

Entropy

All the energy changes we have considered so far have been in terms of enthalpy, and we have been able to predict whether a reaction is likely to occur on the basis of the enthalpy change associated with it. A reaction in which the overall enthalpy change is negative (exothermic) results in more stable products with stronger bonds, and hence is more likely to proceed.

However, we also know that endothermic reactions do happen spontaneously even though they are energetically unfavourable in terms of enthalpy change. We need an explanation for this: we need another energy-related change as well – entropy.

Entropy is the quantitative measure of the **dispersal of energy** in a system.

The symbol used for entropy is **S**. Units are **J K⁻¹ mol⁻¹**

The more disordered a system is, the more different ways in which the energy is dispersed, and the more energetically stable it is.

The idea of dispersal of energy is not immediately obvious, but it is the natural tendency of systems: a gas spreading through a room (diffusion); heat from a fire spreading through a room; ice melting in a warm room. There is always a tendency for energy to spread out and not localised in one place. Entropy refers to the dispersal of energy within the substances making up a chemical system. It can be useful to think of entropy in terms of degree of disorder or randomness.

A perfectly ordered crystal lattice at absolute zero (0K) would have entropy of zero. In reality all substances possess some entropy.

1) The entropy of a pure substance increases with increasing temperature. This is because as we increase temperature the particles vibrate more, making their relative positions a more disordered and random.

It follows that larger molecules, having more bonds to vibrate, have higher entropies than smaller molecules at the same temperature, as there are more different ways for the energy to be dispersed.

2) Entropy also increases during changes of state from solid to liquid (melting) or as a solid lattice dissolves (solution) as the particles are now able to move about within the liquid, becoming even more disordered than they were in the regular solid structure. Energy is dispersed as kinetic as well as vibrational energy.

3) Entropy increases again when a liquid turns into a gas as the particles become able to travel outside the volume originally occupied by the liquid, becoming even more disordered.

4) Entropy increases when a reaction produces more moles of gaseous products than there were moles of gaseous reactants. More molecules means more ways in which the energy can be dispersed between them.

Thus

- entropy is always a positive number
- the more localised or concentrated the energy (the more restricted the particles are in what they can do), the lower the entropy
- the more ways the energy can be dispersed within a system, the higher its entropy

Standard Entropies

The **standard entropy** of a substance, S^\ominus , is the entropy content of one mole of that substance under standard conditions of 298K and 101kPa.

Entropy changes

The energetically favoured direction for entropy changes (ΔS) is for entropy to increase, this corresponds to a more energetically stable situation. [This explains why some ionic substances such as NaCl dissolve in water even though the enthalpy change of solution is endothermic \(\$\Delta H_s = +25 \text{ kJ mol}^{-1}\$ \).](#)

The standard entropy change when a reaction takes place can be calculated using the standard entropies of the reactants and the products:

$$\Delta S^\ominus = \sum S^\ominus_{\text{products}} - \sum S^\ominus_{\text{reactants}}$$

Example:	Substance	$S^\ominus \text{ (J K}^{-1}\text{mol}^{-1}\text{)}$
	O_{3(g)}	+ 237.7
	O_{2(g)}	+ 204.9

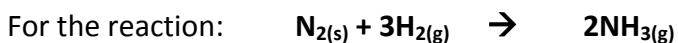
For the reaction: $2\text{O}_3 \rightarrow 3\text{O}_2$

$$\Delta S^\ominus = (3 \times 204.9) - (2 \times 237.7) = +139.3 \text{ J K}^{-1}\text{mol}^{-1}$$

This sign of ΔS here is expected, as three moles of gas are formed from two. The increase in entropy favours this reaction taking place, but we'd also have to consider the enthalpy change for the reaction to predict whether the reaction would be feasible.

The standard entropies of oxygen and ozone are also as expected – ozone has more bonds than oxygen, so more vibrations.

Example:	Substance	S^\ominus ($\text{J K}^{-1}\text{mol}^{-1}$)
	$\text{N}_{2(\text{g})}$	+ 192
	$\text{H}_{2(\text{g})}$	+ 131
	$\text{NH}_{3(\text{g})}$	+ 193



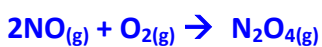
$$\Delta S^\ominus = (2 \times 193) - (192 + (3 \times 131)) = -199 \text{ J K}^{-1}\text{mol}^{-1}$$

So this reaction results in a decrease in entropy, which does not favour the reaction taking place. We'd expect this because we've fewer moles of gas as a result of the reaction, so a more ordered system. We'd have to consider the enthalpy change for the reaction as well before we could say anything about whether the reaction is feasible in practice.

Practice

Calculate the standard enthalpy changes of the following reactions:

Substance	substance	S^\ominus ($\text{J K}^{-1}\text{mol}^{-1}$)
	$\text{NO}_{(\text{g})}$	+ 211
	$\text{O}_{2(\text{g})}$	+205
	$\text{N}_2\text{O}_{4(\text{g})}$	+304
	$\text{C}_6\text{H}_{6(\text{l})}$	+173
	$\text{CO}_{2(\text{g})}$	+214
	$\text{H}_2\text{O}_{(\text{l})}$	+70



$$\Delta S = 304 - (2 \times 211 + 205) = -323 \text{ J K}^{-1}\text{mol}^{-1}$$



$$\Delta S = ((6 \times 214) + (3 \times 70)) - (173 + (7.5 \times 205)) = 1494 - 1710.5 = -216.5 \text{ J K}^{-1}\text{mol}^{-1}$$

Using ΔH and ΔS together

We want to know whether a reaction is feasible, in other words whether it will happen spontaneously. A reaction is spontaneous if a chemical system becomes more stable and its overall energy decreases. The overall energy decrease results from contributions from both enthalpy and entropy.

- We know that when enthalpy decreases (ΔH is negative) a reaction is favoured because the products become more stable than the reactants were.
- We know that when the entropy increases (ΔS is positive) a reaction is favoured because the amount of disorder in the system is increased.

We can conclude that:

- If ΔH is negative AND ΔS is positive, the reaction will always be feasible.
- If ΔH is positive and ΔS is negative, the reaction will never be feasible.

But what if the entropy change favours the reaction but the enthalpy change doesn't, or vice versa?

In these latter two cases we need a way of comparing the effect of entropy and enthalpy, and the way to do this was developed by J.W. Gibbs. Gibbs recognised that the effect of entropy is small at low temperatures, but much larger at high temperatures

He defined a quantity $\Delta G = \Delta H - T\Delta S$

Where T = temp. in K

ΔS = entropy change in $\text{JK}^{-1}\text{mol}^{-1}$

ΔG has units of Jmol^{-1}

ΔH = enthalpy change in Jmol^{-1}

Note: we can also work with ΔS and ΔH in $\text{kJK}^{-1}\text{mol}^{-1}$ and kJmol^{-1} respectively (ΔG will have units of kJmol^{-1}), but the energy must be in THE SAME units for ΔS and ΔH whether we use J or kJ.

The value ΔG is the (Gibbs) **free energy**. A process can take place spontaneously when its ΔG is less than 0, i.e. **when ΔG is negative**.

- If ΔH is positive and ΔS is positive as well, this is an endothermic reaction, but one in which the system becomes more disordered. For the reaction to be feasible ΔG must be negative, so the value of $T\Delta S$ must be larger than the value of ΔH . The reaction will be feasible when T is large, i.e. ABOVE a certain temperature.
- If ΔH is negative and ΔS is negative as well, the reaction may be feasible. This is an exothermic reaction, but resulting in an ordered system. For ΔG to be negative, the value of $T\Delta S$ must be smaller than the value of ΔH . This will be the case at low temperatures – the reaction will be feasible BELOW a certain temperature.

TEMPERATURE CONVERSIONS:

$$^{\circ}\text{C} = \text{K} - 273$$

$$\text{K} = ^{\circ}\text{C} + 273$$

Examples

We can use these ideas to explain why some processes occur as they do.

When ice melts, the enthalpy change associated with breaking the hydrogen bonds in the molecular lattice, $\text{H}_2\text{O}_{(s)} \rightarrow \text{H}_2\text{O}_{(l)}$ $\Delta H = +6.01 \text{ kJ mol}^{-1} = 6010 \text{ J mol}^{-1}$

The standard entropy of ice $S^{\ominus} = +48.00 \text{ J K}^{-1}\text{mol}^{-1}$

The standard entropy of water $S^{\ominus} = +70.05 \text{ J K}^{-1}\text{mol}^{-1}$

So the entropy change on melting ice $\Delta S^{\ominus} = 70.05 - 48.00 = +22.05 \text{ J K}^{-1}\text{mol}^{-1}$

Lets consider what happens at -5°C ($= 268\text{K}$):

$$\Delta G = \Delta H - T\Delta S = 6010 - (268 \times 22.05) = 6010 - 5909.4 = +100.6 \text{ J mol}^{-1}$$

melting of ice is not a process which happens spontaneously at -5°C

Now consider what happens at $+5^{\circ}\text{C}$ ($= 278\text{K}$)

$$\Delta G = \Delta H - T\Delta S = 6010 - (278 \times 22.05) = 6010 - 6129.9 = -119.9 \text{ J mol}^{-1}$$

melting of ice is spontaneous at $+5^{\circ}\text{C}$.

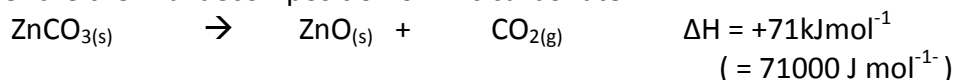
We can go further and say that the process of melting ice becomes feasible when ΔG stops being positive and becomes negative, i.e. at $\Delta G = 0$

$$\Delta G = 0 \text{ when } \Delta H = T\Delta S \quad 6010 = T \times 22.05$$

$$\Rightarrow T = 273\text{K} \text{ (to 3 sf) i.e. } 0^{\circ}\text{C}$$

While this was a change of state, the same thinking can be applied to reactions. Thermal decompositions are endothermic reactions – heating is required - so for them to be feasible at any temperature we know that the enthalpy change will have to be positive.

Consider the thermal decomposition of zinc carbonate



We can see why the entropy change is going to be positive – a gas is being formed, so the products will be more disordered than the solid lattice we started with. The reaction will be feasible ABOVE a certain temperature.

Using the published standard entropies, we can calculate ΔS , and we should then be able to use this to work out the temperature above which the zinc carbonate will thermally decompose.

substance	$S^{\circ} \text{ J K}^{-1}\text{mol}^{-1}$
zinc carbonate	+82
zinc oxide	+44
carbon dioxide	+214

$$\Delta S = (214 + 44) - 82 = 176 \text{ J K}^{-1}\text{mol}^{-1}$$

At room temperature, 298K, the value of ΔG

$$= 71000 - (298 \times 176)$$

$$= +18552 \text{ J mol}^{-1}$$

Clearly ZnCO_3 will not decompose at room temperature because ΔG is positive.

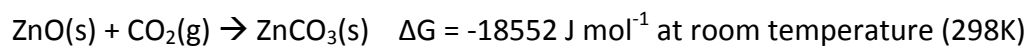
The reaction becomes feasible when $\Delta G = 0$ so $\Delta H = T\Delta S$

$$71000 = T \times 176 \quad \text{so} \quad T = 71000/176 = 403.4\text{K}$$

Converting to $^{\circ}\text{C}$ $T = 403.4 - 273 = 130.4^{\circ}\text{C}$

Reversing a reaction

If the sign of ΔG is positive for the forward reaction, then it is negative (with the same numerical value) for the reverse reaction.



This is feasible. If we leave zinc oxide lying around it may well absorb carbon dioxide from the air, reacting with it to form zinc carbonate.

Summary: If a reaction is not feasible below a certain temperature, the reverse reaction will be feasible below that temperature.

Predictions using free energy

The value of ΔG is useful for predicting the feasibility of reactions, and reactions for which ΔG is positive do not take place. In reality, some reactions have a negative ΔG and still do not appear to take place.

This is because we have considered the energy changes (thermodynamics) but not the kinetics. We have not considered **activation energies** or the **rate of reaction**. If the activation energy is very high, the rate of reaction will be very low (Arrhenius equation). If such reactions were left long enough they would happen, but would be described as not happening over an observable timescale.