O_{(g)}$ $\Delta S^{\ominus} = +103$ J K^{-1} mol^{-1}

Gibbs free energy
   - The energy associated with a chemical reaction that can be used to do work.
   - ΔG must be negative for a spontaneous process.

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

ΔG – Gibbs free energy change (kJ mol^{-1})
ΔH – change in enthalpy (kJ mol^{-1})
T – temperature in kelvin, K
ΔS – change in entropy (J K^{-1} mol^{-1})

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

$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$

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

See video for solution.

Calculate the temperature at which the reaction will be spontaneous:

See video for solution.

Exercises:

1. A reaction has a standard enthalpy change, ΔH, of +10.00 kJ mol^{-1} at 298 K. The standard entropy change, ΔS, for the same reaction is +10.00 J K^{-1} mol^{-1}. What is the value of ΔG for the reaction in kJ mol^{-1}?

$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$ = 10000 – (298 × 10.00) = 7020 J mol^{-1}

$\Delta G^{\ominus}$ = +7.02 kJ mol^{-1}

2. Consider the following reaction:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \quad \Delta H = -92.4 \text{ kJmol}^{-1}$$
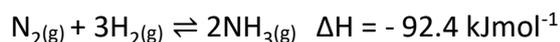
(i) The absolute entropy values, S, at 298 K for $N_{2(g)}$, $H_{2(g)}$ and $NH_{3(g)}$ are 192, 131 and 193 J K^{-1} mol^{-1} respectively. Calculate $\Delta S^{\ominus}$ for the reaction and explain the sign of $\Delta S^{\ominus}$.

$\Delta S^{\ominus}$ = [2 × 193] – [192 + 3 × 131] = –199 J K^{-1} mol^{-1}

$\Delta S^{\ominus}$ is negative - four mol of gas forming two mol of gas

(ii) Calculate $\Delta G^{\ominus}$ for the reaction at 298 K. State and explain whether the reaction is spontaneous.

$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$ = –92.4 – (298 × –0.199) = –33.1 kJ mol^{-1}
Reaction is spontaneous (ΔG is negative)

Standard change in Gibbs free energy (ΔG⁰)

- 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).

$$\Delta G^\ominus = \Sigma \Delta G_f{}^\ominus{}_{products} - \Sigma \Delta G_f{}^\ominus{}_{reactants}$$

- $\Delta G_f{}^\ominus$ - 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.

$$C_2H_5OH_{(l)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(g)}$$
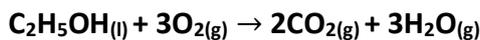
Compound	$\Delta G_f{}^\ominus$ / kJ mol⁻¹
$C_2H_5OH_{(l)}$	−175
$CO_{2(g)}$	−394
$H_2O_{(g)}$	−229
$O_{2(g)}$	0

$\Delta G^\ominus = (3 \times -229 + 2 \times -394) - (-175)$

$\Delta G^\ominus = -1300$ kJ mol⁻¹

The effect of ΔH, ΔS and T on the spontaneity of a chemical reaction

Exothermic reactions

ΔH	ΔS	T	ΔG	spontaneity
negative < 0	positive > 0	any temperature		

- ΔH is negative and ΔS is positive, therefore ΔG will be negative at any temperature.
- An exothermic reaction with an increase in entropy will be spontaneous at any temperature.

ΔH	ΔS	T	ΔG	spontaneity
negative < 0	negative < 0	high		

ΔH	ΔS	T	ΔG	spontaneity
negative < 0	negative < 0	low		

- ΔG will be negative only at low temperatures; at high T, (TΔS) makes ΔG positive.

Endothermic reactions

| ΔH	ΔS	T	ΔG	spontaneity
positive > 0	negative 0 <	any temperature		

- ΔH is positive and ΔS is negative, therefore ΔG will be positive at any temperature.
- An endothermic reaction with a decrease in entropy will be non-spontaneous at any temperature.

ΔH	ΔS	T	ΔG	spontaneity
positive > 0	positive > 0	high		

ΔH	ΔS	T	ΔG	spontaneity
positive > 0	positive > 0	low		

- ΔG will be negative only at high temperatures (TΔS >ΔH); at low temperatures ΔH>TΔS (+ΔG).

Summary

ΔS

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

ΔH
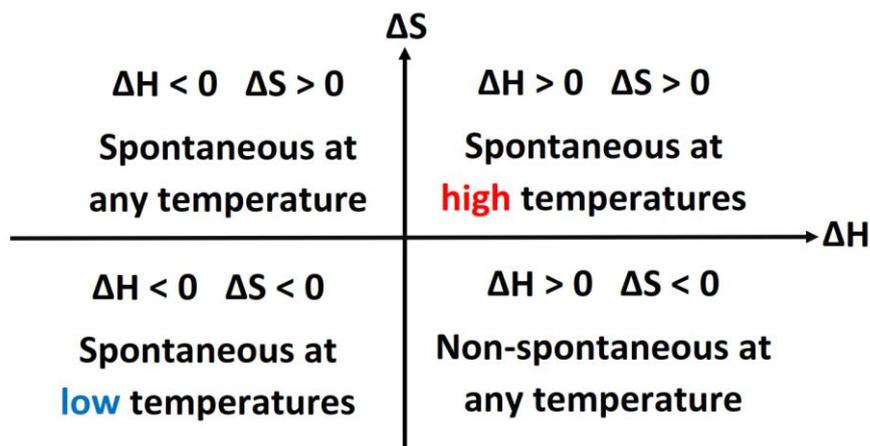
Exercises:

1. 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.
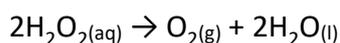
    A reaction that occurs without adding energy beyond that required to overcome the energy barrier.

2. Under what circumstances is a reaction spontaneous at all temperatures?

	$\Delta H^{\ominus}$	$\Delta S^{\ominus}$
A.	+	+
B.	+	−
C.	−	−
D.	−	+

    D

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

    $$2H_2O_{2(aq)} \rightarrow O_{2(g)} + 2H_2O_{(l)}$$

    What are the signs of ΔH, ΔS and ΔG for this reaction? **B**

	ΔH	ΔS	ΔG
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 $+\Delta S^{\ominus}$

D

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.	+	+

D