

## Free-energy change ( $\Delta G$ ) and entropy change ( $\Delta S$ )

A **SPONTANEOUS PROCESS** (e.g. diffusion) will proceed on its own without any external influence.

### A problem with $\Delta H$

A reaction that is exothermic will result in products that are more **thermodynamically stable** than the reactants. This is a driving force behind many reactions and causes them to be **spontaneous** (occur without any external influence).

Some spontaneous reactions, however, are endothermic.

### How can this be explained?

We need to consider something called **entropy**

### Entropy, $S^\circ$

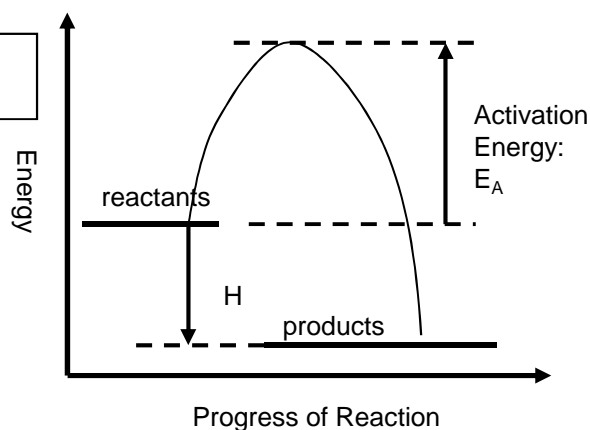
Substances with more ways of arranging their atoms and energy (*more disordered*) have a higher entropy.

Elements	...tend to have lower entropies than...	Compounds
Simpler compounds		Complex compounds
Pure substances		Mixtures

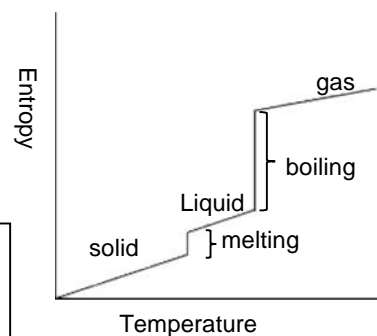
Solids have lower entropies than liquids which are lower than gases. When a solid increases in Temperature its entropy increases as the particles vibrate more.

There is a bigger jump in entropy with boiling than that with melting.

**Gases have large entropies as they are much more disordered**

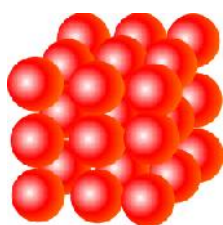


Entropy is a description of the number of ways atoms can share quanta of energy. If number of ways of arranging the energy ( $W$ ) is *high*, then system is *disordered* and entropy ( $S$ ) is *high*.

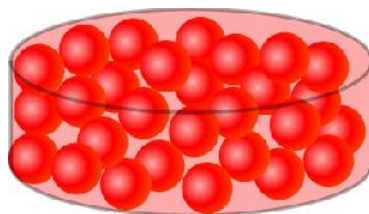


At 0K substances have zero entropy. There is no disorder as particles are stationary

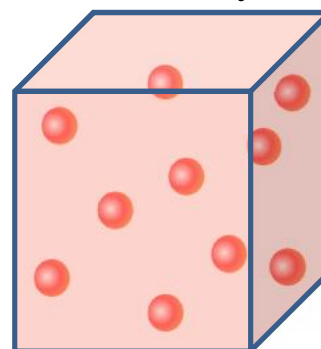
Increasing entropy (disorder)



solid



liquid



gas

## Predicting Change in entropy ' $S_{system}$ ' Qualitatively

An **increase** in disorder and **entropy** will lead to a positive entropy change  $S^\circ = +ve$

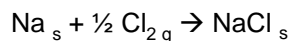
Balanced chemical equations can often be used to predict if  $S^\circ$  is positive or negative.

**In general**, a significant increase in the entropy will occur if:  
 -there is a **change of state** from **solid or liquid to gas**  
 - there is a significant **increase in number of molecules** between products and reactants.



$S^\circ = +ve$

- change from solid reactant to gaseous products
  - increase in number of molecules
- both will increase disorder



$S^\circ = -ve$

- change from gaseous and solid reactant to solid
  - decrease in number of molecules
- both will decrease disorder

### Calculating $S_{system}^\circ$ quantitatively

Data books lists standard entropies ( $S^\circ$ ) **per mole** for a variety of substances. It is not possible for a substance to have a standard entropy of less than zero.

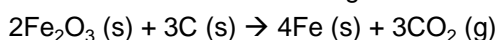
Elements in their standard states do *not* have zero entropy. **Only perfect crystals at absolute zero ( $T = 0$  K) will have zero entropy:**

The unit of entropy is  $\text{J K}^{-1} \text{ mol}^{-1}$

$$S_{system}^\circ = S^\circ_{\text{products}} - S^\circ_{\text{reactants}}$$

#### Example

Calculate  $S^\circ$  for the following reaction at  $25^\circ\text{C}$ :



$$\begin{aligned} S^\circ &= S^\circ_{\text{products}} - S^\circ_{\text{reactants}} \\ &= (3 \times 213.6 + 4 \times 27.3) - (2 \times 87.4 + 3 \times 5.7) \\ &= + 558.1 \text{ J K}^{-1} \text{ mol}^{-1} = \underline{\underline{+ 558 \text{ J K}^{-1} \text{ mol}^{-1}}} \text{ (3 S.F.)} \end{aligned}$$

$$S [\text{Fe}_2\text{O}_3] = 87.4 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$S [\text{C}] = 5.7 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$S [\text{Fe}] = 27.3 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$S [\text{CO}_2] = 213.6 \text{ J K}^{-1} \text{ mol}^{-1}$$

Note: the entropy change is very positive as a large amount of gas is being created increasing disorder

## Entropy of the Surroundings $US_{surrounding}$

The surroundings are the container, air, solvent.

In an exothermic reaction energy is given out into the surroundings. The number of ways of arranging the energy therefore increases and so  $\Delta S_{surrounding}$  increases and is positive.

In an endothermic reaction energy is transferred from the surroundings. The number of ways of arranging the energy in the surroundings therefore decreases and so  $\Delta S_{surrounding}$  decreases and is negative.

$$US_{surrounding} = \frac{-\Delta H_{\text{reaction}}}{T}$$

converted into  $\text{J mol}^{-1}$  by x1000

in K  
Convert  $^\circ\text{C}$  into K by +273

## Total Entropy change $\Delta S_{\text{total}}^{\ominus}$

$$\Delta S_{\text{total}}^{\ominus} = \Delta S_{\text{system}}^{\ominus} + \Delta S_{\text{surrounding}}^{\ominus}$$

For any reaction to be **spontaneous then  $\Delta S_{\text{total}}$  must be positive**. If a reaction is not spontaneous i.e. it doesn't go, then  $\Delta S_{\text{total}}$  will be negative.

**Example :** Data for the following reaction, which represents the reduction of aluminium oxide by carbon, are shown in the table.



Calculate the values of  $S_{\text{system}}$ ,  $H^{\circ}$ ,  $S_{\text{surroundings}}$  and  $S_{\text{Total}}$  for the above reaction at 298 K

Substance	$H_f^{\circ}$ / $\text{kJ mol}^{-1}$	$S^{\circ}$ / $\text{JK}^{-1}\text{mol}^{-1}$
$\text{Al}_2\text{O}_3(\text{s})$	-1669	51
$\text{C}(\text{s})$	0	6
$\text{Al}(\text{s})$	0	28
$\text{CO}(\text{g})$	-111	198

### 1. Calculate $S_{\text{system}}$

$$\begin{aligned} S^{\circ} &= S^{\circ}_{\text{products}} - S^{\circ}_{\text{reactants}} \\ &= (2 \times 28 + 3 \times 198) - (51 + 3 \times 6) \\ &= +581 \text{ J K}^{-1} \text{ mol}^{-1} \text{ (3 S.F.)} \end{aligned}$$

### 2. Calculate $H^{\circ}$

$$\begin{aligned} H^{\circ} &= H_f^{\circ}[\text{products}] - H_f^{\circ}[\text{reactants}] \\ &= (3 \times -111) - -1669 \\ &= +1336 \text{ kJ mol}^{-1} \end{aligned}$$

### 3. Calculate $S_{\text{surroundings}}$

$$\begin{aligned} \Delta S_{\text{surrounding}}^{\ominus} &= -\frac{\Delta H_{\text{reaction}}}{T} \\ &= -1336000/298 \\ &= -4483 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

### 4. Calculate $S_{\text{Total}}$

$$\begin{aligned} \Delta S_{\text{total}} &= \Delta S_{\text{system}} + \Delta S_{\text{surrounding}} \\ &= 581 - 4483 \\ &= -3902 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

$S_{\text{Total}}$  is negative. The reaction is not feasible

## Gibbs Free Energy Change, $G$

Gibbs free energy is a term that combines the effect of enthalpy and entropy into one number

The balance between entropy and enthalpy determines the feasibility of a reaction.

This is given by the relationship :

$$G = H - T S_{\text{system}}$$

For any spontaneous change,  $G$  will be **negative**.

A reaction that has increasing entropy (+ve  $S$ ) and is exothermic (-ve  $H$ ) will make  $G$  be **negative** and will almost always be feasible

If  $G$  is negative there is still a possibility, however, that the reaction will not occur or will occur so slowly that effectively it doesn't happen. If the reaction has a high activation energy the reaction will not occur.

**Convert from °C to K (+ 273)**

Unit of  $S = \text{J K}^{-1} \text{mol}^{-1}$

**Need to convert to  $\text{KJ K}^{-1} \text{mol}^{-1}$  ( $\div 1000$ )**

$$G = H - T S$$

Units:  $\text{KJ mol}^{-1}$       Units:  $\text{KJ mol}^{-1}$

**Example :** Data for the following reaction, which represents the reduction of aluminium oxide by carbon, are shown in the table.



Calculate the values of  $H^\circ$ ,  $S^\circ$  and  $G^\circ$  for the above reaction at 298 K

### 1. Calculate $S^\circ$

$$S^\circ = S^\circ_{\text{products}} - S^\circ_{\text{reactants}}$$
$$= (2 \times 28 + 3 \times 198) - (51 + 3 \times 6)$$
$$= +581 \text{ J K}^{-1} \text{ mol}^{-1} \quad (3 \text{ S.F.})$$

### 2. Calculate $H^\circ$

$$H^\circ = H^\circ_f[\text{products}] - H^\circ_f[\text{reactants}]$$
$$= (3 \times -111) - (-1669)$$
$$= +1336 \text{ kJ mol}^{-1}$$

Substance	$H_f^\circ / \text{kJ mol}^{-1}$	$S^\circ / \text{JK}^{-1} \text{mol}^{-1}$
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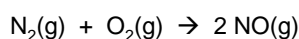
### 3. Calculate $G^\circ$

$$G^\circ = H^\circ - T S^\circ$$
$$= +1336 - 298 \times 0.581$$
$$= +1163 \text{ kJ mol}^{-1}$$

$G^\circ$  is positive. The reaction is not feasible

### Calculating the temperature a reaction will become feasible

Calculate the temperature range that this reaction will be feasible



$$H = 180 \text{ kJ mol}^{-1} \quad S = 25 \text{ J K}^{-1} \text{ mol}^{-1}$$

The reaction will be feasible when  $G = 0$

Make  $G = 0$  in the following equation  $G = H - T S$

$$0 = \Delta H - T \Delta S$$

$$\text{So } T = H / S$$

$$T = 180 / (25/1000)$$
$$= 7200 \text{ K}$$

The  $T$  must be  $> 7200 \text{ K}$  which is a high Temp!

### $G$ during phase changes

As physical phase changes like melting and boiling are equilibria, the  $G$  for such changes is zero.

What temperature would methane melt at?



Make  $G = 0$  in the following equation  $G = H - T S$

$$0 = H - T S$$

$$\text{So } T = H / S$$

$$T = 0.94 / (10.3 \div 1000)$$

$$T = 91 \text{ K}$$

## Effect of Temperature on feasibility

$$G = H - T S$$

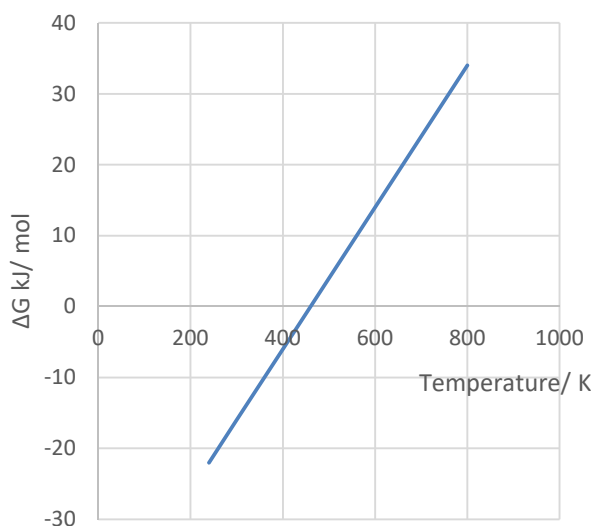
Changing Temperature will change the value of  $-T S$  in the above equation

If the reaction involves an increase in entropy ( $S$  is +ve) then increasing Temperature will make it more likely that  $G$  is negative and more likely that the reaction occurs e.g.  $\text{NaCl} + \text{aq} \rightarrow \text{Na}^+_{(\text{aq})} + \text{Cl}^-_{(\text{aq})}$

If the reaction involves a decrease in entropy ( $S$  is -ve) then increasing Temperature will make it more less likely that  $G$  is negative and less likely for the reaction to occur. E.g.  $\text{HCl}(\text{g}) + \text{NH}_3(\text{g}) \rightarrow \text{NH}_4\text{Cl}(\text{s})$

If the reaction has a  $S$  close to zero then temperature will not have a large effect on the feasibility of the reaction as  $-T S$  will be small and  $G$  won't change much  
e.g.  $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}(\text{g})$

This graph shows how the free-energy change for formation of ammonia varies with temperature above 240 K.  
 $\frac{1}{2} \text{N}_2(\text{g}) + \frac{3}{2} \text{H}_2(\text{g}) \rightarrow \text{NH}_3(\text{g})$



Applying the equation of a straight line  
 $y = mx + c$  to the  $G = H - T S$  equation.  
 $c = H$   
The gradient of this graph is equal to  $-S$

The positive gradient means  $S$  is negative which corresponds to the equation above showing increasing order.

When  $G < 0$  then the reaction is spontaneous. In this case at Temperatures below around 460K

The slope of the line would change below 240K because ammonia would be a liquid and the entropy change would be different