

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

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Spontaneity

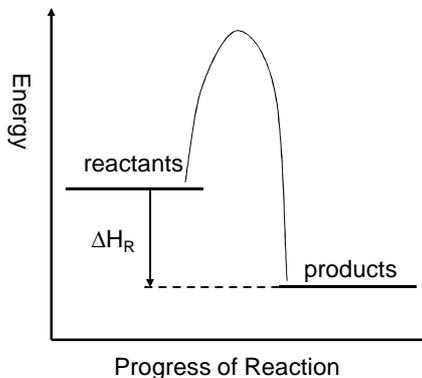
- A **SPONTANEOUS PROCESS** (e.g. diffusion) will proceed on its own without any external influence.
- Spontaneous processes have the greatest probability of occurring i.e. the greatest number of ways of happening.
- **SPONTANEITY** and **SPEED** are unrelated: a spontaneous reaction may occur very slowly.

key

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**

key

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*.
- To avoid large numbers, **ENTROPY** is used:

$$S = k \ln W$$

- $\ln W$: natural log of number of ways of arranging
- k : Boltzmann constant = $1.381 \times 10^{-23} \text{ J K}^{-1}$
- S : Entropy (**units: $\text{J mol}^{-1} \text{ K}^{-1}$**)

Extra

Entropy

The easiest way to think about entropy is to look at how 'ordered' the substance is.

The substance with the lowest entropy is a perfect crystal of diamond. Why?

Only one type of atom in one regular giant structure

A perfect crystal of diamond at absolute zero ($T = 0$ K) will have zero entropy

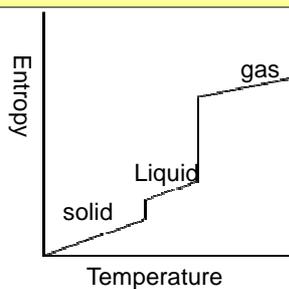
Elements	<i>...tend to have lower entropies than...</i>	Compounds
Simpler compounds		Complex compounds
Pure substances		Mixtures

Entropy

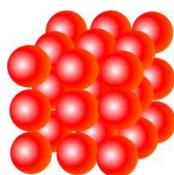
Solids have lower entropies than liquids which are lower than gases.

At 0K substances have no entropy as there is no disorder

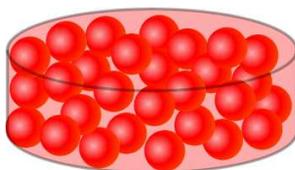
When a solid increases in Temperature its entropy increases as the particles vibrate more



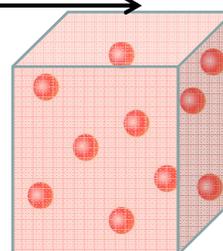
Increasing entropy (disorder) →



solid



liquid



gas

Which has the highest entropy ?

- Cl_2 (g) or HCl (g)
- HCl (g) or HCl (aq)
- ice or steam
- ZnO or ZnCO_3

Entropy Change in Reactions

There is a tendency for entropy to increase in chemical reactions.

Entropy change is shown by the symbol ΔS .

ΔS is positive when entropy increases, signifying an **increase in disorder** in a reaction

There will be a significant increase in the entropy change of the system if there is:

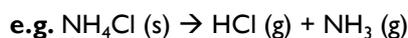
- a **change of state** from solid or liquid to gas
- increase **in the number of moles of substance** between products and reactants.

Predicting ΔS^\ominus

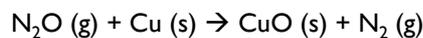
Balanced chemical equations can often be used to predict if ΔS^\ominus is positive or negative.

There will be a significant increase in the entropy change of the system if there is:

- a **change of state** from solid or liquid to gas
- increase **in the number of moles of substance** between products and reactants.



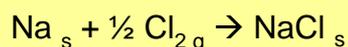
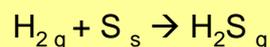
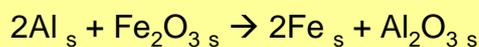
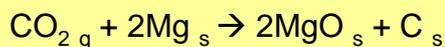
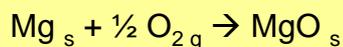
$\Delta S^\ominus = +\text{ve}$ [change from **solid** reactant to **gaseous** products; **increase in number of molecules**: both will increase disorder]



$\Delta S^\ominus = \text{little change}$ [1 gaseous reactant and 1 solid reactant going to 1 gaseous product and 1 solid product]

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Predict the sign for ΔS for these reactions



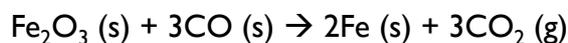
Calculating ΔS°

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.

N.B. Elements in their standard states do *not* have zero entropy. **Only perfect crystals at absolute zero ($T = 0 \text{ K}$) will have zero entropy**

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

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



$$\begin{aligned} \Delta S^\circ &= \Sigma S^\circ_{\text{products}} - \Sigma S^\circ_{\text{reactants}} \\ &= (3 \times 213.6 + 2 \times 27.3) - (1 \times 87.4 + 3 \times 197.6) \\ &= +15.2 \text{ J K}^{-1} \text{ mol}^{-1} = \underline{+15.2 \text{ J K}^{-1} \text{ mol}^{-1}} \text{ (3 S.F.)} \end{aligned}$$

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Gibbs Free Energy Change, ΔG

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

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

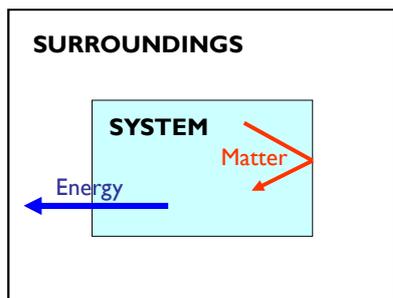
For a spontaneous change, ΔG will be negative.

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Linking ΔH to ΔG

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

EXOTHERMIC REACTION

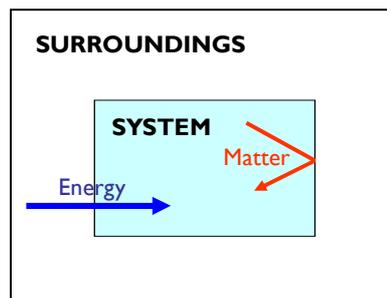


Energy transferred **TO** surroundings

$$\Delta H^\circ = -ve$$

More likely to make ΔG -ve

ENDOTHERMIC REACTION



Energy transferred **FROM** surroundings

$$\Delta H^\circ = +ve$$

More likely to make ΔG +ve

Calculating ΔG

Convert from $^\circ\text{C}$
to **K (+ 273)**

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

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

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

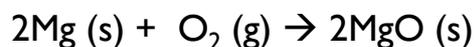
Units: **KJ mol^{-1}**

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

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Example 1

Calculate ΔG for the following reaction at 25°C:



1. Calculate ΔS

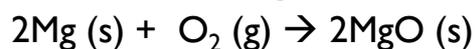
$$\begin{aligned}\Delta S^\circ &= \Sigma S^\circ_{\text{products}} - \Sigma S^\circ_{\text{reactants}} \\ &= (2 \times 26.9) - (2 \times 32.7 + 205) \\ &= -216.6 \text{ J K}^{-1} \text{ mol}^{-1} = \underline{\underline{-217 \text{ J K}^{-1} \text{ mol}^{-1}}} \text{ (3 S.F.)}\end{aligned}$$

2. Calculate $\Delta H^\circ_{\text{reaction}}$

$$\begin{aligned}\Delta H^\circ_r &= \Sigma \Delta H^\circ_f [\text{products}] - \Sigma \Delta H^\circ_f [\text{reactants}] \\ &= -601.7 \times 2 - 0 = \underline{\underline{-1203.4 \text{ kJ mol}^{-1}}}\end{aligned}$$

Example 1

Calculate ΔG for the following reaction at 25°C:



3. Put numbers into ΔG equation

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

$$\begin{aligned}\Delta G &= -1203.4 - [298 \times (-216.6/1000)] \\ &= \underline{\underline{-1139 \text{ KJ mol}^{-1}}}\end{aligned}$$

Would this reaction proceed spontaneously at 25°C?

Yes, because ΔG is negative

Example 2

Calculate ΔG for the following reaction at 25°C:



1. Calculate ΔS

$$\begin{aligned} \Delta S^\circ &= \sum S^\circ_{\text{products}} - \sum S^\circ_{\text{reactants}} \\ &= (192.3 + 186.8) - (94.6) \\ &= +284.5 \text{ J K}^{-1} \text{ mol}^{-1} = \underline{\underline{+285 \text{ J K}^{-1} \text{ mol}^{-1}}} \text{ (3 S.F.)} \end{aligned}$$

2. Calculate $\Delta H^\circ_{\text{reaction}}$

$$\begin{aligned} \Delta H^\circ_r &= \sum \Delta H^\circ_f [\text{products}] - \sum \Delta H^\circ_f [\text{reactants}] \\ &= -46.2 - 92.3 - (-315.0) = \underline{\underline{+176.5 \text{ kJ mol}^{-1}}} \end{aligned}$$

Example 2

Calculate ΔG for the following reaction at 25°C:



3. Put numbers into ΔG equation

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

$$\begin{aligned} \Delta G &= +176.5 - [298 \times (285/1000)] \\ &= \underline{\underline{+91.6 \text{ kJ mol}^{-1}}} \end{aligned}$$

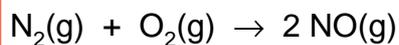
Would this reaction proceed spontaneously at 25°C?

No, because ΔG is positive

Would the reaction become more feasible at higher temperatures?

Calculating the temperature a reaction will become feasible

Calculate the temperature range that this reaction will be feasible



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

The reaction will be feasible when $\Delta G \leq 0$

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

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

$$T\Delta S = \Delta H$$

$$T = \Delta H / \Delta S$$

$$T = 180 / (25/1000)$$

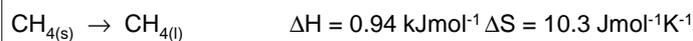
$$= 7200\text{K}$$

The T must be $>7200\text{K}$

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?



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

As $\Delta G = 0$

$$T\Delta S = \Delta H$$

$$T = \Delta H / \Delta S$$

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

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

In conclusion

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

ΔG must be $-ve$ for a reaction to occur

ΔG will be more likely to be $-ve$ if the reaction is exothermic ($\Delta H -ve$) and if ΔS is positive.

ΔS will be positive in reactions where more moles of products are made than there were reactants and/or if solids change to liquids or gases

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Effect of Temperature on feasibility

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

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

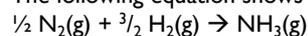
If the reaction involves an increase in entropy (ΔS is **+ve**) then increasing Temperature will make it more likely that ΔG is **negative and more likely that the reaction occurs** e.g. $\text{NaCl} + \text{aq} \rightarrow \text{Na}^+_{(\text{aq})} + \text{Cl}^-_{(\text{aq})}$

If the reaction involves a decrease in entropy (ΔS is **-ve**) then increasing Temperature will make it more **less likely that ΔG 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 ΔS **close to zero** then temperature will not have a large effect on the feasibility of the reaction as $-T\Delta S$ **will be small** and ΔG **won't change much** e.g. $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}(\text{g})$

Effect of changing Temperature

The following equation shows the formation of ammonia.

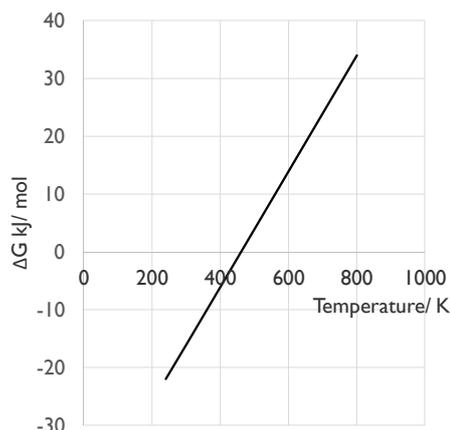


The graph shows how the free-energy change for this reaction varies with temperature above 240 K.

a) The gradient of this slope represents what thermodynamic quantity?

b) Why does ΔG **increase** as the temperature increase?

The line is not drawn below a temperature of 240 K because its slope (gradient) changes at this point. Suggest what happens to the ammonia at 240 K that causes the slope of the line to change.



Problems for discussion

1. The evaporation of water takes place spontaneously at room temperature. This process absorbs heat. Why then does this take place and under what conditions would this be reversed?
2. Explain why it is that most reactions which take place readily at room temperature are exothermic whilst endothermic reactions are favoured at temperatures of about 3000 °C

Problems for discussion

3. Explain why the denser form of an element which exhibits allotropy is expected to have the smaller heat of combustion

4. Why does the solubility of potassium chlorate in water increase with increasing temperature?

5. Why do gases get less soluble as temperature increases?