

1. Details of Module and its structure

Module Detail	
Subject Name	Chemistry
Course Name	Chemistry 01 (Class XI, Semester 01)
Module Name/Title	Thermodynamics: Part 4
Module Id	kech_10604
Pre-requisites	Enthalpy , exothermic and endothermic reactions.
Objectives	After learning this module learner will be able to <ol style="list-style-type: none">1. Define spontaneous and non-spontaneous processes;2. Explain entropy as a thermodynamic state function and apply it for spontaneity;3. Calculate Gibbs energy change (ΔG)4. Establish relationship between ΔG and spontaneity, ΔG and equilibrium constant.5. Predict spontaneity of a reaction in a given condition.
Keywords	Entropy, Gibb's free energy, equilibrium constant

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1. Introduction

The first law of thermodynamics tells us about the relationship between the heat absorbed and the work performed on or by a system. It puts no restrictions on the direction of heat flow. However, the flow of heat is unidirectional from higher temperature to lower temperature. In fact, all naturally occurring processes whether chemical or physical will tend to proceed spontaneously in one direction only. For example, a gas expanding to fill the available volume, burning carbon in dioxygen giving carbon dioxide etc. But heat will not flow from colder body to warmer body on its own, the gas in a container will not spontaneously contract into one corner or carbon dioxide will not form carbon and dioxygen spontaneously.

These and many other spontaneously occurring changes show unidirectional change. We may ask 'what is the driving force of spontaneously occurring changes? What determines the direction of a spontaneous change? In this section, we shall establish some criterion for these processes whether these will take place or not.

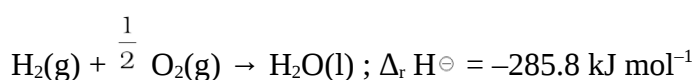
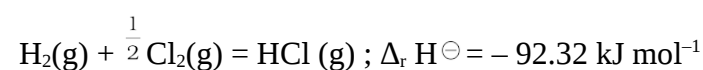
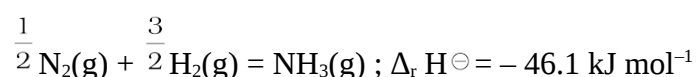
2. Spontaneity

Let us first understand what do we mean by spontaneous reaction or change? You may think by your common observation that spontaneous reaction is one which occurs immediately when contact is made between the reactants. Take the case of combination of hydrogen and oxygen. These gases may be mixed at room temperature and left for many years without observing any perceptible change. Although the reaction is taking place between them, it is at an extremely slow rate. It is still called spontaneous reaction. So spontaneity means 'having the potential to proceed without the assistance of external agency'. However, it does not tell about the rate of the reaction or process. Another aspect of spontaneous reaction or process, as we see is that these cannot reverse their direction on their own. We may summarise it as follows:

A spontaneous process is an irreversible process and may only be reversed by some external agency.

(i) Is decrease in enthalpy a criterion for spontaneity?

If we examine the phenomenon like flow of water downhill or fall of a stone on to the ground, we find that there is a net decrease in potential energy in the direction of change. By analogy, we may be tempted to state that a chemical reaction is spontaneous in a given direction, because decrease in energy has taken place, as in the case of exothermic reactions. For example:



The decrease in enthalpy in passing from reactants to products may be shown for any exothermic reaction on an enthalpy diagram as shown in Fig. 1(a).

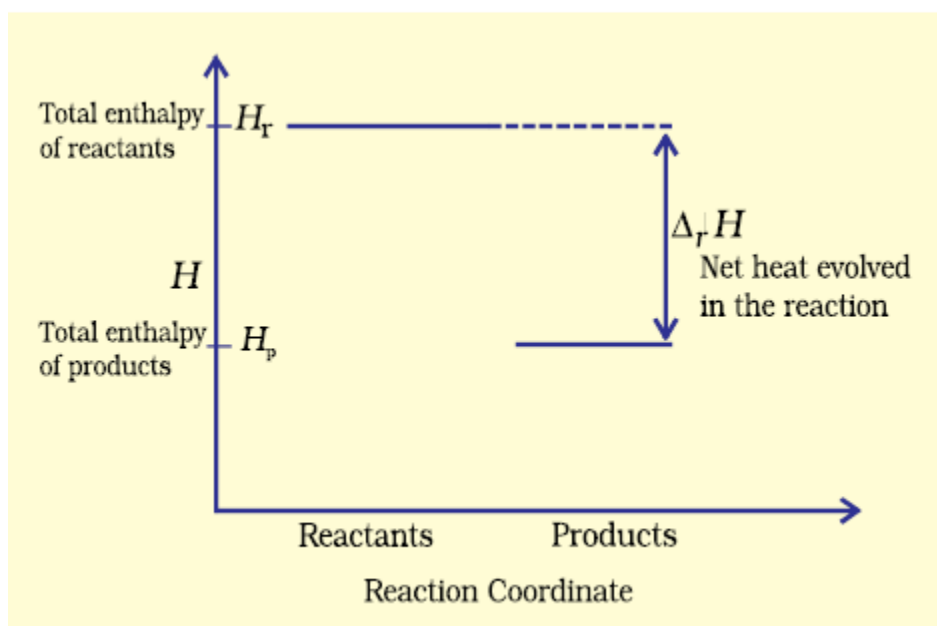
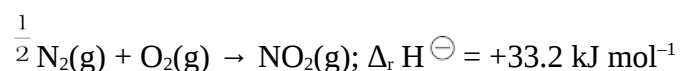
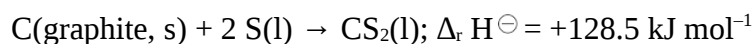


Fig. 1 (a) Enthalpy diagram for exothermic reactions

Thus, the postulate that driving force for a chemical reaction may be due to decrease in energy sounds 'reasonable' as the basis of evidence so far !

Now let us examine the following reactions:





These reactions though endothermic, are spontaneous. The increase in enthalpy may be represented on an enthalpy diagram as shown in Fig. 1(b).

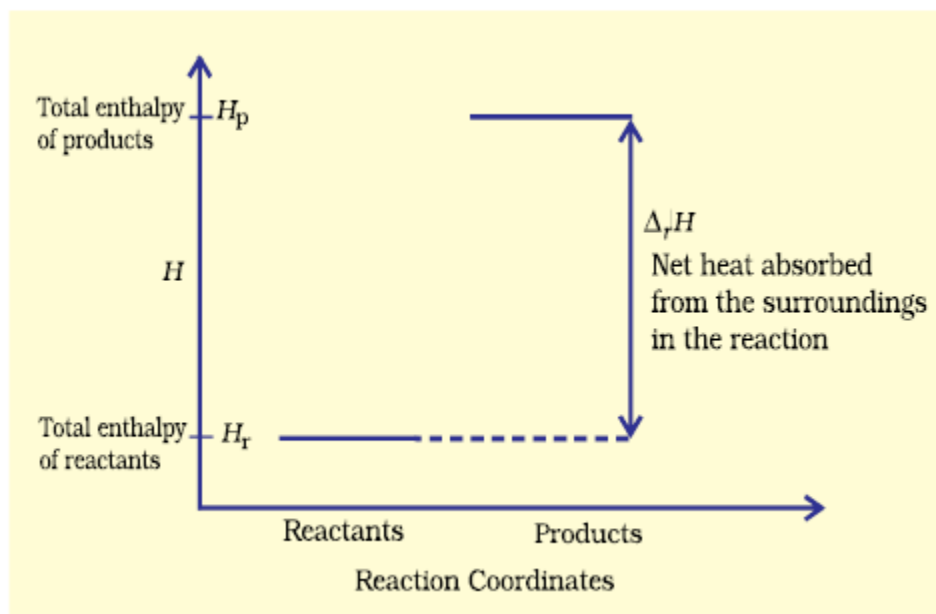


Fig. 1 (b) Enthalpy diagram for endothermic reactions

Therefore, it becomes obvious that while decrease in enthalpy may be a contributory factor for spontaneity, but it is not true for all cases.

3. Entropy and spontaneity

Then, what drives the spontaneous process in a given direction? Let us examine such a case in which $\Delta H = 0$ i.e., there is no change in enthalpy, but still the process is spontaneous.

Let us consider diffusion of two gases into each other in a closed container which is isolated from the surroundings as shown in Fig. 2.

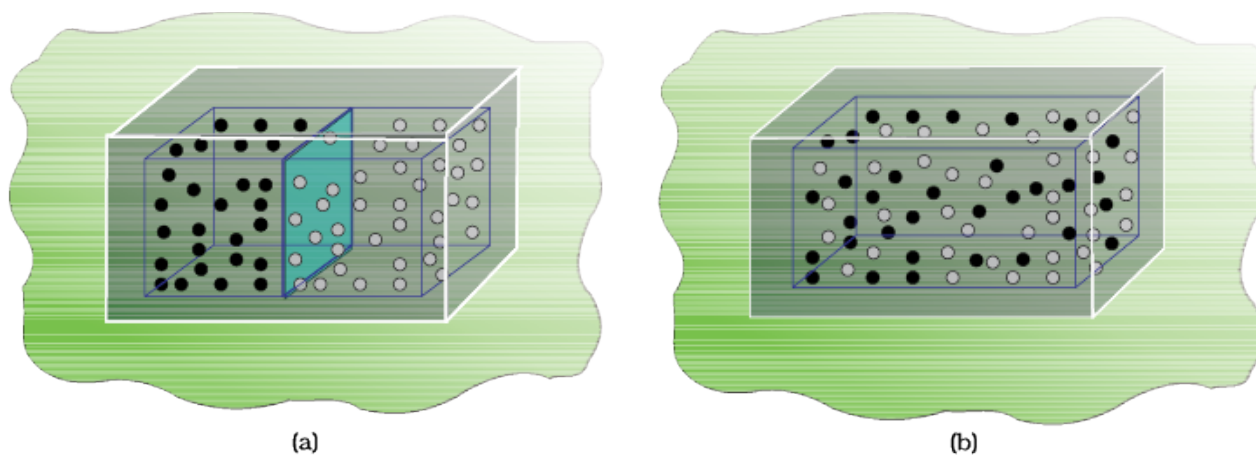


Fig. 2 Diffusion of two gases

The two gases, say, gas A and gas B are represented by black dots and white dots respectively and separated by a movable partition [Fig. 2 (a)]. When the partition is withdrawn [Fig. 2 (b)], the gases begin to diffuse into each other and after a period of time, diffusion will be complete.

Let us examine the process. Before partition, if we were to pick up the gas molecules from left container, we would be sure that these will be molecules of gas A and similarly if we were to pick up the gas molecules from right container, we would be sure that these will be molecules of gas B. But, if we were to pick up molecules from container when partition is removed, we are not sure whether the molecules picked are of gas A or gas B. We say that the system has become less predictable or more chaotic.

We may now formulate another postulate: in an isolated system, there is always a tendency for the systems' energy to become more disordered or chaotic and this could be a criterion for spontaneous change!

At this point, we introduce another thermodynamic function, **entropy** denoted as S . The above mentioned disorder is the manifestation of entropy. To form a mental picture, one can think of entropy as a measure of the degree of randomness or disorder in the system. The greater the disorder in an isolated system, the higher is the entropy. As far as a chemical reaction is concerned, this entropy change can be attributed to rearrangement of atoms or ions from one pattern in the reactants to another (in the products). If the structure of the products is very much disordered than that of the reactants, there will be a resultant increase in entropy. The change in entropy accompanying a chemical reaction may be estimated qualitatively by a consideration of the structures of the species taking part in the reaction. Decrease of regularity in structure would mean increase in entropy. For a given substance, the crystalline solid state is the state of lowest entropy (most ordered), The gaseous state is state of highest entropy.

Now let us try to quantify entropy. One way to calculate the degree of disorder or chaotic distribution of energy among molecules would be through statistical method which is beyond the scope of this treatment. Other way would be to relate this process to the heat involved in a process which would make entropy a thermodynamic concept. Entropy, like any other thermodynamic property such as internal energy U and enthalpy H is a state function and ΔS is independent of path.

Whenever heat is added to the system, it increases molecular motions causing increased randomness in the system. Thus **heat (q) has randomising influence** on the system. Can we then equate ΔS with q ? Wait ! Experience suggests us that the distribution of heat also depends on the temperature at which heat is added to the system. A system at higher temperature has greater randomness in it than one at lower temperature. Thus, **temperature is the measure of average**

chaotic motion of particles in the system. Heat added to a system at lower temperature causes greater randomness than when the same quantity of heat is added to it at higher temperature. This suggests that the entropy change is inversely proportional to the temperature. ΔS is related with q and T for a reversible reaction as:

$$\Delta S = \frac{q_{rev}}{T} \quad (1)$$

The total entropy change (ΔS_{total}) for the system and surroundings of a spontaneous process is given by

(2)

When a system is in equilibrium, the entropy is maximum, and the change in entropy, $\Delta S = 0$.

We can say that entropy for a spontaneous process increases till it reaches maximum and at equilibrium the change in entropy is zero. Since entropy is a state property, we can calculate the change in entropy of a reversible process by

$\Delta S_{sys} =$

We find that both for reversible and irreversible expansion for an ideal gas, under isothermal conditions, $\Delta U = 0$, but ΔS_{total} i.e., $\Delta S_{sys} + \Delta S_{surr}$ is not zero for irreversible process. Thus, ΔU does not discriminate between reversible and irreversible process, whereas ΔS does.

Example 1

Predict in which of the following, entropy increases/decreases:

- (i) A liquid crystallizes into a solid.
- (ii) Temperature of a crystalline solid is raised from 0 K to 115 K.
- (iii) $2\text{NaHCO}_3(\text{s}) \rightarrow \text{Na}_2\text{CO}_3(\text{s}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$

(iv)

Solution

- (i) After freezing, the molecules attain an ordered state and therefore, entropy decreases.
- (ii) At 0 K, the constituent particles are static and entropy is minimum. If temperature is raised to 115 K, these begin to move and oscillate about their equilibrium positions in the lattice and system becomes more disordered, therefore entropy increases.
- (iii) Reactant, NaHCO_3 is a solid and it has low entropy. Among products there are one solid and two gases. Therefore, the products represent a condition of higher entropy.

(iv) Here one molecule gives two atoms i.e., number of particles increases leading to more disordered state. Two moles of H atoms have higher entropy than one mole of dihydrogen molecule.

Example 2

For oxidation of iron,



entropy change is $-549.4 \text{ JK}^{-1}\text{mol}^{-1}$ at 298 K. In spite of negative entropy change of this reaction, why is the reaction spontaneous?

($\Delta_r H^\ominus$ for this reaction is $-1648 \times 10^3 \text{ J mol}^{-1}$)

Solution

One decides the spontaneity of a reaction by considering

$\Delta S_{\text{total}} (\Delta S_{\text{sys}} + \Delta S_{\text{surr}})$. For calculating ΔS_{surr} , we have to consider the heat absorbed by the surroundings which is equal to $-\Delta_r H^\ominus$. At temperature T, entropy change of the surroundings is

$$\begin{aligned}\Delta S_{\text{surr}} &= -\frac{\Delta_r H^\ominus}{T} \text{ (at constant pressure)} \\ &= -\frac{(-1648 \times 10^3 \text{ J mol}^{-1})}{298 \text{ K}} \\ &= 5530 \text{ JK}^{-1}\text{mol}^{-1}\end{aligned}$$

Thus, total entropy change for this reaction

This shows that the above reaction is spontaneous.

4. Gibbs energy and spontaneity

We have seen that for a system, it is the total entropy change, ΔS_{total} which decides the spontaneity of the process. But most of the chemical reactions fall into the category of either closed systems or open systems. Therefore, for most of the chemical reactions there are changes in both enthalpy and entropy. It is clear from the discussion in previous sections that neither decrease in enthalpy nor increase in entropy alone can determine the direction of spontaneous change for these systems.

For this purpose, we define a new thermodynamic function the Gibbs energy or Gibbs function, G, as

$$G = H - TS \quad (3)$$

Gibbs function, G is an extensive property and a state function.

The change in Gibbs energy for the system, ΔG_{sys} can be written as

$$\Delta G_{\text{sys}} = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}} - S_{\text{sys}}\Delta T$$

At constant temperature,

$$\therefore \Delta G_{\text{sys}} = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}}$$

Usually the subscript 'system' is dropped and we simply write this equation as

(4)

Thus, Gibbs energy change = enthalpy change – temperature × entropy change, and is referred to as the Gibbs equation, one of the most important equations in chemistry. Here, we have considered both terms together for spontaneity: energy (in terms of ΔH) and entropy (ΔS , a measure of disorder) as indicated earlier. Dimensionally if we analyse, we find that ΔG has units of energy because, both ΔH and the $T\Delta S$ are energy terms, since $T\Delta S = (\text{K})(\text{J/K}) = \text{J}$.

Now let us consider how ΔG is related to reaction spontaneity.

We know,

$$\Delta S_{\text{total}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

If the system is in thermal equilibrium with the surrounding, then the temperature of the surrounding is same as that of the system. Also, increase in enthalpy of the surrounding is equal to decrease in the enthalpy of the system.

Therefore, entropy change of surroundings,

$$\Delta S_{\text{surr}} = \frac{\Delta H_{\text{surr}}}{T} = -\frac{\Delta H_{\text{sys}}}{T}$$

$$\Delta S_{\text{total}} = \Delta S_{\text{sys}} + \left(-\frac{\Delta H_{\text{sys}}}{T}\right)$$

Rearranging the above equation:

$$T\Delta S_{\text{total}} = T\Delta S_{\text{sys}} - \Delta H_{\text{sys}}$$

For spontaneous process, $\Delta S_{\text{total}} > 0$, so

$$T\Delta S_{\text{sys}} - \Delta H_{\text{sys}} > 0$$

$$\Rightarrow -(\Delta H_{\text{sys}} - T\Delta S_{\text{sys}}) > 0$$

Using equation (4), the above equation can be written as

$$-\Delta G > 0$$

(5)

ΔH_{sys} is the enthalpy change of a reaction, $T\Delta S_{\text{sys}}$ is the energy which is not available to do useful work. So ΔG is the net energy available to do useful work and is thus a measure of the 'free energy'. For this reason, it is also known as the free energy of the reaction.

ΔG gives a criteria for spontaneity at constant pressure and temperature.

(i) If ΔG is negative (< 0), the process is spontaneous.

(ii) If ΔG is positive (> 0), the process is non-spontaneous.

Note: If a reaction has a positive enthalpy change and positive entropy change, it can be spontaneous when $T\Delta S$ is large enough to outweigh ΔH . This can happen in two ways; (a) The positive entropy change of the system can be 'small' in which case T must be large. (b) The positive entropy change of the system can be 'large', in which case T may be small. The former is one of the reasons why reactions are often carried out at high temperature. Table 1 summarises the effect of temperature on spontaneity of reactions.

5. Gibbs energy change and equilibrium

We have seen how knowledge of the sign and magnitude of the free energy change of a chemical reaction allows:

(i) Prediction of the spontaneity of the chemical reaction.

(ii) Prediction of the useful work that could be extracted from it.

So far we have considered free energy changes in irreversible reactions. Let us now examine the free energy changes in reversible reactions.

'Reversible' under strict thermodynamic sense is a special way of carrying out a process such that system is at all times in perfect equilibrium with its surroundings. When applied to a chemical reaction, the term 'reversible' indicates that a given reaction can proceed in either direction simultaneously, so that a dynamic equilibrium is set up. This means that the reactions in both the directions should proceed with a decrease in free energy, which seems impossible. It is possible only if at equilibrium the free energy of the system is minimum. If it is not, the system would spontaneously change to configuration of lower free energy.

So, the criterion for equilibrium $A + B \rightleftharpoons C + D$ is $\Delta_r G = 0$

Gibbs energy for a reaction in which all reactants and products are in standard state, $\Delta_r G^\ominus$ is related to the equilibrium constant of the reaction as follows:

$$0 = \Delta_r G^\ominus + RT \ln K$$

$$\text{or } \Delta_r G^\ominus = -RT \ln K$$

$$\text{or } \Delta_r G^\ominus = -2.303 RT \log K \quad (6)$$

We also know that

(7)

For strongly endothermic reactions, the value of $\Delta_r H^\ominus$ may be large and positive. In such a case, value of K will be much smaller than 1 and the reaction is unlikely to form much product. In case

of exothermic reactions, $\Delta_r H^\ominus$ is large and negative, and $\Delta_r G^\ominus$ is likely to be large and negative too. In such cases, K will be much larger than 1. We may expect strongly exothermic reactions to have a large K , and hence can go to near completion. $\Delta_r G^\ominus$ also depends upon $\Delta_r S^\ominus$, if the change in the entropy of reaction is also taken into account, the value of K or extent of chemical reaction will also be affected, depending upon whether $\Delta_r S^\ominus$ is positive or negative.

Using equation (7),

(i) It is possible to obtain an estimate of ΔG^\ominus from the measurement of ΔH^\ominus and ΔS^\ominus , and then calculate K at any temperature for economic yields of the products.

(ii) If K is measured directly in the laboratory, value of ΔG at any other temperature can be calculated.

Table 1 : Effect of Temperature on Spontaneity of Reactions

$\Delta_r H^\ominus$	$\Delta_r S^\ominus$	$\Delta_r G^\ominus$	Description*
-	+	-	Reaction spontaneous at all temperature
-	-	- (at low T)	Reaction spontaneous at low temperature
-	-	+ (at high T)	Reaction nonspontaneous at high temperature
+	+	+ (at low T)	Reaction nonspontaneous at low temperature
+	+	- (at high T)	Reaction spontaneous at high temperature
+	-	+ (at all T)	Reaction nonspontaneous at all temperatures

* The term low temperature and high temperature are relative. For a particular reaction, high temperature could even mean room temperature.

Example 3

Calculate $\Delta_r G^\ominus$ for conversion of oxygen to ozone, $3/2 \text{ O}_2(\text{g}) \rightarrow \text{O}_3(\text{g})$ at 298 K. if K_p for this conversion is 2.47×10^{-29} .

Solution

We know $\Delta_r G^\ominus = -2.303 RT \log K_p$ and $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

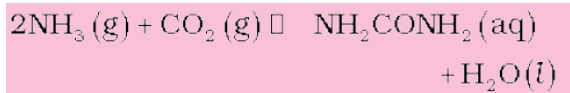
Therefore, $\Delta_r G^\ominus = -2.303 (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) (\log 2.47 \times 10^{-29})$

= $163000 \text{ J mol}^{-1}$

= 163 kJ mol^{-1} .

Example 4

Find out the value of equilibrium constant for the following reaction at 298 K.



Standard Gibbs energy change, $\Delta_r G^\ominus$ at the given temperature is $-13.6 \text{ kJ mol}^{-1}$.

Solution

We know, $\log K =$

$=$

$= 2.38$

Hence $K = \text{antilog } 2.38 = 2.4 \times 10^2$.

Example 5

At 60°C , dinitrogen tetroxide is fifty percent dissociated. Calculate the standard free energy change at this temperature and at one atmosphere.

Solution



If N_2O_4 is 50% dissociated, the mole fraction of both the substances is given by

$$x_{\text{N}_2\text{O}_4} = \frac{1 - 0.5}{1 + 0.5}; \quad x_{\text{NO}_2} =$$

$$= \frac{0.5}{1.5} \times 1 \text{ atm}, \quad p_{\text{NO}_2} =$$

The equilibrium constant K_p is given by

$$K_p =$$

$$= 1.33 \text{ atm.}$$

$$\text{Since } \Delta_r G^\ominus = -RT \ln K_p$$

$$\Delta_r G = (-8.314 \text{ JK}^{-1} \text{ mol}^{-1}) \times (333 \text{ K}) \times (2.303) \times (0.1239)$$

$$= -763.8 \text{ kJ mol}^{-1}$$

6. Conclusion

Chemical reactions are generally carried at constant pressure, so we define another state function Gibbs energy, G , which is related to entropy and enthalpy changes of the system by the equation: $\Delta_r G = \Delta_r H - T \Delta_r S$

For a spontaneous change, $\Delta G_{\text{sys}} < 0$ and at equilibrium, $\Delta G_{\text{sys}} = 0$.

Standard Gibbs energy change is related to equilibrium constant by

$$\Delta_r G^\ominus = -RT \ln K.$$

K can be calculated from this equation, if we know $\Delta_r G^\ominus$ which can be found from $\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus$. Temperature is an important factor in the equation. Many reactions which are non-spontaneous at low temperature, are made spontaneous at high temperature for systems having positive entropy of reaction.