

## 1.5 Reaction Feasibility

Chemical reactions can be used to provide energy to do work  
e.g. petrol/diesel in car engines or an engine in a rocket

- Chemicals are burned and their energy converted into work

However, conversion of energy into work is never 100% efficient

- Work energy derived from a chemical reaction is **always** less than the heat energy ( $\Delta H$ ) that is used
- A small part of the enthalpy change is never converted into work. It is referred to as *unavailable energy*.

$$\Delta H = \text{work energy} + \text{'unavailable energy'}$$

- In thermodynamic terms:

$$\Delta H = \text{free energy} + \text{entropy change}$$

### Entropy

In nature, there is a tendency towards disorder

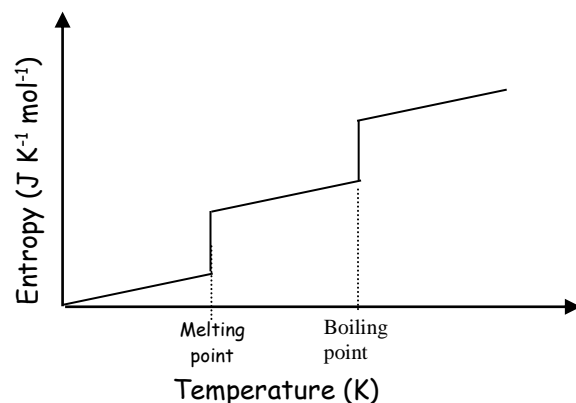
- A brick wall changes into a disordered heap of bricks with age
- The reverse process will not happen spontaneously (but will with outside help to build it)

In thermodynamic terms

- Disorder is called *entropy*
- Entropy is a measure of the degree of disorder in a system
- The greater the disorder, the greater the entropy.

Entropy increases with temperature

- Solids only have vibrational energy
- Gases have vibrational and rotational motion
- Changes of state, like melting and boiling, increase entropy
  - Changes of state have no temperature change

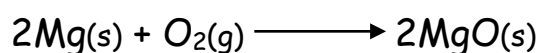


At absolute zero temperature (0K or -273°C), crystal lattice has perfect order and zero entropy

- This is (one version of) the 3<sup>rd</sup> Law of Thermodynamics
- As solid is heated, Kinetic Energy and Entropy (S) increase
- Rapid increase in Entropy (S) at melting and boiling points (bpt>mpt)
- Entropy of a system is temperature dependant

### The 2<sup>nd</sup> Law of Thermodynamics

- Total entropy of a reaction system and its surroundings always increases for a spontaneous process
- A spontaneous process is one which is thermodynamically possible
  - Can take place on its own, irrespective of time taken



- Decrease in entropy as "chaotic gas" is turned into a solid product.
- Heat energy released by reaction compensates by increasing the disorder in the surrounding air molecules.

Process	Entropy Change		
	System	Surroundings	Overall
Mixing	Increase	No change	Increase
Crystallisation	Decrease	Increase	Increase
Polymerisation	Decrease	Increase	Increase
Combustion of fuels	Increase	Increase	Increase

### Units of Entropy

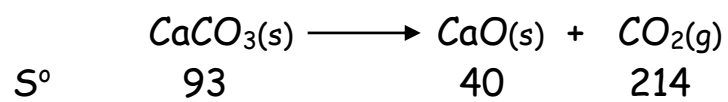
Entropy is given the symbol S

- Standard entropy of a substance is the entropy of that substance under standard conditions
  - 1 mole of a substances at 1atm pressure at a specified temperature
- values used to calculate standard entropy change

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

units of entropy are Joules per Kelvin per mole ( $\text{J K}^{-1} \text{mol}^{-1}$ )

e.g.



$$\begin{aligned} \Delta S^{\circ} &= \Sigma S^{\circ}_{\text{products}} - \Sigma S^{\circ}_{\text{reactants}} \\ &= (40+214) - (93) \\ &= 141 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

## Free Energy

In a thermodynamically-feasible endothermic reaction, there is a favourable entropy change *inside* the reaction mixture

- endothermic reaction can only take place if the entropy change is sufficiently favourable to overcome the less favourable endothermic enthalpy change

The combination of enthalpy and entropy change is known as the **Free Energy Change**.

- Free energy change is given the symbol  $\Delta G$

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

- The sign of the free energy change  $\Delta G$  can be used to predict the possibility of a reaction proceeding
  - If change in free energy  $\Delta G$  is a negative value then reaction is likely to happen spontaneously
  - If a positive  $\Delta G$  value shows that a reaction is unlikely to happen unless external energy is available (i.e. it is heated)
- If measure under standard conditions, equation becomes:

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

Where  $\Delta G^\circ$  = Standard Free Energy change (kJ mol<sup>-1</sup>)  
 $\Delta H^\circ$  = Standard Enthalpy change (kJ mol<sup>-1</sup>)  
T = Temperature (K)  
 $\Delta S^\circ$  = Standard Entropy change (J K<sup>-1</sup>mol<sup>-1</sup>)

### Question

1. Using the data given below, calculate the  $\Delta G^\circ$  at 298K and 1atm pressure for the reaction:  $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \longrightarrow \text{H}_2\text{O}(\text{l})$

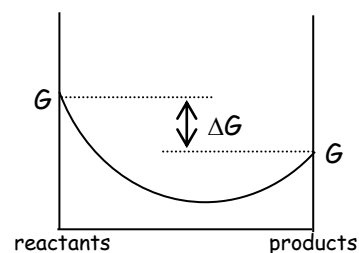
Chemical	$\Delta H^\circ_f$ (kJ mol <sup>-1</sup> )	$S^\circ$ (J K <sup>-1</sup> mol <sup>-1</sup> )
H <sub>2</sub> (g)	0	131
O <sub>2</sub> (g)	0	205
H <sub>2</sub> O(l)	-286	70

## Free Energy and Equilibrium

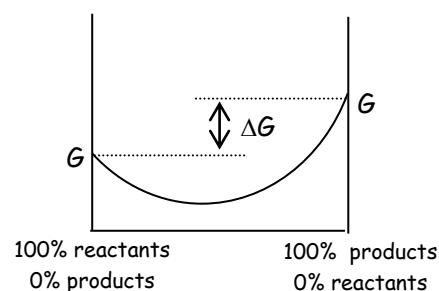
At equilibrium, the free energy of the system has reached minimum value

- free energy of products formed is equal to the free energy of the reactants left

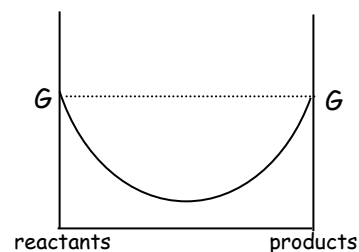
- $\Delta G$  is large and negative
- equilibrium lies on the side of the products



- $\Delta G$  is large and positive
- equilibrium lies on the side of the reactants



- $\Delta G$  is zero
- reactants and products are equally favoured

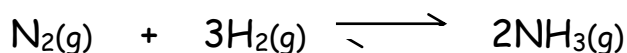


- at equilibrium,  $\Delta G = 0$
- reaction will only proceed spontaneously in the forward direction until the reactant/product composition is achieved where  $\Delta G=0$

### Reaction Feasibility

- the feasibility of a chemical reaction, under standard conditions, can be predicted from the calculated value of the change in standard free energy  $\Delta G^\circ$ .

Example 1: At what temperature does the Haber Process become feasible?



$$\Delta H_f^\circ \text{ (kJ mol}^{-1}\text{)} \quad 0 \quad 0 \quad 2 \times 46.4 \quad \Delta H_{\text{reaction}}^\circ = -92.8 \text{ kJ mol}^{-1} \\ = -92800 \text{ J mol}^{-1}$$

$$S^\circ \text{ (J K}^{-1} \text{ mol}^{-1}\text{)} \quad 191.6 \quad 3 \times 130.7 \quad 2 \times 193.2 \quad \Delta S^\circ = -197.3 \text{ J K}^{-1} \text{ mol}^{-1}$$

When  $\Delta G^\circ = 0$ , products are favoured as much as reactants

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 0$$

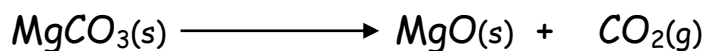
$$T\Delta S^\circ = \Delta H^\circ$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{-92800 \text{ J mol}^{-1}}{-197.3 \text{ J K}^{-1} \text{ mol}^{-1}} \\ = 470 \text{ K } (=197^\circ\text{C})$$

i.e. At 470K, reactants and products are equally favoured

- at temperature below 470K
  - $-T\Delta S^\circ$  is positive (i.e.  $\Delta S^\circ$  is negative)
  - the lower the Temperature, the lower the  $\Delta G^\circ$
  - Haber Process become feasible at Temperatures *below* 470K

Example 2: At what temperature does the decomposition of  $\text{MgCO}_3$  take place?



$$\Delta H_f^\circ \text{ (kJ mol}^{-1}\text{)} \quad -1117.2 \quad -604.1 \quad -394$$

$$S^\circ \text{ (JK}^{-1}\text{mol}^{-1}\text{)} \quad 65.9 \quad 26.9 \quad 213.8$$

$$\Delta H_{\text{reaction}}^\circ = (-604.1) + (-394) - (-1117.2) = +119.1 \text{ kJ mol}^{-1} = \underline{+119100 \text{ J mol}^{-1}}$$

$$\Delta S^\circ = (26.9) + (213.8) - (65.9) = \underline{+174.8 \text{ J K}^{-1} \text{ mol}^{-1}}.$$

Reaction becomes feasible when  $\Delta G^\circ = 0$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 0$$

$$T\Delta S^\circ = \Delta H^\circ$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{-119100 \text{ J mol}^{-1}}{-174.8 \text{ JK}^{-1}\text{mol}^{-1}}$$

$$= \underline{681.35 \text{ K}} \text{ (} = 408^\circ\text{C)}$$