

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.



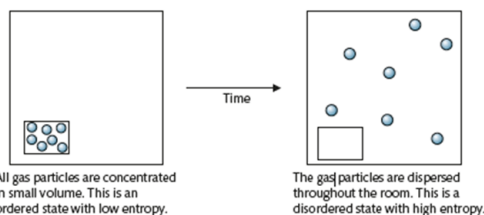
Use the second law of thermodynamics to guess what happens next?

"Any spontaneous process increases the disorder of the universe"

Entropy

Spontaneous changes occur without the need to do work. A spontaneous reaction occurs without adding energy (beyond that required to overcome the activation energy barrier – see Chapter 6).

We measure the degree of disorder in a system using entropy . S



Entropy (S) refers to the distribution of available energy among the particles.



Predicting entropy changes

As the solid state is the most ordered state and the gaseous state the most disordered, we can predict that the entropy of a system increases as a solid changes to a liquid and as a liquid changes to a gas.

Change	ΔS
solid \rightarrow liquid	increase (+)
solid \rightarrow gas	increase (+)
liquid \rightarrow gas	increase (+)
liquid \rightarrow solid	decrease (-)
gas \rightarrow solid	decrease (-)
gas \rightarrow liquid	decrease (-)



We must also take into account the number of moles of reactants and products involved in a reaction.

Worked example

Predict the entropy change ΔS for the following changes.

- (a) $\text{Br}_2(l) \rightarrow \text{Br}_2(g)$ $+$
- (b) $2\text{Cu}(s) + \text{O}_2(g) \rightarrow 2\text{CuO}(s)$ $-$
- (c) $\text{Ag}^+(aq) + \text{Br}^-(aq) \rightarrow \text{AgBr}(s)$ $-$
- (d) $\text{H}_2(g) + \text{Cl}_2(g) \rightarrow 2\text{HCl}(g)$ 0
- (e) $\text{CH}_4(g) + 2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(l)$ $-$
- (f) $\text{Cu}^{2+}(aq) + \text{Zn}(s) \rightarrow \text{Cu}(s) + \text{Zn}^{2+}(aq)$ 0

$+, 0, -$

Exercises

- 54 Identify the process expected to have a value of ΔS closest to zero?
- A $\text{C}_2\text{H}_4(g) + \text{H}_2(g) \rightarrow \text{C}_2\text{H}_6(g)$ C $\text{CaCO}_3(s) \rightarrow \text{CaO}(s) + \text{CO}_2(g)$
 B $\text{H}_2(g) + \text{Cl}_2(g) \rightarrow 2\text{HCl}(g)$ D $\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(g)$
- 55 Identify the processes which have an associated increase in entropy.
- I $\text{Br}_2(g) \rightarrow \text{Br}_2(l)$
 II $\text{Br}_2(g) \rightarrow 2\text{Br}(g)$
 III $\text{KBr}(s) \rightarrow \text{K}^+(aq) + \text{Br}^-(aq)$
- A I and II B I and III C II and III D I, II, and III
- 56 Which is the best description of the entropy and enthalpy changes accompanying the sublimation of iodine: $\text{I}_2(s) \rightarrow \text{I}_2(g)$?
- A $\Delta S +$, $\Delta H +$, reaction is endothermic
 B $\Delta S +$, $\Delta H -$, reaction is exothermic
 C $\Delta S -$, $\Delta H +$, reaction is endothermic
 D $\Delta S -$, $\Delta H -$, reaction is exothermic
- 57 Identify the reaction which has the largest increase in entropy?
- A $\text{AgNO}_3(aq) + \text{NaCl}(aq) \rightarrow \text{AgCl}(s) + \text{NaNO}_3(aq)$
 B $\text{H}_2(g) + \text{Cl}_2(g) \rightarrow 2\text{HCl}(g)$
 C $\text{C}_2\text{H}_4(g) + \text{H}_2(g) \rightarrow \text{C}_2\text{H}_6(g)$
 D $\text{Mg}(s) + \text{H}_2\text{SO}_4(aq) \rightarrow \text{MgSO}_4(aq) + \text{H}_2(g)$
- 58 Predict the entropy change ΔS for the following reactions.
- (a) $\text{N}_2(g) + 3\text{H}_2(g) \rightarrow 2\text{NH}_3(g)$
 (b) $3\text{Fe}(s) + 4\text{H}_2\text{O}(g) \rightarrow \text{Fe}_3\text{O}_4(s) + 4\text{H}_2(g)$
 (c) $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}(s) + 2\text{NH}_4\text{SCN}(s) \rightarrow \text{Ba}(\text{SCN})_2(aq) + 2\text{NH}_3(aq) + 10\text{H}_2\text{O}(l)$

Absolute entropy

The absolute entropy of different substances can be calculated. As entropy depends on the temperature and pressure, tabulated entropy values refer to standard conditions and are represented as S^\ominus . Some values are shown in the table below.

Substance	Formula	$S^\ominus / \text{J K}^{-1} \text{mol}^{-1}$
hydrogen	$\text{H}_2(\text{g})$	+131
oxygen	$\text{O}_2(\text{g})$	+205
nitrogen	$\text{N}_2(\text{g})$	+191
graphite	$\text{C}(\text{graphite})$	+5.7
methane	$\text{CH}_4(\text{g})$	+186
ammonia	$\text{NH}_3(\text{g})$	+193
water	$\text{H}_2\text{O}(\text{l})$	+70.0
steam	$\text{H}_2\text{O}(\text{g})$	+188.8
ethane	$\text{C}_2\text{H}_6(\text{g})$	+230
ethene	$\text{C}_2\text{H}_4(\text{g})$	+220
ethanol	$\text{C}_2\text{H}_5\text{OH}(\text{l})$	+161

A perfectly ordered solid at absolute zero has zero entropy. All other states, which are more disordered, have positive entropy values.

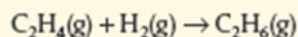
Calculating entropy changes

$$\sum S^\ominus(\text{reactants}) \xrightarrow{\Delta S_{\text{reaction}}} \sum S^\ominus(\text{products})$$

$$\Delta S_{\text{reaction}} = \sum S^\ominus(\text{products}) - \sum S^\ominus(\text{reactants})$$

Worked example

Calculate the entropy change for the hydrogenation of ethene



using the entropy values given in section 12 in the IB data booklet and the table above.

$$\sum S^\ominus(\text{products}) = +230 \text{ J K}^{-1} \text{mol}^{-1}$$

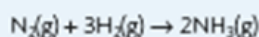
$$\sum S^\ominus(\text{reactants}) = +220 + 131 = 351 \text{ J K}^{-1} \text{mol}^{-1}$$

$$\Delta S_{\text{reaction}}^\ominus = +230 - 351 = -121 \text{ J K}^{-1} \text{mol}^{-1}$$

Exercises

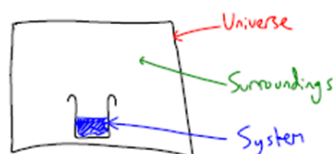
59 Sketch a graph to show how the entropy of a solid changes as the temperature increases.

60 Calculate the entropy change ΔS for the Haber process, shown below, using tabulated standard molar entropies at 25 °C.



61 Calculate the standard entropy change associated with the formation of methane from its elements.

Spontaneity



A chemical process can happen spontaneously (without requiring energy) if the total disorder in the universe is higher after it occurs. So we must consider 2 factors:

- Entropy
- Enthalpy

We describe this 'driving force' for spontaneity *Gibbs free energy, G.*

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

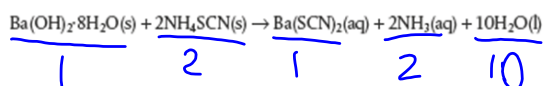
If ΔG is negative \rightarrow the reaction can happen spontaneously.

If ΔG is positive \rightarrow it ~~can't~~ is not spontaneous

Handwritten notes: $\Delta H = - \text{big}$, $\Delta S = + \text{big}$, $\Delta G = 0$ (with a red arrow pointing down from 0).

This equation explains why most exothermic reactions can be spontaneous.

Why might this endothermic reaction still be spontaneous?



Worked example

- (a) Give an equation for the boiling of water. $\text{H}_2\text{O(l)} \rightarrow \text{H}_2\text{O(g)}$
- (b) Predict a sign for the enthalpy change and entropy change for this process.
- (c) Predict a value for the sign of ΔG at low and high temperatures.
- (d) Suggest why water boils at 100 °C. \rightarrow
- (e) Use the entropy values in the table on page 252 to calculate the entropy change for this process.
- (f) Use the data below to calculate the enthalpy change for the process.

	$\Delta H_f^\circ / \text{kJ mol}^{-1}$
$\text{H}_2\text{O(l)}$	-286
$\text{H}_2\text{O(g)}$	-242

- (g) Deduce the boiling point of water from your calculations. Describe any assumptions you have made.

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

Solution

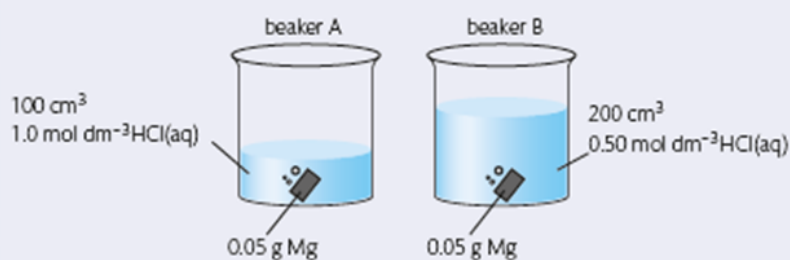
- (a) $\text{H}_2\text{O(l)} \rightarrow \text{H}_2\text{O(g)}$
- (b) As there is an increase in moles of gas, $\Delta S(\text{system})$ is positive. The process involves the breaking of intermolecular (hydrogen) bonds so $\Delta H(\text{system})$ is positive.
- (c) At low temperature: $\Delta G(\text{system}) \approx \Delta H(\text{system})$ and so is positive.
At high temperature: $\Delta G(\text{system}) \approx -T\Delta S(\text{system})$ and so is negative.
- (d) The change only occurs at higher temperatures where ΔG is negative.
- (e)
- $$\Delta G = 0 \text{ at } 100^\circ\text{C}$$
- $$\text{H}_2\text{O(l)} \rightarrow \text{H}_2\text{O(g)}$$
- $$+70.0 \quad +188.8$$
- $$\Delta S^\circ / \text{J K}^{-1} \text{ mol}^{-1}$$
- $$\Delta S_{\text{reaction}}^\circ = \sum S^\circ(\text{products}) - \sum S^\circ(\text{reactants})$$
- $$= +188.8 - (70) = +118.8 \text{ J K}^{-1} \text{ mol}^{-1}$$
- (f)
- $$\Delta H_{\text{reaction}}^\circ = \sum \Delta H_f^\circ(\text{products}) - \sum \Delta H_f^\circ(\text{reactants})$$
- $$= -242 - (-286) = +44 \text{ kJ mol}^{-1}$$
- (g) At the boiling point: $\Delta G(\text{system}) = \Delta H(\text{system}) - T\Delta S(\text{system}) = 0$

$$T = \frac{\Delta H(\text{system})}{\Delta S(\text{system})}$$

$$T = \frac{44 \text{ kJ mol}^{-1}}{118.8 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}} = 370 \text{ K}$$

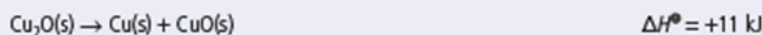
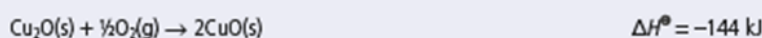
It is assumed that $\Delta H(\text{system})$ and $\Delta S(\text{system})$ do not change with temperature.

- 3 Identical pieces of magnesium are added to two beakers, A and B, containing hydrochloric acid. Both acids have the same initial temperature but their volumes and concentrations differ.



Which statement is correct?

- A The maximum temperature in A will be higher than in B.
 B The maximum temperature in A and B will be equal.
 C It is not possible to predict whether A or B will have the higher maximum temperature.
 D The temperature in A and B will increase at the same rate.
- 4 Consider the following reactions.

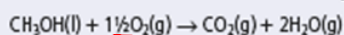


What is the value of ΔH^\ominus , in kJ, for this reaction?



- A -144 + 11 B +144 - 11 C -144 - 11 D +144 + 11
- 5 Which equation best represents the bond enthalpy of HCl?
- A $\text{HCl(g)} \rightarrow \text{H}^\cdot\text{(g)} + \text{Cl}^\cdot\text{(g)}$ C $\text{HCl(g)} \rightarrow \frac{1}{2}\text{H}_2\text{(g)} + \frac{1}{2}\text{Cl}_2\text{(g)}$
 B $\text{HCl(g)} \rightarrow \text{H(g)} + \text{Cl(g)}$ D $2\text{HCl(g)} \rightarrow \text{H}_2\text{(g)} + \text{Cl}_2\text{(g)}$

- 9 Methanol is made in large quantities as it is used in the production of polymers and in fuels. The enthalpy of combustion of methanol can be determined theoretically or experimentally.

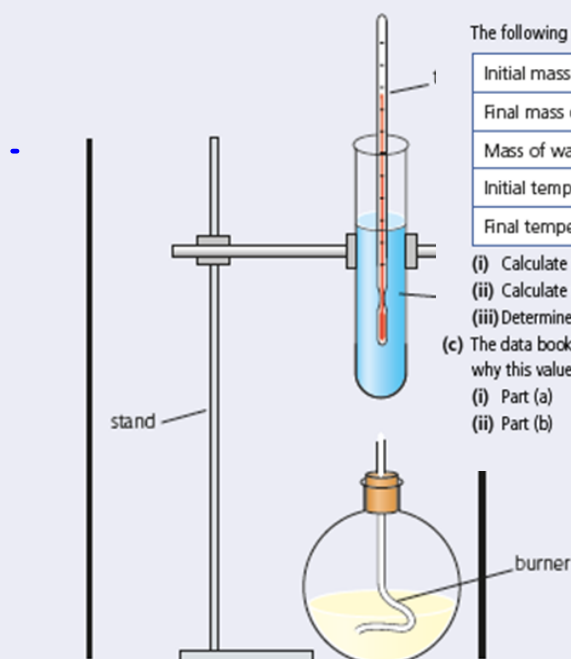


- (a) Using the information from section 11 of the IB data booklet, determine the theoretical enthalpy of combustion of methanol.
 (b) The enthalpy of combustion of methanol can also be determined experimentally in a school laboratory. A burner containing methanol was weighed and used to heat water in a test tube, as illustrated below.

$$C_{\text{H}_2\text{O}} = 4.18 \text{ J g}^{-1} \text{ K}^{-1}$$

(3) (Exothermic) -650 kJ mol⁻¹

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



The following data were collected.

Initial mass of burner and methanol / g	80.557
Final mass of burner and methanol / g	80.034
Mass of water in test tube / g	20.000
Initial temperature of water / °C	21.5
Final temperature of water / °C	26.4

- (i) Calculate the amount, in mol, of methanol burned. (2)
 (ii) Calculate the heat absorbed, in kJ, by the water. (3)
 (iii) Determine the enthalpy change, in kJ mol⁻¹, for the combustion of 1 mole of methanol. (2)

- (c) The data booklet value for the enthalpy of combustion of methanol is -726 kJ mol⁻¹. Suggest why this value differs from the values calculated in parts (a) and (b). (1)

- (i) Part (a) (1)
 (ii) Part (b) (1)

$$0.0163 \text{ mol} \rightarrow 410 \text{ J}$$

$$1 \text{ mol} \rightarrow x$$

$$-25153 \text{ J}$$

(Total 12 marks)

9. ¿Qué significado tienen los siguientes datos? Escribe las ecuaciones termoquímicas correspondientes a cada apartado.

- a) $\Delta H_f^\circ \text{SO}_2(g) = -296,8 \text{ kJ}$
 b) $\Delta H_f^\circ \text{CO}_2(g) = -393,5 \text{ kJ}$
 c) $\Delta H_f^\circ \text{C}_2\text{H}_2(g) = +227,5$

10. Sabiendo que la combustión de 1 kg de TNT libera 4600 kJ y teniendo en cuenta los datos que se adjuntan, calcule:

- a) La entalpía estándar de combustión del metano.
 b) El volumen de metano medido a 25 °C y 1 atm de presión que es necesario para producir la misma energía que 1 kg de TNT.

Datos: ΔH_f° (kJ/mol): $\text{CH}_4(g) = -75$; $\text{CO}_2(g) = -394$;
 $\text{H}_2\text{O}(g) = -242$.

$$\begin{aligned} \text{CH}_4(g) + 2 \text{O}_2(g) &\rightarrow \text{CO}_2(g) + 2 \text{H}_2\text{O}(g) \\ \Delta H_f^\circ &= \sum (n_p \cdot \Delta H_f^\circ) - \sum (n_r \cdot \Delta H_f^\circ) \\ \Delta H &= (-394 \text{ kJ/mol} + 2 \cdot (-242 \text{ kJ/mol})) - (-75 \text{ kJ/mol}) \\ &= -891 \text{ kJ/mol} \end{aligned}$$

$$V = \frac{n \cdot R \cdot T}{P}$$

11. Calcule la entalpía de formación del agua utilizando energías de enlace promedio y luego calcule la energía producida en los motores de un cohete por la combustión de los 150 m³ de hidrógeno de sus depósitos (200 atm y 10 °C), suponiendo un comportamiento ideal del gas.

Datos: energías de enlace promedio en kJ/mol: O=O, 498;
 O—H, 463; H—H, 436.

A partir
 (241 kJ)

Gibbs free energy and equilibrium

In the calculations so far, we have assumed that all reactions have gone to **completion**. This means that all reactants are turned into products.

In reality this is not always the case. We can quantify the **extent of reaction** using a ratio between $\frac{[\text{products}]}{[\text{reactants}]}$. As ΔG becomes more negative, the reaction produces more products.

Experimentally we find that

- Values of ΔG below -30 kJ/mol mean that a reaction has gone to completion.
- Values between -30 and 0 there will be some reactants remaining.

$$\text{Ratio} = \frac{[\text{Products}]}{[\text{Reactants}]}$$

$\Delta G_{\text{reaction}}^{\circ}$	Extent of reaction
$\Delta G_{\text{reaction}}^{\circ} > +30 \text{ kJ mol}^{-1}$	spontaneous change impossible : no reaction $\frac{[\text{products}]}{[\text{reactants}]} \ll 1$
$0 \text{ kJ mol}^{-1} < \Delta G_{\text{reaction}}^{\circ} < +30 \text{ kJ mol}^{-1}$	partial reaction producing equilibrium mixture $\frac{[\text{products}]}{[\text{reactants}]} < 1$
$\Delta G_{\text{reaction}}^{\circ} = 0 \text{ kJ mol}^{-1}$	partial reaction producing equilibrium mixture $\frac{[\text{products}]}{[\text{reactants}]} = 1$
$0 \text{ kJ mol}^{-1} > \Delta G_{\text{reaction}}^{\circ} > -30 \text{ kJ mol}^{-1}$	partial reaction producing equilibrium mixture $\frac{[\text{products}]}{[\text{reactants}]} > 1$
$\Delta G_{\text{reaction}}^{\circ} < -30 \text{ kJ mol}^{-1}$	complete reaction $\frac{[\text{products}]}{[\text{reactants}]} \gg 1$

