FREE ENERGY & ENTROPY

Problem

- a **spontaneous change** occurs in one particular direction and not the other
- exothermic reactions are usually spontaneous - go from higher to lower enthalpy

However ...

Why should reactions with a positive ΔH value take place spontaneously ?
e.g. some salts dissolve readily in water and the temperature of the solution drops

- Surely, this means that energy has to be put in for the reaction to take place
- The answer is that enthalpy change ΔH **does not give the full story**.
- **Free energy changes, ΔG, give a better picture**.

Free energy

- A reaction is only spontaneous if it can do work - *it must generate free energy*
- A negative ΔG indicates a reaction capable of proceeding of its own accord

ΔG < 0 (- ive)	Spontaneous reaction
ΔG > 0 (+ ive)	Non-spontaneous reaction (spontaneous in reverse direction)
ΔG = 0	The system is in equilibrium

Entropy

- Entropy (symbol **S**) is **a measure of the disorder** of a system
- The more the disorder, the greater the entropy
- If a system becomes more disordered, the value of ΔS is positive
- Values tend to be in **JOULES** - not kJ

$$\Delta S = S_{final} - S_{initial}$$

$\Delta S^\circ = S^\circ_{final} - S^\circ_{initial}$ if standard conditions are used

2nd Law

The Second Law of Thermodynamics is based on entropy ...

"Entropy tends to a maximum"

infers... "all chemical and physical changes involve an overall increase in entropy"

Entropy increases when

- solids melt
- liquids boil
- solids dissolve in water
- the number of gas molecules increases
- the temperature increases

Free energy, enthalpy and entropy are related ... $\Delta G = \Delta H - T\Delta S$

Special case For a **reversible reaction at equilibrium** the value of **ΔG is zero**

If ΔG = **ZERO** then $\Delta S = \frac{\Delta H}{T}$

Worked Example *Calculate the entropy change when water turns to steam at 100°C. The enthalpy of vaporisation of water is +44 kJ mol^{-1}*

$$\Delta S = \frac{\Delta H}{T} = \frac{+44\ kJ\ mol^{-1}}{373\ K} = +118\ J\ K^{-1}\ mol^{-1}$$

Q.1 *Element X melts reversibly at 400K. If the enthalpy change of fusion of X is 2.84 kJ mol^{-1}, what is the entropy change? [Fusion is the same as melting]*

Will a reaction work?

Theory A reaction should be **spontaneous if ΔG is negative**, so ...

- Work out if it is exothermic (ΔH -ive) or endothermic (ΔH +ive)
- Is there an increase in disorder ? If YES then ΔS will be positive.
- Is the temperature high or low ? This can affect the value of $T\Delta S°$

Examples

General
- **If ΔH is -ive and ΔS is +ive then ΔG must be negative**
- **If ΔH is +ive and ΔS is -ive then ΔG must be positive**

Specific *i)* **H_2**(g) + **F_2**(g) ——> **2HF**(g)

ΔH -ive highly exothermic process
ΔS 0 same number of gas molecules

$\therefore$ ΔG must be negative

ii) **Na^+**(g) + **Cl^-**(g) ——> **NaCl**(s)

ΔH -ive highly exothermic (Lattice Enthalpy)
ΔS -ive more order in a solid

$\therefore$ ΔG is negative (mostly due to the high value of lattice enthalpy)

iii) $NH_4NO_3(s) \longrightarrow NH_4^+(aq) + NO_3^-(aq)$

ΔH +ive endothermic (the solution goes colder)
ΔS +ive more disorder as aqueous ions

$\therefore$ ΔG will be negative if T is high **or** the value of ΔS is big enough

Q.2

*What is the sign of the **entropy** change in the following reactions ? Give reasons for your decision.*

a) $NH_4NO_{3(s)} \longrightarrow N_2O_{(g)} + 2H_2O_{(g)}$

b) $NH_{3(g)} + HCl_{(g)} \longrightarrow NH_4Cl_{(s)}$

c) $Na_{(s)} \longrightarrow Na_{(g)}$

d) $COCl_{2(g)} \longrightarrow CO_{(g)} + Cl_{2(g)}$

e) $PCl_{3(g)} + Cl_{2(g)} \longrightarrow PCl_{5(g)}$

f) $C_6H_{12(l)} + 9O_{2(g)} \longrightarrow 6CO_{2(g)} + 6H_2O_{(g)}$

g) $C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$

*State the sign for the **enthalpy** change in* *c) f) g)*