

Raffles Institution Year 5 H2 Chemistry 2022

Lecture Notes 5b – Chemical Energetics 2

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

Content

- Entropy
- · Free energy change, spontaneity of reactions

Learning Outcomes

Candidates should be able to:

- (a) explain and use the term *entropy*
- (b) discuss the effects on the entropy of a chemical system by the following:
 - (i) change in temperature
 - (ii) change in phase
 - (iii) change in the number of particles (especially for gaseous systems)
 - (iv) mixing of particles

[quantitative treatment is not required]

- (c) predict whether the entropy change for a given process or reaction is positive or negative
- (d) state and use the equation involving standard Gibbs free energy change of reaction, ΔG^Θ, ΔG^Θ = ΔH^Θ TΔS^Θ [the calculation of standard entropy change, ΔS^Θ, for a reaction using standard entropies, S^Θ, is **not** required]
- (e) state whether a reaction or process will be spontaneous by using the sign of ΔG^{Θ}
- (f) understand the limitations in the use of ΔG^{Θ} to predict the spontaneity of a reaction
- (g) predict the effect of temperature change on the spontaneity of a reaction, given standard enthalpy and entropy changes

Lecture Outline

- 1 Direction of chemical change
- 2 Entropy and Entropy Change
- 3 Gibbs Free Energy Change
- 4 Effect of Temperature on the Spontaneity of Reaction

1 Direction of Chemical Change

 When a piece of hot sodium metal and chlorine gas come in contact, a violent reaction occurs and sodium chloride is formed.

 $2Na(s) + Cl_2(g) \longrightarrow 2NaCl(s)$

Why do sodium and chlorine react readily to form sodium chloride? Why does sodium chloride not form sodium and chlorine on its own accord?

Chemists are always interested in the direction of change. By understanding the factors that
make a reaction go in a particular direction, it is possible to predict the conditions which might
allow a reluctant reaction to go the way that is wanted.

1.1 Spontaneous Change

• What is a spontaneous process?

A spontaneous process is one that, once started, will continue without any external assistance.

- Conversely, a non-spontaneous process will not occur unless some external assistance is continuously applied.
- Examples of spontaneous processes: $H_2O(s) \longrightarrow H_2O(l)$ at 298 K and 1 atm NaOH(aq) + HCl(aq) \longrightarrow NaCl(aq) + H₂O(l) CH₄(g) + 2O₂(g) \longrightarrow CO₂(g) + 2H₂O(l)
- If a process is spontaneous, the reverse process is non-spontaneous. Both spontaneous and non-spontaneous processes are possible, but only spontaneous processes will occur without intervention. Non-spontaneous processes require the system to be acted on by an external agent.
- Note: The term "spontaneous" signifies nothing about how fast a process occurs and has nothing to do with how long a process takes to occur. A spontaneous process can either be slow or fast.

1.2 Criteria for Spontaneity

- In early days of physical chemistry, it was thought that systems reacted or changed so as to minimize their energy. In the 19th century, Marcellin Berthelot suggested that all exothermic reactions are spontaneous.
- However, things are not quite simple since many endothermic processes do take place spontaneously. Examples include the following:

0	$NH_4NO_3(s) + aq. \longrightarrow NH_4NO_3(aq)$	ΔH^{Θ} = +26 kJ mol ⁻¹
0	$H_2O(s) \longrightarrow H_2O(l)$	ΔH^{\oplus} = +6.01 kJ mol ⁻¹

- Since some spontaneous reactions are exothermic and others are endothermic, <u>enthalpy (H)</u> alone cannot account for the direction of spontaneous change; a second factor must be involved. This second thermodynamic factor is termed <u>entropy (S)</u>.
- There are two natural tendencies behind spontaneous processes:
 - o the tendency to achieve a lower energy state and
 - o the tendency toward a state of greater entropy.

2 Entropy and Entropy Change

2.1 What is Entropy?

Candidates should be able to:

(a) explain and use the term entropy

Definition

The entropy (symbol: S) of a system is a measure of the disorder of matter and energy in the system. The more ways matter in the system can be arranged, and the more ways energy in the system can be dispersed, the more disordered the system is and the larger is its entropy.

Simplified version:

The entropy (symbol: S) of a system is a measure of the disorder in the system. The more disordered the system is, the larger is its entropy.

- The entropy of a system is related to the number of ways the particles (atoms, molecules or ions) in the system can be arranged or distributed and also the number of ways the energy in the system can be dispersed or spread out.
- Example: For any substance, the entropy increases as the substance changes from solid to liquid to gas.



entropy increases

The solid state

- has the lowest entropy
- is the least disordered
- has a regular and ordered structure in which the particles are only able to vibrate about fixed positions in the lattice
- has the least energy dispersed within it

The liquid state

- has a higher entropy than the solid state but lower than that of the gas
- is more disordered than the solid state
- the particles have sufficient kinetic energy to undergo translational motion to some extent
- more ways to arrange the particles
- the particles are more randomly arranged than those in the solid
- more ways to disperse the greater amount of energy in the liquid

The gaseous state

- has the highest entropy
- is the most disordered
- the particles in the gas have greater freedom of motion than those in the liquid
- more ways to arrange the particles
- the particles in the gas are even more randomly arranged than those in the liquid
- more ways to disperse the greater amount of energy in the gas

2.2 Some Entropy Values

Using a variety of experimental methods, it is possible to work out the absolute entropy values
of elements and compounds under different conditions. The tables below list the standard
entropies, S^e, of some substances at 298 K.

Element	S ^e / J K ⁻¹ mol ⁻¹	Compound	S ^e / J K ⁻¹ mol ⁻¹	
C(graphite)	5.6	CH₄(g)	186	$\Pi_2 O(3) \longrightarrow \Pi_2 O(1)$
C(diamond)	2.4	C ₂ H ₆ (g)	229	$\Delta S^{\Theta} = S^{\Theta}_{H2O(I)} - S^{\Theta}_{H2O(s)}$
C(g)	158	C ₃ H ₈ (g)	270	= +70 - 48 = +22 mol ⁻¹ K ⁻¹
Ca(s)	41.6	CH ₃ OH(I)	127	= 122 5 1101 1
Ar(g)	155	CO(g)	198	
$H_2(g)$	131	CO ₂ (g)	214	
O ₂ (g)	205	H ₂ O(s)	48.0	$C(g) \longrightarrow C(graphite)$
$N_2(g)$	192	H ₂ O(I)	70.0	$\Delta S^{\Theta} = S^{\Theta}_{C(\text{graphite})} - S^{\Theta}_{C(\text{graphite})}$
F ₂ (g)	203	H ₂ O(g)	189	= +5.6 - 158
$Cl_2(g)$	223	NaCl(s)	72.1	= –152.4 J mol ⁻¹ K ⁻¹
Br ₂ (I)	152	MgO(s)	26.9	
I ₂ (S)	116	CaCO ₃ (s)	91.7	

- When comparing the same or similar substances, entropies of gases are much larger than those for liquids, and entropies of liquids are larger than those for solids. For example, the standard entropies of I₂(s), Br₂(l) and CI₂(g) are 116, 152 and 223 J K⁻¹ mol⁻¹ respectively.
- For a series of related compounds, entropy increases with increasing molecular complexity.

2.3 Entropy Change

- The entropy change (△S) for a reaction or a process is a measure of the change in disorder in a system.
- This entropy change (△S) depends only on the entropy of the initial state (S_{initial}) and entropy of the final state (S_{final}) of the system (its composition, volume, pressure, temperature).



- The entropy change (△S) for a reaction can be worked out using tabulated standard entropy values but this is <u>not</u> required as stated under learning outcome (d) in the syllabus.
- Note:

	entropy change is positive (Δ S > 0)		entropy change is negative (Δ S < 0)
⇒	final state is <u>more disordered</u> than initial state	⇒	final state is less disordered than initial state

• A qualitative idea of the entropy change can be obtained by inspecting the equation for the reaction, and taking note of the various factors affecting entropy as discussed in the next section.

2.4 Factors Affecting the Entropy of a Chemical System

Candidates should be able to:

- (b) discuss the effects on the entropy of a chemical system by the following:
 - (i) change in temperature
 - (ii) change in phase
 - (iii) change in the number of particles (especially for gaseous systems)
 - (iv) mixing of particles

[quantitative treatment is not required]

- (c) predict whether the entropy change for a given process or reaction is positive or negative
- In general, the following factors affect entropy of a chemical system:
 - 1 change in temperature
 - 2 change in phase
 - 3 change in the number of particles (especially for gaseous systems)
 - 4 mixing of particles

(1) Change in Temperature

- The entropy of a system increases as the temperature increases.
- An increase in temperature increases the average kinetic energy of the particles in the system, giving the particles more energy to move. For liquids and gases, the particles undergo more rapid random motion causing greater disorder. Hence the entropy of the system increases. But this explanation is <u>not</u> sufficient.
- Explanation wanted: When the temperature of a system is increased, the increase in entropy comes about because in the broadening of the Boltzmann energy distribution, there are more ways of arranging energy quanta in the hotter system.
- To understand the explanation, there is a need to know the Maxwell-Boltzmann distribution curve of kinetic energies which is described briefly below.
 - The kinetic energy of any particular molecule in a gas is always changing. This is due to collisions and the resultant change in speed and hence energy.
 - However, at any given instant, due to the large number of molecules involved, the distribution of kinetic energies is always the same at the same temperature and it follows the Maxwell-Boltzmann distribution diagram shown on the right.



- The area under the curve is equal to the total number of particles in the system.
- The peak in the curve corresponds to the number of particles with the most probable energy.

 The Maxwell-Boltzmann distribution diagram below shows the distribution of kinetic energies for a given sample of molecules at different temperatures.



- As the temperature increases, there is a broadening of the energy distribution of the particles. Thus, there are more possible energy states in which the particles can adopt at a higher temperature. Hence, an increase in temperature leads to an increase in entropy. or
- As the temperature increases, there is a **broadening of the energy distribution** of the particles. Thus, there are **more packets of energy** available to **spread out** within the system, resulting in **more ways** to spread out the larger number of packets of energy. Hence, an increase in temperature will lead to an **increase in entropy**.

(2) Change in Phase

• For a substance, the entropy increases in the following order





• Solid to Liquid Phase

When a solid melts into a liquid, the order in the solid is destroyed. Particles in a liquid are more randomly arranged and more disordered than those in the solid, resulting in an increase in entropy.

Liquid to Gas or Solid to Gas Phase

The change from liquid to gas or solid to gas is accompanied by **an even larger increase in entropy**. This is because the gaseous state is the most disordered since the gas particles can move freely and are the most randomly arranged. This change of phase is also accompanied by a large increase in volume.

- (3) Change in the number of particles (especially for gaseous systems)
- The entropy of a system increases as the number of particles in the system increases.
- With more particles, there are more ways to arrange the particles and more ways to distribute the energy in the system, and hence creating greater disorder in the system.
- For processes that result in an increase in the number of moles of gaseous particles in a system, the entropy of the system increases more significantly.

This is because the arrangement of molecules in a **gas** is the most **disordered** amongst the three states of matter as the gas molecules move randomly in all directions.

- Some examples of such reactions include
 - decomposition of CaCO₃: CaCO₃(s) → CaO(s) + CO₂(g)
 - decomposition of N₂O: N₂O(g) \longrightarrow N₂(g) + $\frac{1}{2}O_2(g)$
 - combustion of propane (at 100 °C): C₃H₈(g) + 5O₂(g) → 3CO₂(g) + 4H₂O(g)

(4) Mixing of Particles (without chemical reaction)

- (a) Mixing of gas particles
- (b) Mixing of liquid particles
- (c) Dissolution of an ionic solid in water

(a) Mixing of gas particles

Gases always mix completely to create a more disordered state.



 Upon mixing, each gas expands to occupy the whole container. Hence there is an increase in entropy as there are now more ways for the molecules to arrange themselves in the larger volume.

(b) Mixing of liquid particles

- Liquids of similar polarities, e.g. benzene and hexane, mix together to form a solution in which the molecules are randomly mixed. The solution has greater disorder than the liquids in their unmixed state.
- There is an **increase in entropy** as there are now **more ways** for the molecules to arrange themselves in the larger volume of the solution.

(c) Dissolution of an ionic solid in water

- The dissolution of an ionic solid in water can lead to a net increase or decrease in disorder depending on the constituent ions of the ionic solid.
- Example 1: NaCl(s) + aq. → Na⁺(aq) + Cl⁻(aq)
 - In this case, ∆S > 0.
 - The dissolving of sodium chloride in water involves the disruption of the crystal structure of solid NaCl and hydration of the gaseous Na⁺ and Cl⁻ ions.
 - The **disruption** of the crystal **increases disorder**, since the Na⁺ and C*I*⁻ ions previously rigidly held in the solid lattice are now free to move about.

$$NaCl(s) \longrightarrow Na^{+}(g) + Cl(g)$$

 The hydration process, however, decreases disorder (or increases order) about the Na⁺ and Cl⁻ ions because it puts the hydrating water molecules into an orderly arrangement about the Na⁺ and Cl⁻ ions.

$$Na^{+}(g) + Cl^{-}(g) + aq. \longrightarrow Na^{+}(aq) + Cl^{-}(aq)$$



- It turns out that in this case, the overall dissolution process results in a net increase in disorder and entropy change is greater than zero i.e. ΔS > 0.
- **Example 2:** $CaSO_4(s) + aq. \longrightarrow Ca^{2+}(aq) + SO_4^{2-}(aq)$
 - In this case, $\Delta S < 0$
 - For salts such as CaSO₄, which contain more highly charged ions, more water molecules are ordered about the ions, and the dissolution process often results in a net decrease in entropy.
 - In this case, the decrease in entropy in the hydration process outweighs the increase in entropy due to the disruption of the crystal lattice.

Worked Example 1

For each of the following processes, state, giving a reason in each case, whether the change in entropy of the system is positive or negative.

(a)
$$C_{17}H_{36}(s) \longrightarrow C_{17}H_{36}(l)$$

∆S > 0

The entropy change is positive because the reaction produces a liquid from a solid. The molecules in the liquid can move about and hence there are more ways to arrange the molecules in the liquid state than in the solid state. This results in greater disorder, and hence an increase in the entropy of the system.

(b) $N_2(g) + O_2(g) \longrightarrow 2NO(g)$

 $\Delta S \approx 0$ (very small, can be positive or negative)

The entropy change is close to zero because the reaction does not cause any change in the number of moles of gaseous molecules in the system.

Hence there is little change in the disorder in the system and the entropy of the system remains almost the same.

(c) $2H_2O(I) \longrightarrow 2H_2(g) + O_2(g)$

S > 0

The entropy change is positive because the reaction produces gases from a liquid and results in an increase in the number of moles of gaseous molecules in the system (from 0 to 3 moles).

With more gaseous molecules which can move more randomly, there are more ways to arrange them. Thus, disorder increases and hence entropy increases. (d) $Na^{+}(g) + C\Gamma(g) \longrightarrow NaCI(s)$

∆S < 0

The entropy change is negative because the reaction produces a solid from gaseous particles and results in a decrease in the number of moles of gaseous particles in the system.

In this case, the gaseous ions that are free to move randomly formed a solid in which the ions are confined to fixed positions in the lattice. Thus there is a decrease in disorder and entropy decreases.

(e) $Cl_2(g) \longrightarrow 2Cl(g)$

∆S > 0

The entropy change is positive because the reaction results in an increase in the number of moles of gaseous particles in the system.

With more particles, there are more ways to arrange the particles and more ways to distribute the energy in the system, and hence creating greater disorder and higher entropy in the system.

(f) $Mg(s) + ZnO(s) \longrightarrow MgO(s) + Zn(s)$

 $\Delta S \approx 0$ (very small, can be positive or negative)

The entropy change is close to zero because the reaction does not cause any change in the number of moles of particles in the system and also there is no phase change in any substance.

There is little change in the number of ways to arrange the particles in the system and the entropy of the system remains almost the same.

3 Gibbs Free Energy Change

Candidates should be able to:

- (d) state and use the equation involving standard Gibbs free energy change of reaction, ΔG° , $\Delta G^{\circ} = \Delta H^{\circ} T\Delta S^{\circ}$ [the
- calculation of standard entropy change, ΔS^{o} , for a reaction using standard entropies, S^{o} , is not required]

(e) state whether a reaction or process will be spontaneous by using the sign of ΔG^{ϕ}

- (f) understand the limitations in the use of ΔG^{Φ} to predict the spontaneity of a reaction
- There are two natural tendencies behind spontaneous processes:
 - the tendency to achieve a lower energy state and
 - the tendency toward a state of greater entropy.
- For a process or reaction, neither ΔH nor ΔS alone can be used to predict whether the process or reaction is spontaneous or not. Both ΔH and ΔS affect the spontaneity of a reaction or process.
- How can ΔH and ΔS be considered together to predict whether a reaction or a process is spontaneous? This problem was first solved by J. Willard Gibbs, who introduced a new quantity, now called the **Gibbs free energy** (or just **free energy**) and given the symbol **G**.

3.1 Standard Gibbs Free Energy Change

• The Standard Gibbs Free Energy change, ΔG^{Θ} , of a reaction is given by the equation:



- Standard conditions:
 - ΔG^o is obtained at a pressure of 1 bar and at a specified temperature, which is commonly 298 K.
 - The reactants and products are in their standard states.
- Generally, we can assume that ΔH^{e} and ΔS^{e} do not vary significantly with temperature i.e. ΔH^{e} and ΔS^{e} can be assumed to be constant unless there is a phase change.
- Similarly, at constant temperature and pressure, the Gibbs Free Energy change, ∆G, of a reaction is given by the equation:

$$\Delta \boldsymbol{G} = \Delta \boldsymbol{H} - \mathsf{T} \Delta \boldsymbol{S}$$

Note

	∆G [⊖] or ∆G	∆H [⊖] or ∆H	т	∆S [⊖] or ∆S
Units commonly used	kJ mol⁻¹	kJ mol⁻¹	к	J mol ⁻¹ K ⁻¹

3.2 Relationship between ΔG^{Θ} and the Spontaneity of a Reaction

 The sign of ΔG^o can be used to deduce whether a reaction or process is spontaneous under standard conditions (i.e. 1 bar and a specified temperature, usually 298 K).

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

$\Delta G^{\Theta} < 0$ or ΔG^{Θ} is negative or the reaction/process is exergonic	the forward reaction is spontaneous (or thermodynamically feasible) under standard conditions	
$\Delta G^{\Theta} > 0$ or ΔG^{Θ} is positive or the reaction/process is <i>endergonic</i>	the forward reaction is <u>not</u> spontaneous (or <u>not</u> thermodynamically feasible) under standard conditions	

• Similarly, the sign of ∆G can be used to deduce whether a reaction or process is spontaneous under non-standard conditions (i.e. at a particular temperature and pressure).

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

$\Delta G < 0$ or ΔG is negative or the reaction is exergonic	• the forward reaction is spontaneous (or thermodynamically feasible)	
$\Delta G > 0$ or ΔG is positive or the reaction is endergonic	 the forward reaction is <u>not</u> spontaneous (or <u>not</u> thermodynamically feasible) 	
∆G = 0 *	 the system is at equilibrium there is no net change	
* This part will be discussed in the topic on Chemical Equilibrium.		

3.3 Limitations of the use of ΔG^{\ominus}

- ΔG^e indicates the **thermodynamic feasibility** (**spontaneity**) of a reaction i.e. whether it <u>can</u> occur under standard conditions.
- It gives no information about the **kinetic feasibility** (whether the reaction proceeds at an **observable** rate). The kinetic feasibility of a reaction depends on the **activation energy** of the reaction.
- In practice, a reaction with ∆G^o < 0 may not occur due to the very high activation energy of the reaction.
- Note: The same limitations apply to the use of ∆G under non-standard conditions.

3.4 Calculations involving Standard Gibbs Free Energy Change, ΔG°

Worked Example 2



Worked Example 3

Substance	MgCO ₃ (s)	MgO(s)	CO ₂ (g)
$\Delta G_{\rm f}^{\oplus}$ / kJ mol ⁻¹	-1012	-569	-394

(a) Use the ΔG_f^{Θ} data given and the formula, $\Delta G^{\Theta} = \Sigma m \Delta G_f^{\Theta}$ (products) – $\Sigma n \Delta G_f^{\Theta}$ (reactants), to calculate the standard free energy change, ΔG^{Θ} , for the reaction below.

 $MgCO_3(s) \longrightarrow MgO(s) + CO_2(g)$

Will the above reaction take place spontaneously?

(b) Given that the ΔH° of the above reaction is +101 kJ mol⁻¹, and the ΔS° for the reaction is +159 J mol⁻¹ K⁻¹, determine the temperature above which the reaction will take place spontaneously.

Note: The ΔG^{Φ} of a reaction can be calculated in a similar way (via formula or energy cycle) to that of the ΔH^{Φ} of a reaction, using ΔG_{t}^{Φ} data instead of ΔH_{t}^{Φ} data.

Solution

(a) $\Delta G^{\circ} = -569 - 394 - (-1012) = +49 \text{ kJ mol}^{-1}$ Since $\Delta G^{\circ} > 0$, the reaction will **not** take place spontaneously.

(b)

For reaction to be spontaneous,

$$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus} < 0$$

$$101 - T(\frac{159}{1000}) < 0$$

$$T > \frac{101}{0.159}$$

$$T > 635 \text{ K}$$

$$\therefore \text{ the reaction will take place spontaneously at a temperature above 635 K.}$$

Assumption: ΔH^{\ominus} and ΔS^{\ominus} do not change with temperature.

Worked Example 4

Substance	$C_2H_6(g)$	H ₂ O(I)	CO ₂ (g)
∆Gr ^e / kJ mol ⁻¹	-32.9	-237.2	-394.4

reaction can be

With the aid of the given data and an energy cycle, calculate ΔG^{o} for the combustion of ethane, C₂H₆(g). Note: The ΔG^{Θ} of a

Solution



Worked Example 5

For the reaction, $C_2H_4(g) + HCl(g) \longrightarrow C_2H_5Cl(g)$, at 298 K, $\Lambda H^{\oplus} = -96.7$ kJ mol⁻¹ and $\Delta G^{\oplus} = -25.9$ kJ mol⁻¹.

Determine by calculation, whether the reaction is feasible at 1000 K.

Solution

 $\Lambda G^{\ominus} = \Lambda H^{\ominus} - T \Lambda S^{\ominus}$ At 298 K, $\Delta S^{\ominus} = (\Delta H^{\ominus} - \Delta G^{\ominus}) / T = (-96.7 + 25.9) / 298$ = -0.2376 kJ mol⁻¹ K⁻¹ **Assumption:** ΔH^{\ominus} and ΔS^{\ominus} do not change with temperature. $\Delta G^{\ominus} = \Delta H^{\ominus} - T \Delta S^{\ominus}$ At 1000 K, $\Delta G^{\ominus} = -96.7 - (1000)(-0.2376) = +140.9$ = +141 kJ mol⁻¹ Since $\Delta G^{\Theta} > 0$, the reaction is **not** feasible at 1000 K.

4 Effect of Temperature on the Spontaneity of a Reaction

Candidates should be able to:

- (g) predict the effect of temperature change on the spontaneity of a reaction, given standard enthalpy and entropy changes
- Consider $\Delta G = \Delta H T \Delta S$.
 - ΔG is dependent on temperature, T. So, for some reactions, the spontaneity depends on temperature.
 - ΔH and ΔS change comparatively little with temperature as long as no phase changes occur. As an approximation, both terms can be assumed to be temperature independent as long as no phase changes occur.
 - By comparing the **signs** and the **magnitude** of ΔH and $-T\Delta S$ for a reaction, the **sign of** ΔG for the reaction can be determined, and hence the spontaneity of the reaction can be predicted.
 - There are 4 scenarios to consider.



4.1 The 4 Scenarios

(a) Scenario 1: $\Delta H < 0$ and $\Delta S > 0$

ΔG < 0 at all temperatures	Explanation:
These reactions are spontaneous (i.e thermodynamically feasible) at all temperatures .	$\Delta G = \Delta H - T\Delta S$ Comparing the signs of ΔH and $-T\Delta S$: • $\Delta H < 0$
 Examples of such processes include: decomposition of ozone and dinitrogen monoxide organic combustion combustion of explosives 	• $\Delta H < 0$ • $\Delta S > 0 \Rightarrow -T\Delta S < 0$ Since both ΔH and $-T\Delta S$ are negative, $\Delta G < 0$ for all values of T.

(b) Scenario 2: $\Delta H > 0$ and $\Delta S < 0$

$\Delta G > 0$ at all temperatures	Explanation:
These reactions are not spontaneous at all temperatures . Thus these reactions have to be driven continuously with external assistance .	$\Delta G = \Delta H - T\Delta S$ Comparing the signs of ΔH and $-T\Delta S$: • $\Delta H > 0$ • $\Delta S < 0 \Rightarrow -T\Delta S > 0$
Examples of such processes include: photosynthesis formation of ozone from oxygen 	Since both ΔH and $-T\Delta S$ are positive, $\Delta G > 0$ for all values of T.

(c) Scenario 3: $\Delta H > 0$ and $\Delta S > 0$

$\Delta G > 0$ at low temperatures (T < $\frac{\Delta H}{\Delta S}$)	Explanation:
$\Delta G < 0$ at high temperatures (T > $\frac{\Delta H}{\Delta S}$) These reactions are • not spontaneous at low temperatures, and • spontaneous at high temperatures.	$\Delta G = \Delta H - T\Delta S$ Comparing the signs of ΔH and $-T\Delta S$: • $\Delta H > 0$ • $\Delta S > 0 \Rightarrow -T\Delta S < 0$ At low T, • the <u>sign of ΔG</u> is determined by the <u>sign of ΔH</u> • the positive ΔH outweighs the negative $-T\Delta S$ • $\Delta G > 0$
 Examples of such processes include: melting and boiling most decomposition reactions electrolysis dissolving (for certain solids) 	At high T, • the sign of ΔG is determined by the sign of $-T\Delta S$ • the negative $-T\Delta S$ outweighs the positive ΔH • $\Delta G < 0$

(d) Scenario 4: $\Delta H < 0$ and $\Delta S < 0$

$\Delta G < 0$ at low temperatures (T < $\frac{\Delta H}{\Delta S}$)	Explanation:	
$\Delta G > 0 \text{ at high temperatures } (T > \frac{\Delta H}{\Delta S})$ These reactions are • spontaneous at low temperatures, and • not spontaneous at high temperatures.	$\Delta G = \Delta H - T\Delta S$ Comparing the signs of ΔH and $-T\Delta S$: • $\Delta H < 0$ and • $\Delta S < 0 \Rightarrow -T\Delta S > 0$ At low T, • the <u>sign of ΔG</u> is determined by the <u>sign of ΔH</u> • the negative ΔH outweighs the positive $-T\Delta S$	
Examples of such processes include:	• $\Delta G < 0$	
 condensation and freezing addition and combination reactions electrochemical cells precipitation 	At high T, • the sign of ΔG is determined by the sign of $-T\Delta S$ • the positive $-T\Delta S$ outweighs the negative ΔH • $\Delta G > 0$	

4.2 Worked Examples

Worked Example 6

For the following reaction, explain why ΔH and ΔS have the signs as shown and comment on the feasibility.

 $H_2O_2(I) \longrightarrow H_2O(I) + \frac{1}{2}O_2(g)$

 $\Delta H < 0, \Delta S > 0$

Solution

∆S > 0

The entropy change is positive because the reaction produces a gas (and a liquid) from a liquid, and results in an increase in the number of moles of gaseous molecules (from 0 mole to 0.5 moles) in the system. With more gaseous molecules which can move more randomly, there are more ways to arrange the molecules and hence creating greater disorder and higher entropy in the system.

$\Delta H < 0$

The enthalpy change is negative because $H_2O(I)$ and $O_2(g)$ are energetically more stable compared to $H_2O_2(I)$ or the bonds in $H_2O(I)$ and $O_2(g)$ are overall stronger compared to those in $H_2O_2(I)$.

Comment on feasibility (i.e. comment on sign of ΔG)

 $\Delta G = \Delta H - T\Delta S$ $\Delta H < 0, \Delta S > 0 \Rightarrow -T\Delta S < 0$ Since ΔH and $-T\Delta S$ are both negative, $\Delta G < 0$ at all temperatures. Thus, the reaction is spontaneous (i.e. thermodynamically feasible) at all temperatures.

Worked Example 7

For the following process, explain why ΔH and ΔS have the signs as shown and comment on the thermodynamic feasibility.

 $NH_4NO_3(s) \longrightarrow NH_4^+(aq) + NO_3^-(aq)$ $\Delta H > 0, \Delta S > 0$

Solution

∆S > 0

The entropy change is positive because the increase in disorder due to the breaking up of the solid ionic lattice into mobile ions <u>outweighs</u> the decrease in disorder due to the ordering of water molecules around the ions via ion-dipole interactions.

 $\Delta H > 0$ Recall: $\Delta H_{soln} = \sum \Delta H_{hyd} - LE$

In this case, ΔH is $\Delta H_{soln}[NH_4NO_3(s)]$ and it is positive because the lattice energy of NH_4NO_3 is more negative than the sum of $\Delta H_{hyd}[NH_4^+(g)]$ and $\Delta H_{hyd}[NO_3^-(g)]$.

Comment on feasibility (i.e. comment on sign of ΔG) $\Delta G = \Delta H - T\Delta S$

 $\Delta H > 0, \Delta S > 0 \Rightarrow -T\Delta S < 0$

At low temperatures (i.e. $T < \frac{\Delta H}{\Delta S}$), $\Delta G > 0$ because the **positive** ΔH outweighs the **negative** $-T\Delta S$. \Rightarrow The reaction is **not spontaneous** (i.e. not thermodynamically feasible) **at low temperatures**.

At high temperatures (i.e. $T > \frac{\Delta H}{\Delta S}$), $\Delta G < 0$ because the **negative** $-T\Delta S$ outweighs the **positive** ΔH . \Rightarrow The reaction is **spontaneous** (i.e. thermodynamically feasible) **at high temperatures**.

Worked Example 8

For the following reaction, explain why ΔH and ΔS have the signs as shown and comment on the feasibility of the reaction.

> $\Delta H < 0, \Delta S < 0$ $C_2H_4(g) + H_2(g) \longrightarrow C_2H_6(g)$

- $\Delta S < 0$ The entropy change is negative because the reaction results in decrease in the number of moles of gaseous molecules in the system. With fewer molecules, there are fewer ways of arranging the molecules and fewer ways of distributing the energy in the system, and hence creating less disorder and lower entropy in the system.
- The enthalpy change is negative because the energy consumed to break bonds in the reactant $\Delta H < 0$ molecules is less than the energy released from bonds formed in the product molecules.
- Bonds formed: 1 C–C bond and 2 C–H bonds Bonds broken: 1 C=C bond and 1 H–H bond Note: $\Delta H = +610 + 436 - 350 - (2)(410) = -124 \text{ kJ mol}^{-1} < 0$

Comment on feasibility (i.e. comment on sign of ΔG)

 $\Delta G = \Delta H - T\Delta S$ $\Delta H < 0, \Delta S < 0 \Rightarrow -T\Delta S > 0$

At low temperatures (i.e. $T < \frac{\Delta H}{\Delta S}$), $\Delta G < 0$ because the **negative** ΔH outweighs the **positive** $-T\Delta S$. \Rightarrow The reaction is **spontaneous** (i.e. thermodynamically feasible) at low temperatures.

At high temperatures (i.e. $T > \frac{\Delta H}{\Delta S}$), $\Delta G > 0$ because the **positive** $-T\Delta S$ outweighs the **negative** ΔH . ⇒ The reaction is not spontaneous (i.e. not thermodynamically feasible) at high temperatures.

Worked Example 9

A reaction is non-spontaneous at room temperature but is spontaneous at -40 °C. What can you say about the signs of ΔH and ΔS ?

Solution

 ΔH is negative and ΔS is negative.

At a low temperature of -40 °C, $\Delta G < 0$ (i.e. the reaction is spontaneous) because the negative ΔH outweighs the positive $-T\Delta S$.

At a higher temperature of room temperature, $\Delta G > 0$ (i.e. the reaction is non-spontaneous) because the positive $-T\Delta S$ outweighs the negative ΔH .

4.3 Summary of Effect of Temperature on the Spontaneity of a Reaction

				-T∆S	ΔG		
		ΔΗ	ΔS		At low T	At high T	
1	Temperature-	< 0	> 0	< 0	Always < 0 (Spontaneous at all T)		
2	cases	> 0	< 0	> 0	Always > 0 (Non-spontaneous at all T)		
3	Temperature-	> 0	> 0	< 0	> 0 (Non-spontaneous)	< 0 (Spontaneous)	
4	cases	< 0	< 0	> 0	< 0 (Spontaneous)	> 0 (Non-spontaneous)	

4.4 Graph of ΔG° against temperature T

From the preceding sections, it should be clear that ΔG^{Θ} is strongly dependent on temperature. A graph of ΔG^{Θ} for a reaction against temperature T is sometimes plotted.

$$\Delta G^{\Theta} = (-\Delta S^{\Theta}) \mathbf{T} + \Delta H^{\Theta}$$

y = mx + c

- Note that a graph of ΔG^{Θ} against temperature T is a straight line with a gradient of $-\Delta S^{\Theta}$ and a . y-intercept (at 0 K) of ΔH^{Θ} .
- The plot below shows the variation of ΔG^{Θ} with T for the following reaction: .



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

■ Worked Example 10

In 1944, T. Ellingham published plots of ΔG° against temperature T for a number of reactions. Today, such plots are called Ellingham diagrams.

An Ellingham diagram for three reactions involving the oxidation of C and CO is shown below.



Which of the following shows correctly the three reactions corresponding to I, II and III in the above Ellingham diagram?

	I	п	ш
Α	$2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$	$C + O_2 \rightarrow CO_2$	$2C + O_2 \rightarrow 2CO$
В	$2C + O_2 \rightarrow 2CO$	$2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$	$C + O_2 \rightarrow CO_2$
С	$C + O_2 \rightarrow CO_2$	$2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$	$2C + O_2 \rightarrow 2CO$
D	$2CO + O_2 \rightarrow 2CO_2$	$2C + O_2 \rightarrow 2CO$	$C + O_2 \rightarrow CO_2$



Self-Check Questions

 The reaction, NH₃(g) + HC*l*(g) → NH₄C*l*(s), proceeds spontaneously at 25 °C even though there is a decrease in disorder in the system.

Substance	NH₃(g)	HCI(g)	NH₄C <i>l</i> (s)
∆H _f ^e / kJ mol ⁻¹	-46.2	-92.3	-314.4

Given that ΔS^{Θ} is -284.6 J mol⁻¹ K⁻¹, explain with relevant calculations why the reaction is spontaneous at 25 °C.

2. For each of the following reactions, predict conditions in temperature, if any, in which the reaction will be spontaneous.

(a)	$X(s) \rightarrow Y(s) + Z(g)$	∆ <i>H</i> ^e = +250 kJ mol ⁻¹
(b)	$2X(g) + Y(g) \rightarrow 2Z(g)$	$\Delta H^{\Theta} = -100 \text{ kJ mol}^{-1}$

- (c) $X(I) \rightarrow Y(I) + Z(g)$ $\Delta H^{\Theta} = -200 \text{ kJ mol}^{-1}$
- (d) $2X(s) + 2Y(g) \rightarrow Z(g)$ $\Delta H^{\Theta} = +50 \text{ kJ mol}^{-1}$
- One suggestion for the reduction of greenhouse gas emissions from coal-fired power stations is to separate the CO₂ from the flue gases and pump it into the sea bed, where it will dissolve in water under pressure.

$$CO_2(g) + nH_2O(l) \Rightarrow CO_2(aq)$$

During this process, hydrogen bonds are formed between CO₂ and H₂O molecules.

What will be the signs of ΔH and ΔS for this equilibrium for the forward reaction?

	ΔH	ΔS
Α	-	-
В	-	+
С	+	-
D	+	+

4. When SOCl₂ is added to Ba(OH)₂, a vigorous reaction occurs and the temperature falls from 25 °C to 0 °C.

What are the correct signs of ΔG and ΔS for this reaction?

	ΔG	ΔS
Α	-	-
В	-	+
С	+	-
D	+	+

5. At temperatures below 13 °C, shiny, ductile metallic tin, known as 'white tin', changes slowly into a grey powder which is brittle.

Data for each form of tin are given in the table.

	∆H _f ^e / kJ mol ⁻¹	S ^e / J K ⁻¹ mol ⁻¹	
white	0	51.4	
grey	-2.09	44.1	

What is the expression for ΔG^{Θ} , in J mol⁻¹, for the formation of grey tin from white tin at 12 °C?

A $\Delta G^{\oplus} = -2.09 - 285 (-7.3)$

B $\Delta G^{\oplus} = -2.09 - 12 (+7.3)$

C $\Delta G^{\Theta} = -2090 - 12 (+7.3)$

D $\Delta G^{\oplus} = -2090 - 285 (-7.3)$

Practice Questions

- 6. Describe and explain how the entropy of each of the following systems will change during the stated process. Assume the pressure of each system remains at 1 bar throughout.
 - (a) 1 mol of $Cl_2(g)$ at 298 K is added to 1 mol of $N_2(g)$ at 298 K.
 - (b) 1 mol of Cl₂(g) at 298 K is heated to 373 K.
 - (c) 1 mol of $Cl_2(g)$ at 298 K is reacted with iodine according to the following equation:

$$Cl_2(g) + \frac{1}{3}I_2(s) \rightarrow \frac{2}{3}ICl_3(l)$$

(d) 1 mol of $Cl_2(g)$ at 1000 K is photolysed according to the following equation:

$$Cl_2(g) \rightarrow 2Cl \bullet (g)$$

7. The standard enthalpy change of formation, ΔH_{f}^{Θ} , and the standard free energy of formation, ΔG_{f}^{Θ} , of CO(g) and CO₂(g) are given in the table below.

	CO(g)	CO ₂ (g)
∆H _f ⊖/ kJ mol ⁻¹	-110.5	-393.5
∆G _f ^e / kJ mol ⁻¹	-137.2	-394.4

- (a) (i) Calculate the standard entropy change of formation, ΔS_f^{Θ} , of CO(g) and CO₂(g).
 - (ii) Explain why the two values in (a)(i) are so different.
- (b) Use the formula $\Delta G^{\Theta}(\text{reaction}) = \Sigma m \Delta G_f^{\Theta}(\text{products}) \Sigma n \Delta G_f^{\Theta}(\text{reactants})$ to calculate ΔG^{Θ} for the reaction

$$C(s) + CO_2(g) \longrightarrow 2CO(g)$$

and hence, show that the reaction is not feasible at 298 K but feasible at 1000 K.

 Vaporisation and transport of tungsten normally limit the life of the tungsten filament lamp. The quartz-iodine lamp contains small quantities of iodine which react with deposited tungsten:

 $W(s) + I_2(g) \longrightarrow WI_2(g)$ (on quartz envelope)

Substance	I ₂ (g)	WI ₂ (g)
∧H ^e / kJ mol ⁻¹	+62.43	-8.37

- (a) Given that ΔS^{Θ} for the above reaction is -43.1 J mol⁻¹ K⁻¹, calculate ΔG^{Θ} at 350 °C, the normal temperature of the quartz envelope. Assume that ΔH^{Θ} and ΔS^{Θ} are independent of temperature.
- (b) The WI₂ vapour then decomposes and deposits tungsten on the filament. The iodine is then liberated for further scavenging. Find the temperature of the filament above which WI₂ will decompose.

 $[(a) \Delta G_{623K} = -43.9 \text{ kJ mol}^{-1};(b) T = 1643 \text{ K}]$

9. (a) Bromine and fluorine react together to give bromine trifluoride.

$$Br_2(I) + 3F_2(g) \longrightarrow 2BrF_3(I)$$

(i) Construct a fully labelled energy cycle relating the reactants and products of this reaction to their gas phase atoms. Use your cycle to calculate the average bond energy of the Br–F bond in BF₃.

Your cycle should include relevant data from the *Data Booklet* together with the following data.

standard enthalpy change of formation of $BrF_3(I) = -301 \text{ kJ mol}^{-1}$ enthalpy change of vaporisation of $Br_2(I) = +31 \text{ kJ mol}^{-1}$ enthalpy change of vaporisation of $BrF_3(I) = +44 \text{ kJ mol}^{-1}$

- (ii) The standard Gibbs free energy of formation, ΔG_{f}^{\bullet} , of BrF₃(I) is -241 kJ mol⁻¹. Calculate ΔS_{f}^{\bullet} and comment on its sign with respect to the reaction.
- (b) Chlorine dioxide readily decomposes to its elements.

 $2 O=Cl=O(g) \longrightarrow Cl_2(g) + 2O_2(g)$ $\Delta H^{\Theta} = -204 \text{ kJ mol}^{-1}$

- (i) Construct a suitable energy cycle using this equation and use data from the *Data Booklet* and your cycle to calculate the *CI*=O bond energy in *CI*O₂.
- (ii) Explain how the value and sign of ΔG^{Θ} would compare to the value and sign of ΔH^{Θ} for the decomposition of CIO_2 .

10. When fuel consisting of 2,3,4-trimethylpentane, C₈H₁₈ is combusted in a car engine, it can form either CO₂ or CO, according to the following equations.

$$C_{8}H_{18}(l) + \frac{25}{2}O_{2}(g) \rightarrow 8CO_{2}(g) + 9H_{2}O(l) \qquad (1)$$

$$C_{8}H_{18}(l) + \frac{17}{2}O_{2}(g) \rightarrow 8CO(g) + 9H_{2}O(l) \qquad (2)$$

The following data are available:

...

Reaction	∆ <i>H</i> ^e / kJ mol ⁻¹	∆S ^o / J mol ⁻¹ K ⁻¹	
(1)	-5465	-553	
(2)	-3261	+138	

(a) Calculate ΔG^{Θ} for reactions (1) and (2).

[-5300 kJ mol⁻¹; -3302 kJ mol⁻¹]

- (b) Hence, suggest which reaction predominantly takes place during the combustion of C₈H₁₈ under standard conditions.
- (c) On the axes provided below, sketch how ΔG° for each reaction (1) and (2) will vary with temperature. Label your sketches appropriately.



- (d) Comment on whether CO or CO₂ will be produced when combustion takes place at very high temperatures.
- **11.** The following data relates to the energy changes which occur when sodium hydroxide, NaOH, and magnesium hydroxide, Mg(OH)₂, dissolve in water:

	sodium	magnesium
Hydration energy of metal ion / kJ mol ⁻¹	-390	-1890
Lattice energy of metal hydroxide / kJ mol ⁻¹	-896	-2995
Enthalpy change of solution of metal hydroxide / kJ mol ⁻¹	-44	X
Extent of hydration of metal ion (Average number of attached water molecules per metal ion)	5	15

- (a) Explain why the hydration energy of Mg²⁺ is more negative than that of Na⁺.
- (b) Use the data above, calculate x, the enthalpy change of solution of Mg(OH)₂.

[x= +5 kJ mol⁻¹]

- (c) Solubility is also controlled by the entropy change which accompanies dissolution. Use the extent of hydration from the table to compare qualitatively the entropy changes of solution of Mg(OH)₂ and NaOH.
- (d) Suggest and explain one other factor which contributes to the total entropy change when Mg(OH)₂ dissolves in water.