

ENTROPY AND FREE ENERGY

Is the state of a chemical system such that a rearrangement of its atoms and its molecules would decrease the energy of the system?

Yes, a system that is favoured to react, i.e. a product-favoured system is likely to be exothermic, such a system is often referred to as a *spontaneous* reaction; in general product favoured reactions are exothermic. A spontaneous change is a change that happens naturally; it tends to occur without any external influence. Hence, exothermic reactions occur spontaneously because they involve a **decrease** in the enthalpy of the system. The reverse of a spontaneous process is **nonspontaneous** and takes place only in the presence of some external influence.

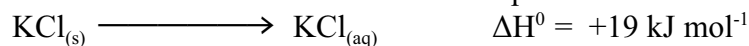
(Note: a process that is spontaneous in one direction is not spontaneous in the other.)

But many spontaneous reactions or processes are endothermic or even have $\Delta H = 0$. Why do these spontaneous reactions occur, since they happen spontaneously with an **increase** in the enthalpy of the system?

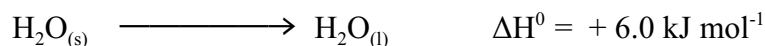
Examples:

a) diffusion of a gas,

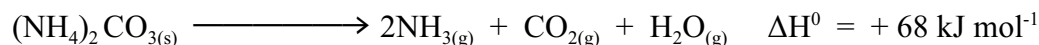
b) dissolution of some ionic solids is an endothermic process:



c) melting of ice



d) sublimation of some solids:



What is the additional factor to the enthalpy change that enables some endothermic reactions to occur spontaneously?

What are the conditions that decide whether a change can occur spontaneously?

A common property of product-favoured processes is **ENTROPY**, (symbol *S*), a *state function* - the final state is more disordered or random than the original. The extent of disorder of a system is measured by the quantity called entropy: it is related to the number of ways of arranging the molecules (or atoms or ions) in a system, or more accurately the number of ways that the energy can be arranged between molecules.

Low entropy means little disorder, high entropy means a high degree of disorder. Natural changes tend to increase the degree of disorder of matter and of energy.

This observation is embodied in the **Second Law of Thermodynamics**, which states that **the total entropy of the universe is continually increasing**. Whenever anything happens, matter, energy, or both become more dispersed or disordered. This means that a **product-favored reaction is accompanied by an increase in the entropy of the universe; $\Delta S_{\text{universe}}$ is positive.**

The direction of all natural events is toward disorder – that is why entropy is sometimes referred to as "time's arrow." (Enrico Fermi)

(Another way of expressing the second Law of thermodynamics: things are getting more screwed up every day, or another way of stating it is: You can't break even. either!!!)

[The mathematical relationship is given by:

$$\text{Entropy, } S = k \ln W$$

where S is entropy, W is the number of ways of arranging both the molecules and energy quanta in a system, (or the number of ways a change can occur, i.e. the number of ways of achieving a physical or chemical change, or simply the probability of that situation arising), and k is a constant called the **Boltzmann Constant**, ($1.38 \times 10^{-23} \text{ J K}^{-1}$), and for any change in the system:

$$\Delta S = k \Delta \ln W$$

where ΔS is the entropy change and $\Delta \ln W$ is the change in the log (to the base e) of the number of ways of arranging the molecules in the system brought about by the change in the system. As $\ln W$ is a pure number with no units, the units of entropy are therefore the same as those of the Boltzmann's constant: J K^{-1} .

The changes that happen of their own accord are those with the greatest probability, i.e. the greatest number of ways, W , of happening. Thus, for all changes that happen spontaneously:

W must increase

But entropy, $S = k \ln W$, hence, for all spontaneous changes:

entropy must increase

or:

entropy change, ΔS , must be positive

At this point you ask yourself: "So what is entropy, really?" On a microscopic level, i.e. at the atomic or molecular level, entropy represents the number of possible ways the particles can be arranged – i.e. the statistical probability for disorder. Example: the larger a molecule, the more possible ways there are for its atoms to rotate and vibrate relative to each other, thus the greater is its entropy.]

The dispersal or disorder in a sample of matter can be measured with a calorimeter. When energy is transferred to matter in very small increments, so that the temperature change is very small, the entropy change can be calculated as:

$$\Delta S = \frac{q}{T} \quad \text{or} \quad \Delta S = \frac{\Delta H}{T}$$

q , the heat absorbed divided by the absolute temperature at which the change occurs.

This makes sense since heating up a system gives the system more quanta of energy, and thus an increase in the entropy of the system. Thus, the more heat (more quanta) we transfer the more ways the energy may be arranged and the more entropy will be gained, hence $\Delta S \propto \Delta H$.

If heat energy is given to a system at low temperature, then it will produce a large increase in entropy. Now, if the same heat energy is given to a system at high temperature, then the change in entropy is less significant. This is to say if we add a fixed amount of heat energy when T is large, the change in entropy, ΔS , is small, and if we add the same amount when T is small, then the change in entropy, ΔS , is large. Hence, the entropy change is inversely proportional to the temperature, i.e. $\Delta S \propto 1/T$

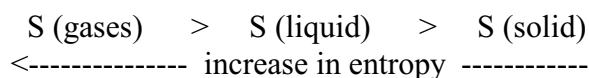
Measurement of entropy depends on the assumption that in a **perfect crystal at the absolute zero** of temperature, (0 K, or - 273.15 °C), all translational motion ceases and there is no disorder; this sets the zero of the entropy scale. Thus, a perfect crystal at temperature zero K has perfect order and zero entropy.

The table of **standard molar entropy, S^0** , values applies to one mole of each substance at the standard pressure of 100 kPa and 298 K, as for enthalpies; and are expressed in units of joules per kelvin per mole (**$\text{J K}^{-1} \text{mol}^{-1}$**).

[Take care with units: entropies are usually given in $\text{J K}^{-1} \text{mol}^{-1}$, where as enthalpies in kJ mol^{-1}]

When comparing the same or very similar substances, entropies of gases are much larger than those of liquids, which are larger than for solids. Gases have much higher entropies than liquids and solids at the same temperature, since gas particles have complete freedom of movement, and thus greater degree of disorder and hence the highest entropy.

In a solid the particles can only vibrate around lattice positions, a solid is an ordered 3-dimensional structure with low entropy. When a solid melts, its particles are freer to move around, and molar entropy increases. When a liquid vaporizes, restrictions due to forces between the particles nearly disappear, and another large increase in entropy occurs:



Example: $I_{2(s)} = 116.1 \text{ J K}^{-1} \text{ mol}^{-1}$, $Br_{2(l)} = 152.2 \text{ J K}^{-1} \text{ mol}^{-1}$, $Cl_{2(g)} = 223.0 \text{ J K}^{-1} \text{ mol}^{-1}$
 $S^0 H_2O_{(g)} = 188.8 \text{ J K}^{-1} \text{ mol}^{-1}$, $S^0 H_2O_{(l)} = 69.91 \text{ J K}^{-1} \text{ mol}^{-1}$, $S^0 H_2O_{(s)} = 48.0 \text{ J K}^{-1} \text{ mol}^{-1}$

Entropy of a substance increases with temperature. Heating increases the motion of particles and therefore the degree of disorder.

Increase in molecular complexity generally leads to increase in entropy:

Example: S^0 : CH_4 : $248.2 \text{ J K}^{-1} \text{ mol}^{-1}$, C_2H_6 : $336.1 \text{ J K}^{-1} \text{ mol}^{-1}$, C_3H_8 : $419.4 \text{ J K}^{-1} \text{ mol}^{-1}$

Entropies of more complex molecules are larger than those of simpler molecules, especially in a series of closely related compounds:

Example: Ar: $154.7 \text{ J K}^{-1} \text{ mol}^{-1}$ CO_2 : $213.7 \text{ J K}^{-1} \text{ mol}^{-1}$ $CH_3CH_2CH_3$: $269.9 \text{ J K}^{-1} \text{ mol}^{-1}$

Entropies of ionic solids become larger as the attractions among the ions become weaker. The weaker the forces between ions, the easier it is for the ions to vibrate about their lattice positions. Examples are $MgO_{(s)}$ and $NaF_{(s)}$ with entropies of 26.8 and $51.5 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively; the $2+$ and $2-$ charges on the magnesium ions and oxide ions result in greater attractive forces and hence lower entropy.

Entropy usually increases when a pure liquid or solid dissolves in a solvent. Matter usually becomes more dispersed or disordered when a substance dissolves and different kinds of molecules mix together.

Entropy increases when a dissolved gas escapes from a solution. Although gas molecules are dispersed among solvent molecules in solution, the very large entropy increase that occurs on changing from the liquid to the gas phase results in a higher entropy for separated gas and liquid than for the mixture.

For a **phase change** :

An increase in the entropy of a system accompanies a change of state, (vaporization or melting), allowing for greater freedom in movement of atoms, molecules, or, ions, a greater degree of disorder of the system.. When a solid melts or a liquid evaporates, the temperature of the system does not increase,; (although heat is being absorbed continuously from the surroundings), but the entropy increases because the particles have more freedom to move. On a molar basis, the entropy change for a phase change is given by:

$$\Delta S = \frac{\Delta H}{T} = \frac{\text{enthalpy change for change of state}}{\text{absolute temperature of the change of state}} = \frac{\text{J mol}^{-1}}{\text{K}}$$

Example: for $\text{H}_2\text{O}_{(l)} \longrightarrow \text{H}_2\text{O}_{(g)}$ $\Delta H = + 40.7 \text{ kJ mol}^{-1}$ at 100°C (373 K)

Hence: $\Delta S = \frac{\Delta H}{T} = + 109 \text{ J K}^{-1} \text{ mol}^{-1}$

CHANGES IN ENTROPY

Entropy can change in chemical reactions because of a change in the:

- 1) number of uncombined atoms, ion, or molecules in the system,
- 2) phase in which the species in the system are present, or
- 3) complexity of the substances involved.

To determine whether a reaction will be spontaneous, it is thus necessary to take into account both the change in enthalpy and the change in the disorder of a system.

Entropy is given the symbol S , standard entropy, S^θ , and change in entropy, ΔS :

$$\Delta S = S_{\text{final}} - S_{\text{initial}}$$

The previous generalizations can be used to predict whether there is an increase in disorder of the substances involved when reactants are converted to products. (Such predictions are much easier to make for entropy changes than for enthalpy changes.)

An increase in the degree of disorder of a system shows in a positive value of ΔS . Thus, an indication of reaction feasibility may be summarized as:

If ΔS is positive, the reaction can go

$\Delta S > 0$ for product favoured -reactions, spontaneous

$\Delta S = 0$ reversible reaction

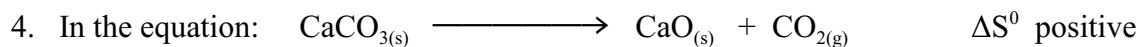
$\Delta S < 0$ impossible

It is often possible to tell whether a reaction has a positive or negative value of ΔS by an inspection of the equation:

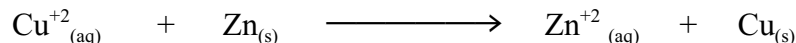
1. For the processes: $\text{H}_2\text{O}_{(s)} \longrightarrow \text{H}_2\text{O}_{(l)}$ and $\text{H}_2\text{O}_{(l)} \longrightarrow \text{H}_2\text{O}_{(g)}$, we expect an entropy increase in each case because water molecules in the solid are more ordered than in the liquid and much more ordered than in the gas.

2. The equation: $\text{NH}_4\text{NO}_{3(s)} \longrightarrow \text{N}_2\text{O}_{(g)} + 2 \text{H}_2\text{O}_{(g)}$ shows that 1 mole of the crystalline solid, ammonium nitrate, forms 1 mole of a gas, nitrogen(I)oxide, and 2 moles of water vapour, a total of 3 moles of gas. Thus, the value of ΔS is positive.

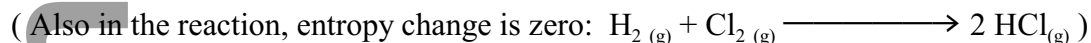
3. In the equation: $\text{CaO}_{(s)} + \text{H}_2\text{O}_{(l)} \longrightarrow \text{Ca(OH)}_{2(s)}$ ΔS^θ negative



In the following reaction, there is no change in the number of moles of substances, nor in the phases of the substances:



One mole of solid plus one mole of ions in solution have been converted to one mole of solid and one mole of ions in solution. For such reactions, it is difficult to predict whether entropy will increase or decrease. The best prediction here is that the entropy change will be small. In fact, it is -21.0 J K^{-1} .



If a process results in an increase in the entropy of a system, the reverse of that process causes an equal decrease in entropy. Entropy decreases when:

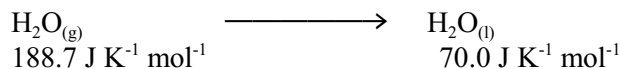
1. the temperature of a system becomes lower,
2. a gas condenses or a liquid freezes,
3. a gas is compressed into a smaller volume, or
4. a dissolved substance crystallizes out of solution.

CAN ENTROPY EVER DECREASE?

For spontaneous changes entropy, S , must always increase.

However, some spontaneous changes involving a decrease in entropy do take place!

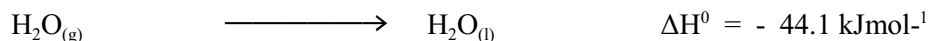
Example the spontaneous condensation of steam at room temperature to liquid water:



For this change, ΔS is negative — the entropy has decreased by $(188.7 - 70.0) = 118.7 \text{ JK}^{-1}\text{mol}^{-1}$

How can we account for this, considering that the entropy must always increase?

Let us look at the enthalpy change when water condenses:



When water condenses, where does this energy go?

If the water condenses on a glass surface, it goes to the glass. If it condenses as droplets in the air, it goes to the air molecules. The atoms in the glass, or the air molecules, or whatever — call them the **surroundings** — gain energy quanta and this increases the number of ways in which they can share energy. Thus, the entropy of the *surroundings increases*, whereas the entropy of the *water decreases*. Hence, there are two entropy changes to consider — the entropy change of the water, ΔS_{water} , and the entropy change of the surroundings, $\Delta S_{\text{surroundings}}$.

$$\Delta S_{\text{Total}} = \Delta S_{\text{water}} + \Delta S_{\text{surroundings}}$$

The positive $\Delta S_{\text{surroundings}}$ outweighs the negative ΔS_{water} , so ΔS_{Total} is positive and the total entropy increases. When the surroundings and the system are taken into account, ΔS is positive. The Second Law of Thermodynamics has not been broken at all !!!

ASSIGNMENT

- Would you predict an increase or a decrease in entropy for the following:
 - the evaporation of alcohol from an open bottle
 - making crystals
 - putting cream in your coffee
- Why is the value of S^0 for $\text{Cl}_{2(g)}$ greater than that for $\text{Br}_{2(l)}$?
- Choose the substance having the larger entropy at 25°C :
 - $\text{O}_{3(g)}$ or $\text{H}_2\text{O}_{(l)}$
 - $\text{HCl}_{(aq)}$ or $\text{HCl}_{(g)}$
 - $\text{H}_2\text{O}_{2(l)}$ or $\text{H}_2\text{O}_{(l)}$
 - $\text{H}_{(g)}$ or $\text{H}_{2(g)}$
- Gallium undergoes a solid–solid phase transformation at 275.6 K for $\Delta H_{275.6}^0 = 2100\text{ J mol}^{-1}$. Calculate ΔS^0 for this change.
- Calculate the standard state entropy change for the vaporization of one mole of argon at the normal boiling point. ΔH^0 (vaporization) = 6519 J mol^{-1} for Ar at 87.5 K . Is this an increase or decrease in entropy? (Answer: $\Delta S^0 = 74.5\text{ JK}^{-1}\text{mol}^{-1}$, increase)
- The normal boiling point of cesium is 690°C and the heat of vaporization is 68.28 kJ mol^{-1} . Calculate ΔS^0 for the condensation of cesium vapour. Is this an increase or decrease in entropy for the cesium? (Answer: $\Delta S^0 = -70.9\text{ JK}^{-1}\text{mol}^{-1}$, decrease)
- Predict whether the entropy change for each of the following reactions will be large and negative, large and positive, or small:
 - $2\text{ZnS}_{(s)} + 3\text{O}_{2(g)} \longrightarrow 2\text{ZnO}_{(s)} + 2\text{SO}_{2(g)}$
 - $\text{C}_{(\text{graphite})} + 2\text{H}_{2(g)} + 1/2\text{O}_{2(g)} \longrightarrow \text{CH}_3\text{OH}_{(l)}$
 - $3\text{NO}_{2(g)} + \text{H}_2\text{O}_{(l)} \longrightarrow 2\text{HNO}_{(aq)} + \text{NO}_{(g)}$

How about calculating ΔS for a reaction?

The standard entropy changes for chemical reactions can be calculated from known standard state entropies in two ways. In the first tabulated values for the absolute entropies of the reactants and products are used, in the same way as the calculation for a reaction using values of ΔH_f^0 :

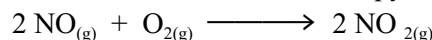
$$\Delta S^0(\text{reaction}) = \Sigma S^0(\text{products}) - \Sigma S^0(\text{reactants})$$

Example 1: $2\text{H}_{2(g)} + \text{O}_{2(g)} \longrightarrow 2\text{H}_2\text{O}_{(l)}$ (See Table 11 of the Data Book)

$$\Delta S^0 = \Sigma S^0(\text{products}) - \Sigma S^0(\text{reactants}) = -326.9\text{ J K}^{-1}$$

Note: there is a decrease in entropy, S , because 3 moles of gas produce 2 moles of liquid.

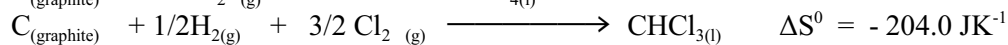
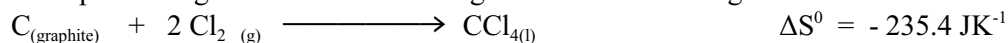
Example 2: Nitrogen dioxide is formed from nitrogen monoxide and oxygen in a product-favored reaction at 25°C . Determine the standard entropy change, ΔS^0 , for the reaction, ΔS^0_{rxn}



Answer: = -146.5 J/K or -73.25 J/K for the formation of 1 mol of NO_2 . Notice that the sign of the entropy change is negative. This is largely due to the fact that the chemical reaction began with 3 mol of gaseous reactants and ended with 2 mol of gaseous product.

The second method of determining the entropy change for a chemical reaction is the same as that used in Hess's Law calculations of enthalpy changes. Since, entropy changes, like enthalpy changes depend only on the initial and final states, and not on the sequence of changes that have taken place, hence, known entropy changes for other chemical reactions may be combined algebraically as for Hess's Law.

Example: Using ΔS^0 values at 25°C given for the following reactions:



find ΔS^0 for the reaction: $\text{CCl}_{4(l)} + \text{H}_{2(g)} \longrightarrow \text{CHCl}_{3(l)} + \text{HCl}_{(g)}$

Gibbs Free Energy

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

The natural direction of many physical and chemical changes is toward minimum energy or toward maximum entropy. When both the enthalpy change and the entropy change of a process are favourable, then the process clearly will be spontaneous. And when changes in both enthalpy and entropy are unfavourable, the process will be nonspontaneous. However, when these driving forces oppose each other, it is necessary to determine which predominates.

A new thermodynamic function, defined by J. Willard Gibbs (1839–1903), a professor at Yale University, combined these two criteria for spontaneity into a single function, called the Gibbs Free energy and is given the symbol G :

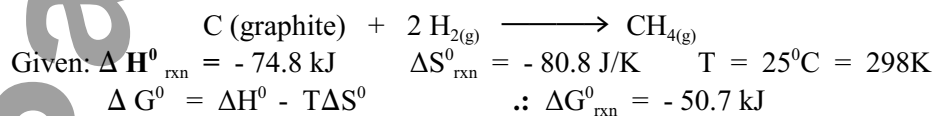
$$\text{Gibbs free energy change} = \text{total energy change for the system} - \text{energy lost in disordering the system}$$

The free energy change, ΔG , is the energy that is available, or free, to do useful work as the result of a chemical or physical change. Not all the energy transferred in a process can be harnessed for useful work because some is lost to the entropy change. (Chemists are more interested in studying chemical reactions than in harnessing energy for useful work such as driving steam engines.)

WHAT IS MEANT BY THE TERM "FREE" ENERGY?

Does it mean that we can get something for nothing?

No, the free energy change of a reaction is a measure of the *maximum magnitude of the net useful work* that can be obtained from a reaction. Consider the formation of methane:



The reaction is exothermic; it has an enthalpy change of -74.8 kJ . Part of this thermal energy, though, is used to bring order to the system (and so the entropy declines). The amount of thermal energy diverted to this is $T \Delta S^0 = 24.1 \text{ kJ}$. Therefore, only 50.7 kJ of energy is “free” or available for useful work.

ΔG tells us if a change is spontaneous or not since it relates a number to the change in entropy of the universe, to predict whether a chemical reaction is spontaneous at given values of T and P , it is necessary only to determine the sign of ΔG :

$\Delta G < 0$ spontaneous process, product-favoured reactions

$\Delta G = 0$ reversible processes, equilibrium reaction

$\Delta G > 0$ non-spontaneous processes

ΔG^0_f : is analogous to the standard molar enthalpy of formation, ΔH^0_f , and is defined as the change in Gibbs free energy for the reaction in which 1 mol of the compound is formed from its elements in their standard states.

$\Delta G^0_f = 0$ for an element that is in its standard state.

Free energy has units of energy, kilojoules, kJ , ΔG has the same units as ΔH : J mol^{-1} or kJ mol^{-1}

[Note: that free energy does not give an indication of kinetic stability or instability – i.e. to say no indication of the rate of a chemical reaction, do not assume that a thermodynamically spontaneous reaction occurs quickly.]

Because G is a state function, chemical equations can be added together, ΔG^0_f values combined in the same way as for enthalpy and entropy.

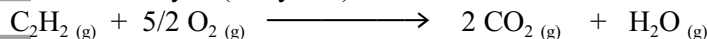
Two ways of calculating ΔG^0

- 1) determine ΔH^0 (rxn) and ΔS^0 (rxn) and then use Gibbs equation: $\Delta G^0 = \Delta H^0 - T\Delta S^0$
- 2) use tabulated values of the free energies of formation, ΔG_f^0 .

$$\Delta G^0 (\text{reaction}) = \Sigma \Delta G_f^0 (\text{products}) - \Sigma \Delta G_f^0 (\text{reactants})$$

Calculating ΔG^0 (reaction)

a) Combustion of ethyne (acetylene):



Use enthalpies of formation to calculate ΔH^0 (reaction) = -1238 kJ

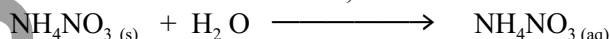
Use standard molar entropies to calculate ΔS^0 (reaction) = -97.4 J K⁻¹ = -0.0974 kJ K⁻¹

$$\Delta G^0 (\text{reaction}) = \Delta H^0 - T\Delta S^0 = -1238 \text{ kJ} - 298 \text{ K} (-0.0974 \text{ kJ K}^{-1}) = -1209 \text{ kJ}$$

Reaction is product-favoured in spite of negative ΔS^0 (reaction).

Reaction is therefore said to be “enthalpy driven”

b) Dissolution of ammonium nitrate;



From tables of thermodynamic data we find ΔH^0 (reaction) = +25.7 kJ

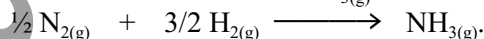
$$\Delta S^0 (\text{reaction}) = +108.7 \text{ JK}^{-1} = +0.1087 \text{ kJ K}^{-1}$$

$$\Delta G^0 (\text{reaction}) = \Delta H^0 - T\Delta S^0 = +25.7 \text{ kJ} - 298 \text{ K} (+0.1087 \text{ kJ K}^{-1}) = -6.7 \text{ kJ}$$

Reaction is product-favoured in spite of positive ΔH^0 (reaction).

Reaction is therefore said to be “entropy driven”

c) Using values of ΔH_f^0 and S^0 to find ΔH^0_{rxn} and ΔS^0_{rxn} , respectively, calculate the free energy change for the formation of 1 mol of $\text{NH}_3(\text{g})$ from the elements at standard conditions (and 25 °C):



Effect of Temperature on ΔG : $\Delta G^0 = \Delta H^0 - T\Delta S^0$

The value of ΔG^0 can depend strongly on T, because of the competition between ΔH^0 and $T\Delta S^0$ in the above equation.

If ΔH^0 is negative and ΔS^0 is positive, then the reaction is spontaneous at all temperatures.

If ΔH^0 is positive and ΔS^0 is negative, then the reaction is never spontaneous.

For the other possible combinations, there exists a special temperature T* defined by :

$$T^* = \frac{\Delta H^0}{\Delta S^0} \text{ at which } \Delta G^0 \text{ equals zero.}$$

If both ΔH^0 and ΔS^0 are positive, the reaction will be spontaneous at temperatures above T*

If both ΔH^0 and ΔS^0 are negative, the reaction will be spontaneous at temperatures below T*

Thus, with knowledge of ΔH^0 and ΔS^0 , the experimenter can manipulate conditions to make a reaction spontaneous. (See Table of Reaction Spontaneity)

ΔH^0	ΔS^0	ΔG^0	Reaction
exo (-)	increases (+)	-	product-favoured
endo(+)	decreases (-)	+	reactant-favoured
exo (-)	decreases (-)	?	T dependent
endo (+)	increases (+)	?	T dependent

Limitations of ΔG

There are many reactions for which ΔG is negative and which should therefore go spontaneously at room temperature, example combustion of fuels, however these reactions are observed not to happen spontaneously.

This is because they have a high activation energy, (see later notes on Kinetics), and until they are heated the reaction is infinitely slow.

Hence, ΔG values provide information only about the thermodynamic or energetic feasibility of a reaction and not about kinetic stability, the reaction rate is too slow. Activation energy, (this is independent of ΔG), provides information about kinetic stability of a reaction.

FREE ENERGY AND EQUILIBRIUM CONSTANTS

The free energy change, ΔG , indicates whether a reaction is likely to proceed spontaneously. However, there are other criteria that can be used to determine the spontaneity of a reaction.

The extent of a reaction can be determined by looking at its equilibrium constant. There is a simple relationship between the equilibrium constant, K , and ΔG° :

$$\Delta G^\circ = -RT \ln K$$

A **large -ive** ΔG° means that K for the reaction is a **large +ive** value, indicating that the reaction goes left to right. A **large +ive** ΔG° means that K for the reaction is a **very small** value, indicating that the reverse reaction is predominant.

If ΔG° is neither small nor large, more of an "equilibrium" situation exists.

FREE ENERGY AND ELECTRODE POTENTIALS

The potential of a cell is related to the change in free energy that accompanies the cell reaction:

$$\Delta G^\circ = -n F E^\circ$$

where: n is the number of moles of electrons transferred during the cell reaction;

F is the value of the Faraday constant (96 487 C),

E° is the emf in volts

Recall that for a spontaneous reaction the free energy decreases or ΔG is negative. Therefore E° must be positive, as we learned before.

These equations are given to you in the I.B. exam.

COMPARISON OF ΔG° , K AND E°

ΔG° (kJ mol ⁻¹)	K	E° (volts)	Extent of reaction
< - 60	> 10 ¹⁰	> + 0.6	reaction complete
0	1	0	reaction balanced between reactants and products
> + 60	< 10 ⁻¹⁰	< - 0.6	reaction 'doesn't go'

Note: A "complete" reaction has been defined arbitrarily as one for which $K > 10^{10}$, and a reaction which "doesn't go" as one with $K < 10^{-10}$. These figures correspond to ΔG° values of - 60 kJmol⁻¹ and + 60 kJ mol⁻¹, respectively.

Ludwig Boltzmann (1844–1906)

Ludwig Boltzmann was an Austrian mathematician and physicist who gave us a useful interpretation of entropy (and who also did much of the work on the kinetic theory of gases). Engraved on his tombstone in Vienna is his equation relating entropy and “chaos,”

$S = k \log W$ (where k is a fundamental constant of nature, now called Boltzmann’s constant).

Boltzmann said the symbol W was related to the number of ways that atoms or molecules can be arranged in a given state, always keeping their total energy fixed. His equation tells us, therefore, that if there are only a few ways to arrange the atoms of a substance— that is, if there are only a few places in which we can put our atoms or molecules — then the entropy is low. On the other hand, the entropy is high if there are many possible arrangements ($W \gg 1$), that is, if the level of chaos is high.

THERMODYNAMICS AND TIME

The **three laws of thermodynamics** are:

First law: The total energy of the universe is a constant.

Second law: The total entropy of the universe is always increasing.

Third law: The entropy of a pure, perfectly formed crystalline substance at absolute zero is zero.

Some cynic long ago paraphrased the first two laws into simpler statements. The first law is a statement that “You can’t win!”, and the second law tells you that “You can’t break even either!” Yet another interpretation of the second law is Murphy’s Law that “Things always tend to go wrong.”

The second law tells us the entropy of the universe increases in a product-favored process.

This is what scientists mean when they say that the second law is an expression in physical — as opposed to psychological — form of what we call *time*. In fact, entropy has been called “time’s arrow.” The second law demands that disorder increases with time. Because all natural processes result in increased disorder, it is evident that entropy and time “point” in the same direction.

Neither of the first two laws of thermodynamics has ever been or can be proven. It is just that there never has been a single, concrete example showing otherwise. No less a scientist than Albert Einstein once remarked that thermodynamic theory “. . . is the only physical theory of the universe content [which], within the framework of applicability of its basic concepts, will never be over-thrown. ”

Einstein’s statement does not mean that people have not tried (and are continuing to try) to disprove the laws of thermodynamics. Someone is always claiming to have invented a machine that performs useful work without expending energy — a perpetual motion machine. Although such a machine was actually granted a patent recently by the U.S. Patent Office (presumably the patent examiner had not had a course in thermodynamics), no workable perpetual motion machine has ever been demonstrated; the laws of thermodynamics are safe.

If you are interested in the theories of the origin of the universe, and in “times arrow,” read *A Brief History of Time, From the Big Bang to Black Holes*, by Stephen W. Hawking, Bantam Books, New York, 1988.