



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

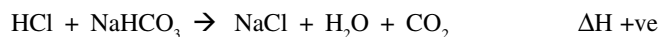
The study of Free Energy and Entropy is concerned with the factors which make reactions occur *spontaneously* – this means they occur without having to input energy *but it does not mean they are necessarily fast*.

Consider the following two reactions:

1. Some dilute hydrochloric acid is added to magnesium ribbon. There is some effervescence as hydrogen is given off and the reaction vessel gets quite warm.



2. Some dilute hydrochloric acid is added to sodium hydrogencarbonate. There is again some effervescence but this time the temperature of the reaction vessel decreases.



Both reactions are spontaneous but while one reaction gives out heat the other takes heat in.

To explain why some reactions are spontaneous even though they have a positive enthalpy change we need to take into account another factor called *entropy*.

Entropy

Entropy is often thought of as being a measure of the *disorder* of a system. For example, a gas in which the molecules are moving more or less completely freely and randomly throughout the system has a high degree of disorder. On the other hand a regular crystal, such as sodium chloride in which all the particles are vibrating about fixed positions, is highly ordered. Systems which have a high degree of disorder are said to have a high entropy; systems which are highly ordered (or have a low degree of disorder) are said to have a low entropy.

Entropy is measured in $\text{J K}^{-1} \text{mol}^{-1}$ and is given the symbol S . A *change* in entropy is given the symbol ΔS . Entropy change which is measured under standard conditions is referred to as *standard entropy change* and is given the symbol ΔS^\ominus . Entropies change with temperature and so the temperature at which they are measured must be specified.

Table 1. Some Examples of Entropy Values

Increasing entropy 	C(diamond)	+5.7 $\text{J K}^{-1} \text{mol}^{-1}$	A relative small value because it is a regular crystalline solid
	H ₂ O(l)	+69.9 $\text{J K}^{-1} \text{mol}^{-1}$	A liquid so it has a higher entropy
	Ne(g)	+146.2 $\text{J K}^{-1} \text{mol}^{-1}$	A gas and so is highly disordered. It has a relatively high entropy

The standard entropies of elements and many compounds can be found in data books.

Calculating Standard Entropy Changes, ΔS^\ominus from Standard Entropies, S^\ominus

Entropy changes for reactions can be calculated in the same way as enthalpy changes. The entropy change for a reaction is the difference between the total (Σ) entropies of the products and the total entropies of the reactants.

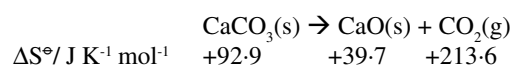
$$\text{i.e.} \quad \Delta S^\ominus = \Sigma S^\ominus_{\text{products}} - \Sigma S^\ominus_{\text{reactants}}$$

Example 1. Calculate the standard entropy change for the following reaction using the given standard entropies:



$$S^\ominus \text{ (298 K) / J K}^{-1} \text{ mol}^{-1}$$

CaCO ₃ (s)	92.9
CaO(s)	39.7
CO ₂ (g)	213.6



$$+92.9 \quad +39.7 \quad +213.6$$

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

$$\Delta S = (39.7 + 213.6) - 92.9 = +160.4 \text{ J K}^{-1} \text{ mol}^{-1}$$

Free Energy

Entropy (in the universe as a whole) tends to *increase*. However, this does not mean that there must be an increase in entropy in any given reaction. A reaction can show a decrease in entropy provided that the surroundings show an appropriate increase in entropy. Entropy and enthalpy by themselves do not help us to decide whether a reaction is spontaneous or not.

A better indication of the feasibility of a reaction is the *free energy change*, ΔG . ΔG is related to the enthalpy change *and* the entropy change in a reaction by the following equation.

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

Free energy change
Enthalpy change
Temperature
Entropy change

The change in free energy does enable us to say whether a reaction is or is not spontaneous:

If the free energy change for a reaction is negative, the reaction is spontaneous.

If the free energy change for a reaction is positive, the reaction is not spontaneous.

For example,



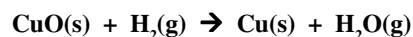
Not spontaneous at 298K because ΔG is positive.



Spontaneous at 298K because ΔG is negative.

As seen above, free energy is usually measured, like enthalpy, in kJ mol^{-1} . This means you must remember to convert S values from $\text{J mol}^{-1} \text{K}^{-1}$ to $\text{kJ mol}^{-1} \text{K}^{-1}$ by dividing by 1000.

Example 2 Calculate the standard free energy change for the following reaction at 500 K and hence determine whether the reaction is spontaneous at 500K:



	$\Delta H_f^\circ / \text{kJ mol}^{-1}$	$S^\circ / \text{J mol}^{-1} \text{K}^{-1}$
CuO(s)	-155	+44
H ₂ (g)	0	+131
Cu(s)	0	+33
H ₂ O(g)	-242	+189

Solution

- Calculate the enthalpy change for the reaction using the given data

$$\begin{aligned} \Delta H_f^\circ &= \sum \Delta H_f^\circ \text{ f, prods} - \sum \Delta H_f^\circ \text{ f, reactants} \\ &= (0 + (-242)) - ((-155) - 0) \\ &= -87 \text{ kJ mol}^{-1} \end{aligned}$$

- Calculate the entropy change for the reaction using the given data

$$\begin{aligned} \Delta S^\circ &= \sum S^\circ \text{ prods} - \sum S^\circ \text{ reactants} \\ &= (33 + 189) - (44 + 131) \\ &= 47 \text{ J K}^{-1} \text{ mol}^{-1} \\ &= 0.047 \text{ kJ K}^{-1} \text{ mol}^{-1} \end{aligned}$$

- Use the enthalpy and entropy changes calculated in 1. and 2. and the equation for free energy to find ΔG at 500K.

$$\begin{aligned} \Delta G^\circ &= \Delta H^\circ - T\Delta S \\ &= -87 - 500 \times 47/1000 \\ &= -110.5 \text{ kJ mol}^{-1} \end{aligned}$$

ΔG is negative therefore the reaction is spontaneous.

Free Energy Changes and Temperature

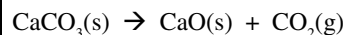
By changing the temperature at which a reaction is carried out it is sometimes possible to change the factor $T\Delta S$ to such an extent that the feasibility of a reaction is changed.

Example 3

(a) Is the following reaction spontaneous at 25°C?

(b) Is it spontaneous at 1000°C?

(c) What is the temperature at which it becomes spontaneous?



$$\Delta S^\circ = +165 \text{ J mol}^{-1} \text{K}^{-1}$$

$$\Delta H^\circ = +178 \text{ kJ mol}^{-1}$$

Solution

(a) At 25°C,

$$\begin{aligned} \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= 178 - 298 \times 165/1000 \\ &= +128.8 \text{ kJ mol}^{-1} \end{aligned}$$

This value for ΔG is positive and so the reaction is not spontaneous at 25°C

(b) At 1000°C

$$\begin{aligned} \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= 178 - 1273 \times 165/1000 \\ &= -32 \text{ kJ mol}^{-1} \end{aligned}$$

This value for ΔG is negative and so the reaction is spontaneous at 1000°C

(c) To find the temperature at which the reaction becomes spontaneous we find the temperature at which the value of ΔG is changing from positive to negative, i.e. $\Delta G = 0$

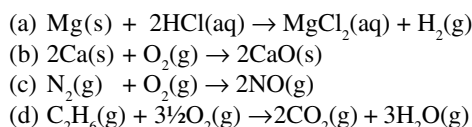
$$\begin{aligned} \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ 0 &= 178 - T \times \frac{165}{1000} \\ T &= 178 \times \frac{1000}{165} \quad (\text{rearranging the equation to give } T) \\ &= 1079 \text{ K} \end{aligned}$$

i.e. The reaction becomes spontaneous at temperatures above 1079K (806°C)

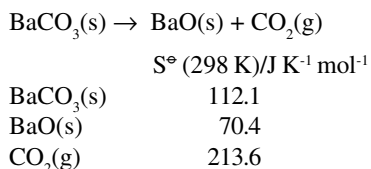
In other words calcium carbonate does not decompose at room temperature but if it is heated to a temperature above 1079 K then it does decompose. This, of course, agrees with what we know about the stability of calcium carbonate.

Practice Questions

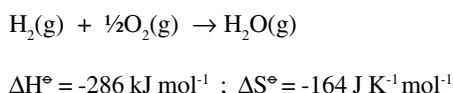
1. Would you expect that the entropy change for the following reactions is positive, negative or approximately zero?



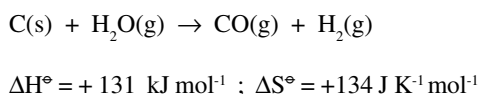
2. Calculate the standard entropy change for the following reaction:



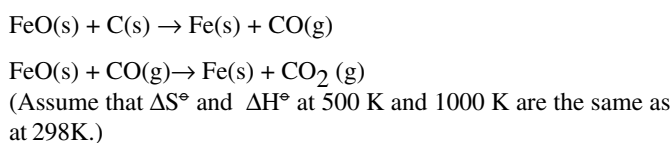
3. Calculate the free energy change for the following reaction at 298 K:



4. Decide whether the following reaction is spontaneous at 25°C. If it is spontaneous, decide at what temperature it would cease to be spontaneous. If it is not spontaneous, decide at what temperature it would become spontaneous.



5. Calculate the free energy change at 500K and 1000K for each of the following reactions:



	FeO(s)	Fe(s)	C (s)	CO(g)	CO ₂ (g)
$\Delta H^\ominus/\text{kJ mol}^{-1}$	-271.9	0	0	-110.5	-393.5
$\Delta S^\ominus/\text{J K}^{-1} \text{ mol}^{-1}$	57.5	27.3	5.7	197.6	213.6

Which of the reactions is spontaneous at 500 K? Which is spontaneous at 1000 K? How does the sign of ΔS^\ominus affect the way in which feasibility changes with temperature?

If the sign of ΔS^\ominus is negative then increasing the temperature makes the reaction less spontaneous because $-T\Delta S^\ominus$, and hence ΔG^\ominus , becomes more positive.

If the sign of ΔS^\ominus is positive then increasing the temperature makes the reaction more spontaneous because $-T\Delta S^\ominus$, and hence ΔG^\ominus , becomes more negative.

5. At 500 K the first reaction is not spontaneous ($\Delta G^\ominus = +81.1 \text{ kJ mol}^{-1}$). At 1000 K the first reaction is spontaneous ($\Delta G^\ominus = -5 \text{ kJ mol}^{-1}$). At 1000 K the second reaction is not spontaneous ($\Delta G^\ominus = +4.1 \text{ kJ mol}^{-1}$).

4. The reaction is not spontaneous at 25°C. The reaction becomes spontaneous at temperatures above 978 K.

3. -237 kJ mol^{-1}

2. $172 \text{ J K}^{-1} \text{ mol}^{-1}$

- (d) positive because $\frac{1}{2}$ moles of disordered gases produce 5 moles of equally disordered gases.

- (c) approximately zero because 2 moles of disordered gases produce 2 moles of equally disordered gases.

- (b) negative because a highly disordered gas is consumed

1. (a) positive because a highly disordered gas is produced

Answers

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