# 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 $\Delta H$ 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 $\Delta H$ **does not give the full story**.
- **Free energy changes, $\Delta G$, give a better picture**.

**Free energy**

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

| | |
|---|---|
| **$\Delta G$ < 0 (- ive)** | Spontaneous reaction |
| **$\Delta G$ > 0 (+ ive)** | Non-spontaneous reaction (spontaneous in reverse direction) |
| **$\Delta G$ = 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 $\Delta S$ is positive
- Values tend to be in **JOULES** - not kJ

$$\Delta S^\circ = S^\circ_{final} - S^\circ_{initial}$$

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

*Special case* For a reversible reaction at equilibrium the value of $\Delta G$ is zero

If $\Delta G$ **= 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$^{-1}$*

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

***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 $\Delta G$ is negative**, so ...

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

**Examples**

*General*

- **If $\Delta H$ is -ive and $\Delta S$ is +ive then $\Delta G$ must be negative**
- **If $\Delta H$ is +ive and $\Delta S$ is -ive then $\Delta G$ must be positive**

*Specific* *i)* $H_2(g) + F_2(g) \longrightarrow 2HF(g)$

$\Delta H$ -ive highly exothermic process
$\Delta S$ 0 same number of gas molecules

$\therefore$ $\Delta G$ must be negative

*ii)* $Na^+(g) + Cl^-(g) \longrightarrow NaCl(s)$

$\Delta H$ -ive highly exothermic (Lattice Enthalpy)
$\Delta S$ -ive more order in a solid

$\therefore$ $\Delta G$ is negative (mostly due to the high value of lattice enthalpy) *iii)* $\mathbf{NH_4NO_3}$(s) ——> $\mathbf{NH_4^+}$(aq) + $\mathbf{NO_3^-}$(aq)

$\Delta H$ +ive endothermic (the solution goes colder)
$\Delta S$ +ive more disorder as aqueous ions

$\therefore$ $\Delta G$ will be negative if T is high **or** the value of $\Delta S$ 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)