

Gibbs Free Energy and Equilibrium

The enthalpy and entropy changes that accompany all chemical reactions, each have a role to play in terms of determining if the reaction will actually occur. Enthalpy (ΔH^\ominus) and entropy (ΔS^\ominus) are brought together in the equation shown below, which is used to calculate the standard Gibbs free energy change of a reaction, ΔG^\ominus .

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

Where T = temperature in Kelvin

Gibbs free energy can be thought of as a measure of how feasible (how likely) a reaction is. A feasible reaction is sometimes called a 'spontaneous' one, but this can be very misleading. Spontaneous, in the literal sense, suggests a reaction that happens instantaneously, but chemical reactions can sometimes be extremely slow. This means that a reaction that has a negative ΔG^\ominus , may still not appear to occur since it is very slow. This is why it is perhaps better to refer to feasible reactions as thermodynamically favourable.

A thermodynamically favoured chemical reaction (i.e., a reaction that will 'go'), will have a value for ΔG^\ominus that is negative. Inspection of the equation above, and knowing that temperature (T) is always given in Kelvin, i.e., it is a positive number, tells us that a negative value for ΔG^\ominus is favoured by a negative value for ΔH^\ominus and a positive value for ΔS^\ominus .

However, temperature has an important role to play in determining whether or not a reaction is ultimately considered thermodynamically favourable. When only one of the entropy or enthalpy terms is favourable to the reaction occurring, relatively low or relatively high temperatures can influence the sign of ΔG^\ominus , and hence the thermodynamic favourability of it. Analysis of the possible sign combinations of ΔH^\ominus , ΔS^\ominus and ΔG^\ominus is summarised below:

ΔH^\ominus	ΔS^\ominus	ΔG^\ominus
+	+	- at high temperatures + at low temperatures
+	-	always +
-	+	always -
-	-	- at low temperatures + at high temperatures

Once a value for Gibbs free energy has been calculated, it can be related to the equilibrium constant (K) for the reaction by use of the equations shown below:

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

Where R = 8.314 J K⁻¹ mol⁻¹, T = temperature in Kelvin, and ln is the natural log

Rearrangement leads to the expression below:

$$K = e^{-\Delta G^\ominus/RT}$$

There is an important mathematical relationship between Gibbs free energy and the equilibrium constant that can be exposed by considering a couple of examples.

Let's start with a positive value of ΔG^\ominus of + 50.0 kJ mol⁻¹, at a temperature of 100°C. It's crucial to understand that a couple of conversions must take place in order for the equation to work correctly. Since R has a unit that includes joules and ΔG^\ominus is usually given in units of kJ, one must be converted in order for them to match. Here we have converted the kJ of ΔG^\ominus , to J.

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

$$+ (50) (1000) = - (8.314) (273 + 100) (\ln K)$$

$$K = 9.90 \times 10^{-8}$$

The important thing to note here is that a positive value of ΔG^\ominus is associated with a value of K which is extremely small. Since K is a ratio of products (the numerator) to the reactants (the denominator), this suggests that there are relatively very few products, and this is consistent with a positive ΔG^\ominus , i.e., a reaction that is not feasible.

Repeating a similar calculation with a value of $\Delta G^\ominus = -50$ kJ mol⁻¹, at the same temperature, and by performing the same, important conversions, we find

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

$$- (50) (1000) = - (8.314) (273 + 100) (\ln K)$$

$$K = 1.01 \times 10^7$$

Of course, this time the value of K is extremely large, this time consistent with a feasible reaction that would product a large number of products.

In summary:

K	ln K	ΔG^\ominus	Situation
> 1	Positive	Negative	Products favoured at equilibrium
1	0	0	Products and reactants equally favoured at equilibrium
< 1	Negative	Positive	Reactants favoured at equilibrium

As the table shows, the equilibrium position can favour reactants or products depending on the chemical reaction in question, and as such, ΔG^\ominus can have either positive or negative values at equilibrium.

The equation $\Delta G^\ominus = -RT \ln K$, shows us how ΔG^\ominus can be influenced by temperature. ΔG^\ominus assumes standard conditions of 100 kPa for gases and 1 mol dm⁻³ for solutions. So, when conditions differ from standard values, a previously positive (or negative) ΔG^\ominus value, will take on a *new* ΔG value under these *new* conditions. In some cases (where ΔG^\ominus is close to 0), not only does the magnitude change, but the sign may change too, causing a previously non-favoured reaction to become feasible, and vice-versa. There is an equation which allows the calculation of the new ΔG value,

$$\Delta G = \Delta G^\ominus + RT \ln Q$$

Where Q = reaction quotient, and is a ratio of products to reactants at a position other than equilibrium.

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Since Q is not necessarily equal to K , and we are not necessarily at the equilibrium position, the sign of ΔG can be thought of as a predictor about in which direction the reaction, will go. Here are the two scenarios:

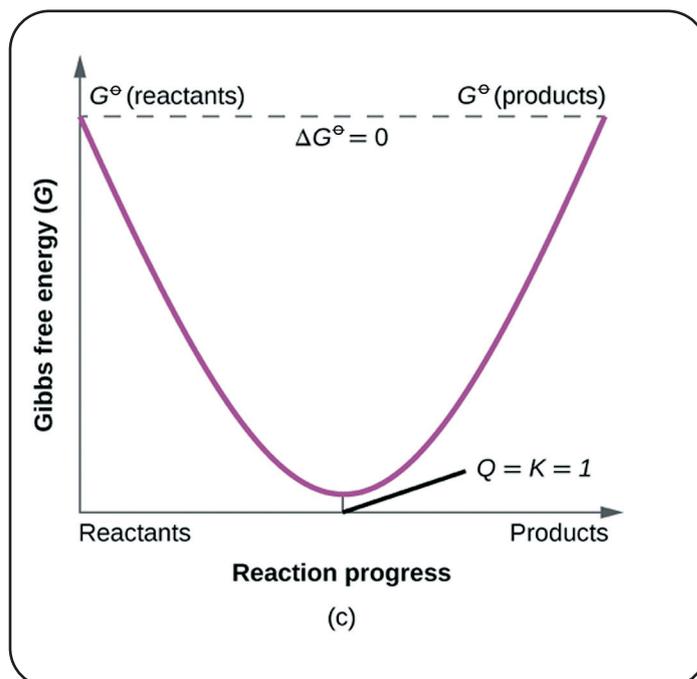
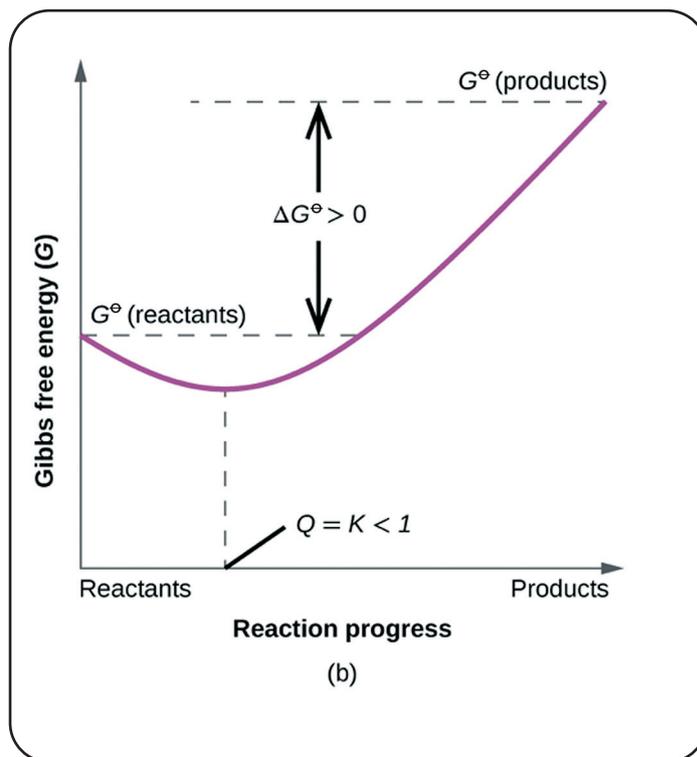
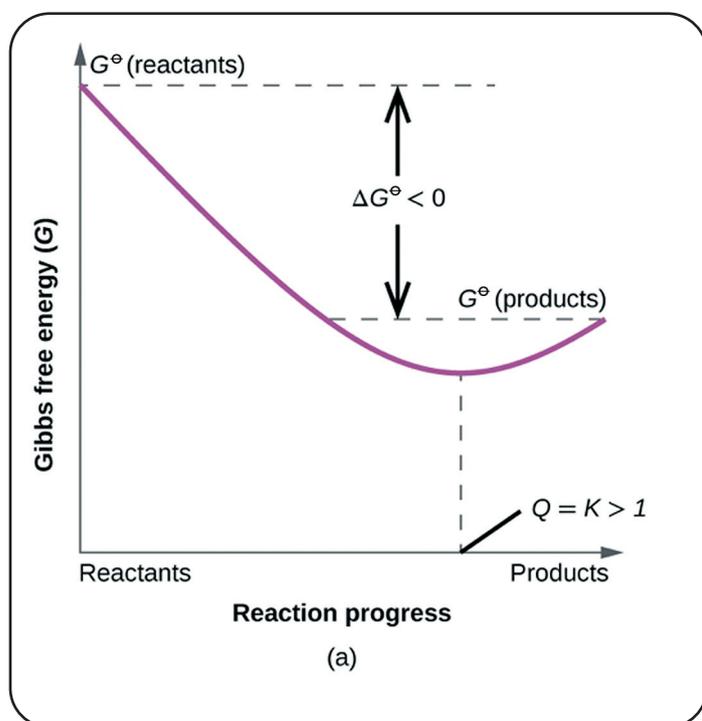
- 1) If ΔG^\ominus is negative at equilibrium, then we will have lots of products at equilibrium, meaning that Q needs to increase in magnitude to approach K . As Q gets larger (i.e., as we get more products), the term ' $RT \ln Q$ ' gets increasingly positive, and eventually adding that term to a negative ΔG^\ominus , will make $\Delta G = 0$, equilibrium will be established and no further change occurs.

It is possible that Q could already be too large and therefore ΔG is positive. If so, then the reaction will need to form more reactants, reduce the value of Q , and allow ΔG to reach zero, i.e., allow equilibrium to be established.

- 2) If ΔG^\ominus is positive at equilibrium, then we will have lots of reactants at equilibrium, meaning Q needs to decrease in magnitude to approach K . As Q gets smaller (i.e., as we get more reactants), the term ' $RT \ln Q$ ' gets increasingly negative, and eventually adding that term to a positive ΔG^\ominus , will make $\Delta G = 0$, equilibrium will be established and no further change occurs.

It is possible that Q could already be too small and therefore ΔG is negative, if so, then the reaction will need more products, increase the value of Q , and allow ΔG to reach zero, i.e., allow equilibrium to be established.

In short, it is ΔG (not ΔG^\ominus) that will be zero at equilibrium and the sign of it at any point in time (generated by the combination of ΔG^\ominus and $RT \ln Q$), that defines the direction that the reaction proceeds. This can be shown graphically, thus:



The above concept can be illustrated by tackling one of the confusing aspects of using ΔG^\ominus to predict the feasibility of a reaction which arises when considering reversible reactions. Take the Haber Process as an example:



As the reaction is written, the forward reaction (forming ammonia) is highly feasible with a negative value for ΔG^\ominus . If we write the backward reaction:



The value of ΔG^\ominus is now positive, giving the impression that the decomposition of ammonia is not feasible. However, we know by

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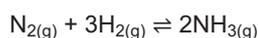
observation that this reaction will reach equilibrium from either direction (i.e., starting with only H₂ and N₂ or starting with only NH₃) and all species are present in the equilibrium mixture. This indicates that both the formation of ammonia and decomposition of ammonia are feasible.

The confusion lies in not realising that ΔG^\ominus refers to a reaction that goes to completion in a single direction, i.e., $\Delta G^\ominus = -33$ kJ if 3 moles of H₂ and 1 mole of N₂ are converted entirely into 2 moles of ammonia. As the reaction reaches equilibrium we know this 100% conversion is not correct.

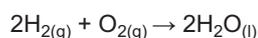
As can be seen in the graphs, moving from pure reactants or pure products to a position of equilibrium always involves a decrease in Gibbs free energy and so both forward and backward reactions are feasible to a point, i.e., until the system reaches equilibrium and Gibbs free energy is at a minimum. Once the reaction has reached equilibrium, moving from this position requires an increase in Gibbs free energy and is therefore not feasible and the system remains in this state until the conditions are altered.

Questions

1. Consider the reaction shown below for the production of ammonia from nitrogen and hydrogen.



- a) Calculate ΔG^\ominus , at 298 K for the reaction, given that the reaction has an equilibrium constant $K = 3.30 \times 10^8$ at 298 K
 - b) Use the value of ΔG^\ominus calculated in (a) above, to calculate the value of ΔG at 800 °C, where all three gases have partial pressures of 2×10^5 Pa and are contained in a 1.00 dm³ container.
2. If a chemical reaction forms an equilibrium mixture where products predominate, what does that suggest about the ΔG^\ominus for the reaction?
 3. Despite having a negative value for ΔG^\ominus , hydrogen gas and oxygen gas can happily co-exist in a mixture together without the reaction shown below occurring. Suggest a reason why the reaction mixture is kinetically stable, despite the formation of water being thermodynamically favourable.



Answers

1. a) -48.6 kJ mol⁻¹
b) 61.0 kJ mol⁻¹
2. A large number of products will suggest a large value for K . In turn, via the equation and the mathematics of \ln , ΔG^\ominus will be a negative number.
3. The activation energy for the reaction must be very high. This means that the reaction is incredibly slow, so despite being feasible (negative ΔG^\ominus), the reaction does not occur.