

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

$\Delta G < 0$ (-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 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"

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 ΔG is zero

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

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

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

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 $T\Delta S^{\circ}$

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

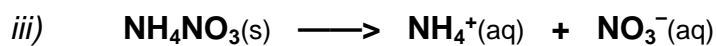
$\therefore \Delta G$ must be negative

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)



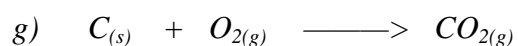
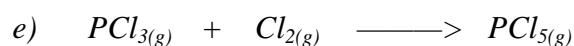
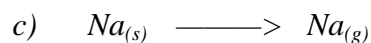
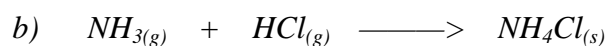
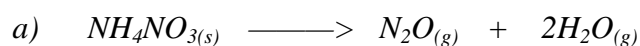
ΔH +ive endothermic (the solution goes colder)

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.2

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)