

## 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  $\Delta H$  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 *i.e. it must generate free energy*
  - A negative value for  $\Delta G$  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  $\Delta S$  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  $\Delta G$  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  $100^\circ\text{C}$  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  $\Delta G$  is negative**, so ...

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

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

$\Delta H$  -ive highly exothermic process

$\Delta S$  0 same number of gas molecules

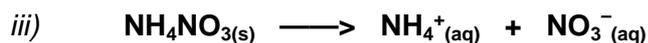
$\therefore \Delta G$  must be negative

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

$\Delta H$  -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)



$\Delta H$  +ive endothermic (the solution goes colder)

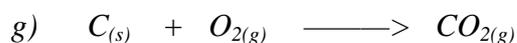
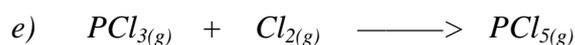
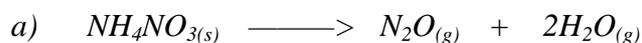
$\Delta S$  +ive more disorder as aqueous ions

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

### Q.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)