

FREE ENERGY & ENTROPY

- Problem**
- a **spontaneous change** occurs in one particular direction and not the other
 - exothermic reactions are usually spontaneous - they 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 *i.e. it must generate free energy*
 - A negative value for ΔG indicates a reaction is capable of proceeding of its own accord

$\Delta G < 0$ (-ive) Spontaneous reaction

$\Delta G > 0$ (+ive) Non-spontaneous reaction (but spontaneous in the 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 ΔS is positive
 - Values tend to be in **JOULES** - not kJ

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

- 2nd Law** The Second Law of Thermodynamics is based on entropy ...

"Entropy tends to a maximum"

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

- Entropy increases** when
- solids melt
 - liquids boil
 - solids dissolve in water
 - there is an increase in the number of gas molecules
 - the temperature of solids, liquids and gases 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 ΔG is zero

$$\text{If } \Delta G = \mathbf{ZERO} \quad \text{then} \quad \Delta S = \frac{\Delta H}{T}$$

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

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

Will a reaction work?

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

- Work out (use common sense) 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 $T\Delta S^{\circ}$

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) $\text{H}_{2(\text{g})} + \text{F}_{2(\text{g})} \longrightarrow 2\text{HF}_{(\text{g})}$

ΔH -ive highly exothermic process

ΔS 0 same number of gas molecules

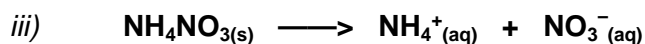
$\therefore \Delta G$ must be negative

ii) $\text{Na}^{+}_{(\text{g})} + \text{Cl}^{-}_{(\text{g})} \longrightarrow \text{NaCl}_{(\text{s})}$

ΔH -ive highly exothermic (Lattice Enthalpy)

ΔS -ive more order in a solid

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



ΔH +ive endothermic (the solution goes colder)

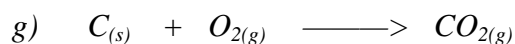
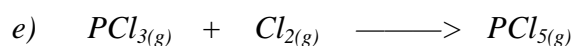
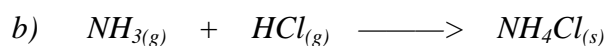
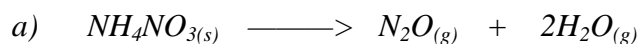
ΔS +ive more disorder as aqueous ions

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

Q.1

What is the sign of the entropy change in the following reactions ?

Give reasons for your decision



State the sign for the enthalpy change in

c)

f)

g)