FACTFILE:

GCE CHEMISTRY

4.2 ENTROPY

Rewarding Learning

Learning Outcomes

Students should be able to:

4.2.1 recall that enthalpy change is not sufficient to explain feasible change, for example the endothermic reaction between ammonium carbonate and ethanoic acid;

4.2.2 recall that the balance between entropy change and enthalpy change determines the feasibility of a reaction;

4.2.3 recall that entropy is a measure of disorder;

4.2.4 calculate the standard entropy change, ΔS, in a chemical reaction using standard entropy data;

4.2.5 use the equation ΔG = ΔH -TΔS to calculate standard free energy changes;

4.2.6 recall that processes are spontaneous when the free energy change is negative; and

4.2.7 recall that when the enthalpy change and the entropy change have the same sign the feasibility of the process depends on the temperature, and calculate the temperature at which these processes start/cease to be feasible.

Feasability

Some reactions occur without having energy supplied from the environment; they are spontaneous. Endothermic reactions take in heat from the surroundings in order to occur, hence they should not occur spontaneously - some do however, for example the reaction between ammonium carbonate and ethanoic acid is endothermic yet spontaneous. A feasible reaction is one which can take place spontaneously without any external help.

The enthalpy change on its own is not enough to determine whether or not a reaction will be feasible, there is another factor besides energy change which determines feasability. This factor is entropy.

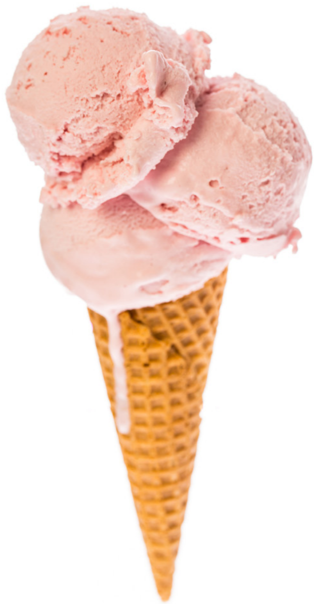
Entropy is a measure of the disorder (randomness) of a system.

In gases the particles are moving freely and randomly so gases are more disordered than liquids and solutions, and have a high entropy. In solids the particles are vibrating about fixed positions, and the system is highly ordered with a low entropy. The reaction between ammonium carbonate and ethanoic acid shows a increase in disorder as a solid and solution produce a gas and solution, hence there is an increase in entropy. The reaction is feasible, despite being endothermic as it results in a change in entropy.

$(NH_4)_2CO_3(s) + 2CH_3COOH(aq) \rightarrow 2CH_3COONH_4(aq) + H_2O(l) + CO_2(g)$

It is the balance between entropy change and enthalpy change that determines the feasibility of a reaction;

Any reaction that results in the formation of a gas, or an increase in the number of gaseous moles will result in an increase in entropy.



The melting of ice cream leads to disorder. There is an increase in entropy!

Calculating change in entropy

Entropy is given the symbol $S^{\ominus}$ and standard entropy change is $\Delta S^{\ominus}$
Entropy is measured in J K^{-1} mol^{-1}.

Entropy values change with temperature and so the temperature at which they are measured must be specified.

The entropy change for a reaction is the difference between the total (∑) entropies of the products and the total entropies of the reactants.

i.e $\Delta S^{\ominus} = \sum S^{\ominus}_{products} - \sum S^{\ominus}_{reactants}$

Example 1: Calculate the standard entropy change for the following reaction using the given standard entropies.

$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(l)$

	$NaHCO_3(s)$	$Na_2CO_3(s)$	$CO_2(g)$	$H_2O(l)$
$S^{\ominus}$ / JK^{-1} mol^{-1}	101.7	135.0	213.6	69.9

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

$\Delta S = (135.0 + 213.6 + 69.9) - (2 \times 101.7) = +215.1$ JK^{-1} mol^{-1}

Note that the entropy values are given per mole, so the molar quantities in the equation must be used i.e $2NaHCO_3$

In this example the entropy has increased because a solid (ordered) produces three new substances two of which is a gas (more disordered) and a liquid (more disordered)

Free Energy

It is not just the enthalpy change in a reaction that determines whether it can occur at a particular temperature, entropy must be considered as well. This produces a new quantity called free energy (G).

A feasible reaction is one with $\Delta G < 0$

Free energy change = $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$

ΔG is measured in kJmol^{-1}
ΔS is usually given in JK^{-1} mol^{-1} and often values given must be changed to kJ $K^{-1}mol^{-1}$ by dividing by 1000, before using the free energy equation.
ΔH is measured in kJmol^{-1}
T is measured in kelvin (K)

Example 1: Calculate the change in standard free energy for the reaction:

$Fe_2O_3(s) + 3H_2(g) \rightarrow 2Fe(s) + 3H_2O(g)$

and determine if it will take place at 293K

	Fe_2O_3 (s)	$3H_2(g)$	2Fe(s)	$3H_2O(g)$
$S^{\ominus}$ / J K^{-1} mol^{-1}	90	131	27	189
$\Delta_f H^{\ominus}$ / kJ mol^{-1}	-822	0	0	-242

$\Delta H^{\ominus} = \sum \Delta_f H^{\ominus}$ of products $- \sum \Delta_f H^{\ominus}$ of reactants
$= (+ 3 \times -242) - (-822) = +96$ kJmol^{-1}

$\Delta S^{\ominus} = \sum S^{\ominus}$ of products $- \sum S^{\ominus}$ of reactants
$= ((2 \times 27) + (3 \times 189)) - (90 + (3 \times 131))$
$= 621 - 483 = +138$ J$K^{-1}mol^{-1}$ $= +0.138$ kJ$K^{-1}mol^{-1}$

$\Delta G^{\ominus} = \Delta H^{\ominus} - T\, \Delta S^{\ominus}$

$= 96 - (293 \times 0.138) = 55.566$ kJmol^{-1}

$\Delta G^{\ominus}$ is positive and greater than zero hence this reaction is not feasible at this temperature.

To determine at what temperature it does become feasible, you need to work out the temperature at which $\Delta G^{\ominus}$ becomes less than zero

$\Delta G^{\ominus} \leq 0$
$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$
so $\Delta H^{\ominus} - T\ \Delta S^{\ominus} \leq 0$
$96 - (T \times 0.138) \leq 0$
$96 - 0.138T \leq 0$
$96 \leq 0.138T$
$696 \leq T$

The temperature must be greater than 696K for the reaction to occur.

Predicting the feasibllity of a reaction

This depends on both enthalpy change and entropy change
(Note temperature T is in K and is always positive)

situation	enthalpy change	entropy change	ΔG	feasibility
1	positive	negative	always positive	not feasible at any temperature
2	negative	positive	always negative	feasible at a any temperature
3	positive	positive	may be positive or negative depending on the temperature	feasible above certain temperatures
4	negative	negative	may be positive or negative depending on temperature	feasible below certain temperatures

If the enthalpy change and entropy change have the same sign, then the feasibility depends on the temperature, and you can use the equation $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$ to calculate the temperature at which the reaction starts/ceases to be feasible.

Credits

? Revision Questions

1 Heat is produced when magnesium reacts with sulfuric acid:

$$Mg + H_2SO_4(aq) \rightarrow MgSO_4(aq) + H_2(g)$$

Which one of the following is true for the reaction?

A	ΔS is negative
B	ΔH is positive
C	ΔG is positive
D	reaction is feasible at any temperature

2 The standard entropy change for the following reaction is $+138 JK^{-1}mol^{-1}$.

$$Fe_2O_3(s) + 3H_2(g) \rightarrow 2Fe(s) + 3H_2O(g)$$

The standard entropies of $Fe_2O_3(s)$, $H_2(g)$ and $Fe(s)$ are 90, 131 and 27 $JK^{-1}\ mol^{-1}$ respectively. Which one of the following is the standard entropy of steam?

A	$332\ JK^{-1}mol^{-1}$
B	$189\ JK^{-1}mol^{-1}$
C	$145\ JK^{-1}mol^{-1}$
D	$85\ JK^{-1}mol^{-1}$

3 The decomposition of calcium carbonate is represented by the following equation:

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

$\Delta H^\ominus = +178\ kJmol^{-1}$

$\Delta S^\ominus = +161\ JK^{-1}mol^{-1}$

What is the standard free energy change, $\Delta G^\ominus$, for this reaction at 25°C (298K)?

A	$-48\ kJ\ mol^{-1}$
B	$+130\ kJ\ mol^{-1}$
C	$+174 kJ\ mol^{-1}$
D	$+339 kJ\ mol^{-1}$

4 Data for the reduction of iron(III) oxide by carbon, are shown in the table below

$$2Fe_2O_3(s) + 3C(s) \rightarrow 4Fe(s) + 3CO_2(g)$$

Which one of the following is true for the reaction?

Substance	$\Delta_f H^\ominus$/kJ mol^{-1}	$S^\ominus$/J K^{-1} mol^{-1}
Fe_2O_3	-824.2	87.4
C	0.0	5.7
Fe	0.0	27.3
CO_2	-393.5	213.6

a (i) Calculate the values of $\Delta H^\ominus$, $\Delta S^\ominus$ and $\Delta G^\ominus$ for the reaction at 298K.

$\Delta H^\ominus$ ....

....

.... [2]

$\Delta S^\ominus$ ....

....

.... [2]

$\Delta G^\ominus$ ....

....

.... [1]

(ii) Using your results from part (i) explain why this reaction is not feasible at 298 K.

....

.... [1]

b Calculate the temperature above which this reaction is feasible.

....

....

.... [2]

5 Ammonium nitrate decomposes on heating to form nitrogen(I) oxide and water.

(i) Write an equation for this decomposition.

.... [1]

(ii) This reaction is exothermic and has a positive entropy change.
Explain why this process is spontaneous at all temperatures.

....

.... [1]

6 Zinc is manufactured by the reduction of its oxide using carbon.

$$ZnO(s) + C(s) \rightarrow Zn(s) + CO(g)$$

$\Delta H^{\ominus} = +237\ kJ\ mol^{-1}$

$\Delta S^{\ominus} = +\ 190\ JK^{-1}\ mol^{-1}$

What is the minimum temperature needed for this reaction to become feasible?

A	154 K
B	427 K
C	975 K
D	1248 K