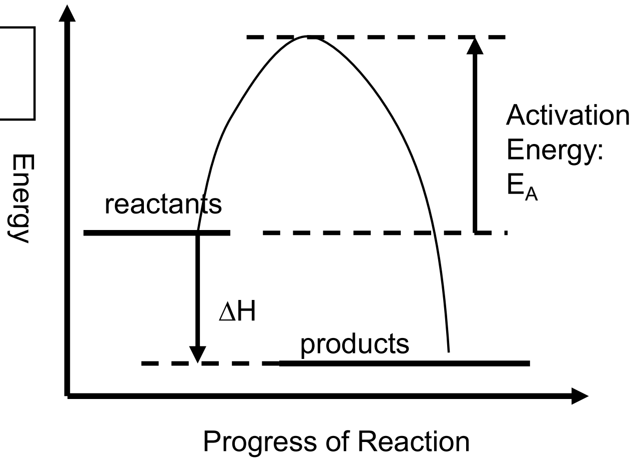
Free-energy change (ΔG) and entropy change (ΔS)

A spontaneous process (e.g. diffusion) will proceed on its own without any external influence.

A problem with ΔH

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.**

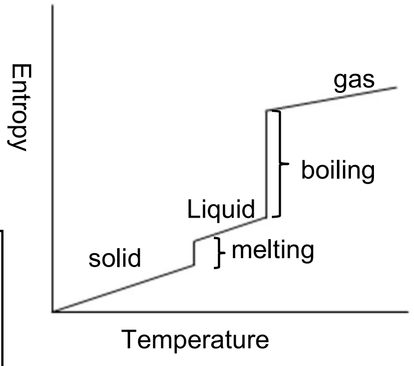
Entropy, S°

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

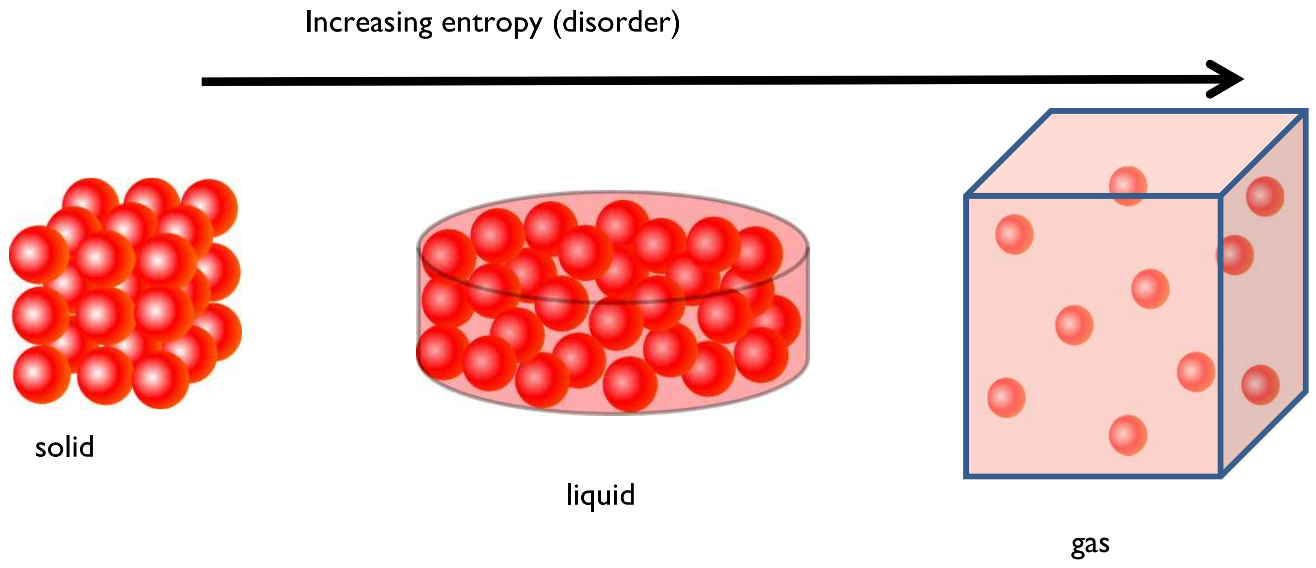
Entropy is a description of the number of ways atoms can share quanta of energy. If number of ways of arranging the energy (**W**) is high, then system is disordered and entropy (**S**) is high.

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.



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



Predicting Change in entropy 'ΔS_{system}' Qualitatively

An **increase** in disorder and **entropy** will lead to a positive entropy change **ΔS° = +ve**

Balanced chemical equations can often be used to predict if ΔS° 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.

$NH_4Cl\ (s) \rightarrow HCl\ (g) + NH_3\ (g)$
ΔS° = +ve
•change from solid reactant to gaseous products
•increase in number of molecules
both will increase disorder

$Na_{\ s} + \frac{1}{2}\ Cl_{2\ g} \rightarrow NaCl_{\ s}$
ΔS° = -ve
•change from gaseous and solid reactant to solid
•decrease in number of molecules
both will decrease disorder

Calculating ΔS_{system}° quantitatively

Data books lists standard entropies (***S***˚) **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 **J K^{-1} mol^{-1}**

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

Example

Calculate ΔS° for the following reaction at 25˚C:

$2Fe_2O_3\ (s) + 3C\ (s) \rightarrow 4Fe\ (s) + 3CO_2\ (g)$

$\Delta S^\circ = S^\circ_{products} - S^\circ_{reactants}$

$= (3 \times 213.6 + 4 \times 27.3) - (2 \times 87.4 + 3 \times 5.7)$

$= +\ 558.1$ J K^{-1} mol^{-1} = **<u>+ 558 J K^{-1} mol^{-1}</u>** (3 S.F.)

S [Fe_2O_3] = 87.4 J K^{-1} mol^{-1}
S [C] = 5.7 J K^{-1} mol^{-1}
S [Fe] = 27.3 J K^{-1} mol^{-1}
S [CO_2] = 213.6 J K^{-1} mol^{-1}

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

Entropy of the surroundings $\Delta S^{\ominus}_{surrounding}$

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.

$$\Delta S^{\ominus}_{surrounding} = \frac{-\ \Delta H\ \text{reaction}}{T}$$

converted into J mol^{-1} by x1000

in K
Convert ^{o}C into K
by +273

Total entropy change $\Delta S^{\ominus}_{\text{total}}$

$$\boxed{\Delta S^{\ominus}_{\text{total}} = \Delta S^{\ominus}_{\text{system}} + \Delta S^{\ominus}_{\text{surrounding}}}$$

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

Example : Data for the following reaction, which represents the reduction of aluminium oxide by carbon, are shown in the table.
$Al_2O_3(s) + 3C(s) \rightarrow 2Al(s) + 3CO(g)$

Substance	**$\Delta_f H$ / kJmol^{-1}**	**S / JK^{-1}mol^{-1}**
$Al_2O_3(s)$	-1669	51
C(s)	0	6
Al(s)	0	28
CO(g)	-111	198

Calculate the values of $\Delta S_{system,}$ ΔH , $\Delta S_{surroundings}$ and ΔS_{Total} for the above reaction at 298 K

1. Calculate ΔS_{system}

$\Delta S^{\circ} = \Sigma S^{\circ}_{\text{products}} - \Sigma S^{\circ}_{\text{reactants}}$

$= (2 \times 28 + 3 \times 198) - (51 + 3 \times 6)$

$= +581 \text{ J K}^{-1} \text{ mol}^{-1}$ (3 S.F.)

2. Calculate ΔH°

$\Delta H^{\circ} = \Sigma\Delta_f H^{\circ} \text{ [products]} - \Sigma\Delta_f H^{\circ} \text{ [reactants]}$

$= (3 \times -111) - -1669$

$= +1336 \text{ kJ mol}^{-1}$

3. Calculate $\Delta S_{surroundings}$

$$\Delta S^{\ominus}_{\text{surrounding}} = \frac{-\Delta H_{\text{reaction}}}{T}$$

$= -1336000/298$
$= -4483 \text{ J K}^{-1} \text{ mol}^{-1}$

4. Calculate ΔS_{Total}

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

$= 581 - 4483$
$= -3902 \text{J K}^{-1} \text{ mol}^{-1}$

ΔS_{Total} is negative. The reaction is not feasible

Gibbs Free Energy Change, Δ*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 :

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

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

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

If Δ*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= **J K^{-1} mol^{-1}**

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

Need to convert to **kJ K^{-1} mol^{-1}** **(÷1000)**

Units: **kJ mol^{-1}**

Units: **kJ mol^{-1}**

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

$Al_2O_3(s) + 3C(s) \rightarrow 2Al(s) + 3CO(g)$

Calculate the values of Δ*H* , Δ*S* and Δ*G* for the above reaction at 298 K

Substance	Δ*fH* / kJ mol^{-1}	*S* / JK^{-1}mol^{-1}
$Al_2O_3(s)$	-1669	51
C(s)	0	6
Al(s)	0	28
CO(g)	-111	198

1. Calculate ΔS

$\Delta S^\circ = \Sigma S^\circ_{products} - \Sigma S^\circ_{reactants}$

= (2 x 28 + 3x198) – (51 + 3 x 6)

= +581 J K^{-1} mol^{-1} (3 S.F.)

2. Calculate ΔH˚

$\Delta H^\circ = \Sigma\Delta_f H^\circ$ [products] - $\Sigma\Delta_f H^\circ$ [reactants]

= (3 x -111) – -1669

= +1336 kJ mol^{-1}

3. Calculate ΔG

ΔG = ΔH - TΔS
= +1336 – 298x 0.581
= +1163 kJ mol^{-1}

ΔG 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.

$N_2(g) + O_2(g) \rightarrow 2\,NO(g)$

Δ H = 180 kJ mol^{-1} ΔS = 25 J K^{-1} mol^{-1}

The reaction will be feasible when Δ G ≤0

Make ΔG = 0 in the following equation ΔG = ΔH - TΔS

0 = ΔH - TΔS

So T= ΔH / ΔS

T = 180/ (25/1000)
= 7200 K

The T must be >7200 K which is a high temperature.

ΔG during phase changes

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

What temperature would methane melt at?

$CH_{4(s)} \rightarrow CH_{4\,(l)}$ ΔH = 0.94 kJ mol^{-1} ΔS = 10.3 J mol^{-1} K^{-1}

Make ΔG = 0 in the following equation ΔG = ΔH - TΔS
0 = ΔH - TΔS
So T= ΔH / ΔS

T= 0.94 / (10.3÷1000)

T= 91K

Effect of temperature on feasibility

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

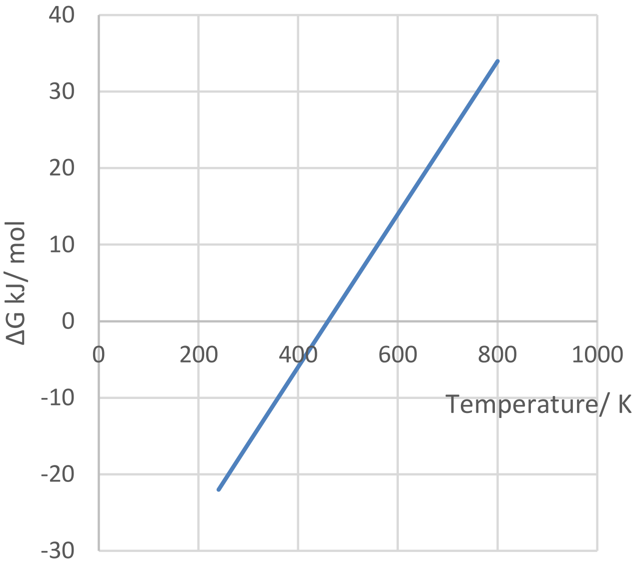
Changing temperature will change the value of **- TΔ*S*** in the above equation

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

If the reaction involves an decrease in entropy (Δ***S* is -ve)** then increasing temperature will make it more **less likely** that Δ**G is negative and less likely for the reaction to occur.** E.g. $HCl(g) + NH_3\ (g) \rightarrow NH_4Cl(s)$

If the reaction has a Δ***S* close to zero** then temperature will not have a large effect on the feasibility of the reaction as **- TΔ*S* *will be small*** and Δ**G won't change much.**
e.g. $N_{2\ (g)} + O_{2\ (g)} \rightarrow 2NO_{\ (g)}$

This graph shows how the free-energy change for formation of ammonia varies with temperature above 240 K.
$\frac{1}{2} N_2(g) + {}^3/_2\ H_2(g) \rightarrow NH_3(g)$



Applying the equation of a straight line:

y = mx + c to the Δ**G = ΔH - TΔS** equation.

c = Δ**H**
The gradient of this graph is equal to **-ΔS**

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

When Δ**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.