

## 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

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

$\Delta S^\circ = S^\circ_{\text{final}} - S^\circ_{\text{initial}}$ <p>if standard conditions are used</p>
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### 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  $\Delta G$  is zero

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

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

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

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

### Will a reaction work?

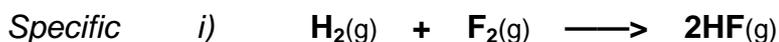
**Theory** A reaction should be **spontaneous if  $\Delta G$  is negative**, so ...

- 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  $T\Delta S^\circ$

### 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



$\Delta H$  -ive highly exothermic process

$\Delta S$  0 same number of gas molecules

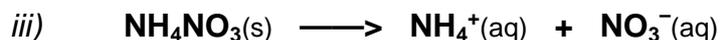
$\therefore \Delta G$  must be negative



$\Delta H$  -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)



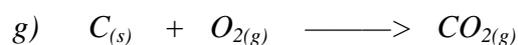
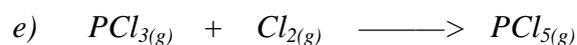
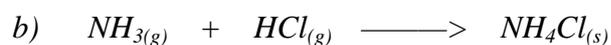
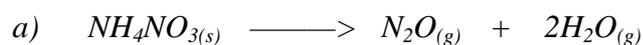
$\Delta H$  +ive endothermic (the solution goes colder)

$\Delta S$  +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.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)