

Physical Chemistry 1 (Thermodynamics) Module 4

Open Source Textbook

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## **Chapter 16 Spontaneity and Free Energy**

## Chapter 16 Spontaneity

### Summary

Free energy changes occurring during a spontaneous process or a natural process or an irreversible process are examined here. The thermodynamic criterion for spontaneity under constant temperature conditions is defined by the decrease in the Helmholtz free energy (A), while the Gibbs free energy (G) defines the spontaneity under constant temperature and pressure conditions. The latter is of prime importance when all the work produced is only of pV work and the reactions occur under constant temperature and pressure conditions. Both these free energy terms are examined as a function of pressure, temperature, and volume to gain a deeper insight into the control of the spontaneity of a chemical reaction or a physical process.

### Goals

We will examine what drives a natural process or a spontaneous process. To that end, we will begin with Clausius inequality and figure out a way to replace the dS term present in the inequality with a property of the system, independent of the surroundings. Along these lines we will discover Helmholtz free energy and Gibbs free energy. Subsequently, we will investigate the properties of these two new state functions and examine the equilibrium constant from these vantage points.

### 16.1 Why Study this?

Gibbs free energy (G) is the primary thermodynamic property that can predict successfully if a given process is spontaneous (direction), when the experiment is carried out under constant pressure conditions. G also provides an excellent access to predicting when the equilibrium is achieved and predict the value of the equilibrium constant. All spontaneous processes happening under constant pressure conditions, in the universe, is characterized by a decrease in the G value of the system. Thus, this chapter describing its discovery and discussion of its properties are of immense importance. These are strong but important reasons to study this section.

### 16.2 Spontaneity

We will continue our quest to discover thermodynamic quantities which drive natural processes, such as entropy but these properties should only depend on the system and not dependent on the changes in the surroundings. Naturally, such a property would also predict if the forward direction of the process is natural. For example, thermodynamic quantities such as temperature, work, heat, energy, and enthalpy, all been tested in our previous discussions, and none of them can predict the spontaneity of given a process. So far, our champion has been entropy, which can predict if a given process would occur spontaneously or not, as an absolute, standard, and reliable approach. The only caveat is that the total entropy (system + surroundings) is the metric, and we will have to monitor both the system and the surroundings, unless it is an isolated system. Isolated system is not very convenient for laboratory measurements and therefore, we are looking for any property of the system, and that of the system only, which can predict if a given process is spontaneous, without examining the surroundings. We begin with Clausius inequality.

### 16.3 Clausius Inequality

We begin with the Clausius inequality because it predicts the spontaneity of a process but our strategy is to find a way to replace entropy term with equivalent properties of the system, and not involve the surroundings.

$$T dS \geq dQ$$

When the process is reversible, the equality sign is valid and when the process is irreversible, the greater than sign is valid. Thus, this applies to all processes and our first step is to apply the first law to examine it. We replace, for example, dQ with dU – dw<sub>total</sub> and get the following equation.

$$T dS \geq dU - dw_{total} \quad , \quad \text{all processes}$$

The work  $dw_{total}$  includes the pressure-volume work and all other forms of work such as the mechanical, electrochemical, photochemical or some other form. Since we focus on gases for most of our discussions, we will factor out the  $pV$  work and write all other forms of work separately, as  $dw_{other}$ .

$$T dS > dU + p_{opp} dV - dw_{other}$$

We will be clear that  $p_{opp}$  is the opposing pressure on the gas,  $dV$  is change in the volume of the gas and  $-p_{opp}dV$  is the  $pV$  work term. If we were to examine chemical reactions, as in a battery for example, we will be interested in the electrochemical work as  $dw_{other}$ . We take the  $TdS$  term to the right side and write the following.

$$0 \geq dU + p_{opp} dV - dw_{other} - T dS$$

This is a powerful expression because for all irreversible processes taking place, the sum on the right side of the inequality should be less than zero and for all reversible processes or equilibria, the equality sign applies. Still, there are terms in the above expression that require us to look in the surroundings. If we have only condensed phases, then  $p_{opp} dV$  will be small and can be neglected as shown below.

$$0 \geq dU - dw_{other} - T dS \quad (\text{condensed phases})$$

When we have only gases, and have  $pV$  work as the only form of work, which is often the case with gases, then we can write the following expression.

$$0 \geq dU + p_{opp} dV - T dS \quad (\text{pV work only})$$

All the above expressions still require the evaluation of the system and the surroundings and hence, we need to continue our search for a property of the system that will predict the spontaneity of a process. We will impose specific restrictions on the above expression, such as constant temperature or constant pressure and then re-examine if we can write the above in terms of the property of the system alone.

### 16.3.1 Constant temperature conditions

When we keep the temperature constant, isothermal processes, which is experimentally quite convenient,  $dT = 0$ . Then we write the following.

$$dU - dw_{total} - T dS \leq 0$$

Under constant temperature conditions, we write  $dU - TdS$ , as a single composite function, and get the following key relation.

$$d(U - T S) \leq dw_{total} \quad (\text{constant } T)$$

Since  $U$ ,  $T$ , and  $S$  are all state functions, we can replace this composite term ( $U - TS$ ) with a new state function  $A$ , where  $A = U - TS$ , and after moving the negative sign to the left, we get the following.

$$-dA \geq dw_{total} \quad (A \equiv U - TS)$$

$A$  is the new state function, Helmholtz free energy. For all processes at constant temperature, the decrease in this property of the system ( $-dA$ ) is greater than or equal to all forms of work produced. Thus, for the first time, we arrived at an inherent property of the system that decreases when spontaneous processes and equals to zero when the system equilibrates. Thus, we write three specific sets of conditions.

$$dA = 0, \quad \text{at equilibrium}$$

$$-dA > dw_{total} \quad \text{the system moves forward}$$

$$-dA < dw_{total} \quad \text{the system moves in the reverse direction}$$

$A$  is a new type of energy that we have discovered because it is the difference between the internal energy and the  $TS$  energy. We recognize  $TS$  has the units of energy. Therefore,  $A$  has the units of energy, and Helmholtz free energy is the energy we can extract as total amount of work from the system during an isothermal process. This is the reason it is coined as the free energy.

We recognize that this form of work can be pV work as well as all other forms of work. If we are interested in work that is other than pV work, then A is the quantity we will be examining. We can write three separate conditions, using this condition.

When  $-dA > 0$ , the forward process is spontaneous and decrease in A sponsors the system to carry out the spontaneous process or the irreversible process. When there is no more decrease in A, then  $dA = 0$ , the system is at equilibrium, and when  $-dA < 0$ , the reverse process is spontaneous. Note that all these occur under isothermal conditions.

In summary, we have discovered a new state function,  $A = U - TS$ , which can predict the direction of spontaneous process ( $-dA > dW_{total}$ ) or the establishment of equilibrium ( $dA = 0$ ). One drawback of A is that we must carry out the process under isothermal conditions, but the pressure can vary. The work term includes all forms of work. We finally found a thermodynamic state function that can predict if a given process is spontaneous or when will equilibrium will be achieved that is dependent on the properties of the system and system alone. The surroundings are not involved in evaluating A of the system. Now, we will investigate what would be the case if we held pressure constant, in an isothermal process. Since most of the natural processes occur under constant T & p conditions, it is convenient to make laboratory measurements under these conditions as well. Thus, the need to keep these two variables constant.

### 16.3.2 Constant temperature and pressure conditions

We start with the modified Clausius inequality that we examined before.

$$dU - dw_{total} - T dS \leq 0$$

We will first split  $dw_{total}$  into pV work and  $dw_{other}$ , where the latter accounts for all forms of work other than the pV work, and we get the following.

$$dU + p_{opp} dV - dw_{other} - T dS \leq 0, \text{ all processes, constant T and p}$$

Under constant pressure conditions, we can adjust the  $p_{opp}$  to be equal to p and then, the equation simplifies as following.

$$-(dU + p dV - dw_{other} - T dS) \geq 0$$

Since p and T are constant, we can write the differential form, as following.

$$-(dU + p dV - T dS) - dw_{other} \geq 0$$

By imposing constant temperature conditions, we can group the above three terms in the parenthesis and write the two following equations.

$$-d(U + pV - TS) - dw_{other} \geq 0, \text{ (constant T, p)}$$

We replace  $U + pV - TS$  by a single variable G, for convenience, to get the following.

$$-dG \geq dw_{other} \text{ (constant T, p)}$$

Since, U, p, V, T, and S are all state functions, G is must be a state function. We recognize three specific conditions, when  $dw_{other} = 0$  or all the work is pV work only. The decrease in G is the maximum amount of work other than the pV work that can be produced. Thus, for a spontaneous process, the Gibbs free energy of the system decreases, a hall mark of all natural process, under constant pressure and temperature conditions, when all the work is the pressure volume work.

For finite changes, when all other work is zero or all work is only pV work, we write the corresponding following equations.

- $-dG = 0$       Equilibrium is achieved
- $-dG > 0$       Spontaneous processes
- $-\Delta G < 0$       Reverse process is spontaneous

For finite changes, when  $w_{other}$  is zero, and involves only the pV work, at constant T and p, we get the following criteria, and these are also illustrated in Figure 16.1.

- $-\Delta G = 0$       Equilibrium
- $-\Delta G > 0$       Spontaneous processes
- $-\Delta G < 0$       Reverse process is spontaneous

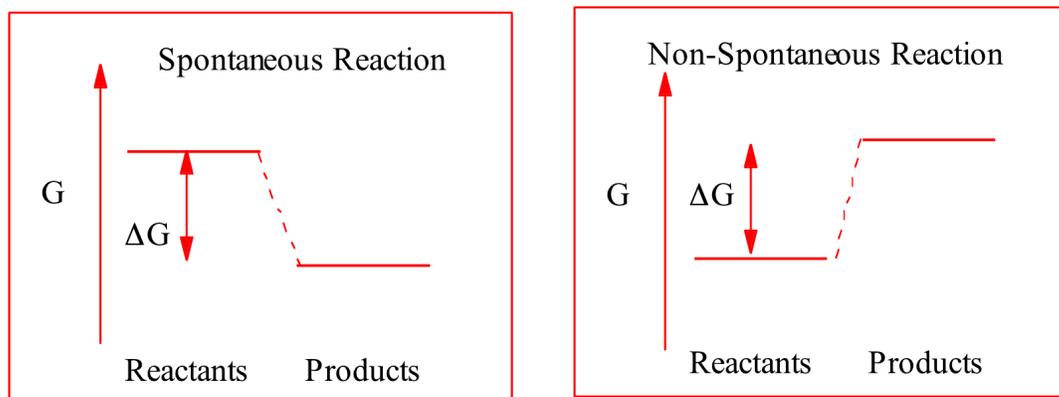


Figure 16.1 The changes in the Gibbs free energy of the system for spontaneous process (left) and for processes that are spontaneous in the opposite direction (right). When  $\Delta G < 0$ , the process is spontaneous and the reaction progresses forward. When  $\Delta G > 0$ , then the reverse reaction occurs spontaneously (right).

The decrease in  $G$  drives the spontaneous process and when there is no further decrease, the system is at equilibrium. When the change in  $G$  is greater than zero, then the reverse process is spontaneous.

In summary, we finally arrived at a thermodynamic property that is only dependent on the system and a decrease in this property is characteristic of all natural processes under constant temperature and pressure conditions.

#### 16.4 Properties of Helmholtz free energy (A)

Helmholtz free energy is an intrinsic property of the system that is a measure of all work that can be extracted from it, and we will discuss properties of Helmholtz free energy here. The relation between  $A$  and temperature and volume are important considerations.

We start with our initial identity  $A = U - TS$  that we defined and write the differential form.

$$A = U - TS$$

$$dA = dU - TdS - SdT$$

We use the first law of thermodynamics,  $dU = dq_{rev} + dw$ , and choose a reversible process. Then, we replace  $dq_{rev}$  with  $TdS$ .

$$dU = dq_{rev} - pdV = TdS - pdV$$

We replace  $dU$  with these new terms, as follows.

$$dA = TdS - pdV - TdS - SdT$$

The  $TdS$  terms cancel away, leaving a tidy small equation that connects  $A$  with changes in  $V$  and  $T$ , as given here.

$$dA = -pdV - SdT$$

We now write the exact differential of  $A$ , and obtain tidy expressions for volume and pressure dependencies as below.

$$dA = \left(\frac{\partial A}{\partial V}\right)_T dV + \left(\frac{\partial A}{\partial T}\right)_V dT$$

The exact differentials are of the property that the first and second terms in the two above equations are identical. Thus, we get two separate relations, one of  $V$  and the other for  $T$ , as follows.

$$\left(\frac{\partial A}{\partial V}\right)_T = -p$$

$$\left(\frac{\partial A}{\partial T}\right)_V = -S$$

Therefore, the rate of change of  $A$  with respect to  $V$ , at constant  $T$  is equal to  $-p$ , and the rate of change of  $A$  with respect to  $T$  at constant  $V$  is  $-S$ . These are discussed further below.

#### 16.4.1 $A$ as a function of $V$ , for an isothermal process

The relation between  $A$ ,  $V$  and  $p$ , from above tells us that as we increase volume,  $A$  decreases and the slope of the plot will be equal to  $-p$ . Thus,  $A$  and  $V$  are inversely related at constant temperature.

$$\left(\frac{\partial A}{\partial V}\right)_T = -p$$

Plot of  $A$  vs  $V$  at constant  $T$  is a curve, with a negative slope equal to gas pressure (Figure 16.2, constant  $T$ ). The slope of the line is steep at low volume, higher pressure, and the slope diminishes as the pressure drops at larger volumes.

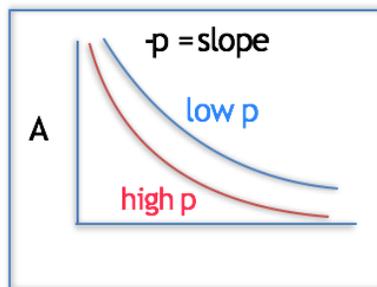


Figure 16.2 The decrease in Helmholtz free energy ( $A$ ) with increasing volume is shown for a gas at a constant temperature (red curve). The plot will not be linear, because pressure decreases with increase in volume at constant temperature (delete the blue curve, x-label missing).

When  $V$  increases in an isothermal process, pressure must decrease (Boyle's law), and an example is the expansion of a gas into the room from a compressed gas cylinder. The decrease in  $A$  ensures that it is a spontaneous process. However, the expansion must be slow enough to keep the temperature of the gas in the cylinder, constant.

#### 16.4.2 $A$ as a function of $T$ , for an isochoric process

Analysis similar to the above with the relation between  $A$ ,  $T$  at constant  $V$  will also provide insight into the behavior of  $A$  in an isochoric process. Helmholtz free energy is inversely related to temperature at constant  $V$ . The rate of change in  $A$  with  $T$  at constant  $V$  is equal to  $-S$ , as shown below.

$$\left(\frac{\partial A}{\partial T}\right)_V = -S$$

Thus,  $A$  decreases with increase in temperature with slope equals to  $-S$ , because there is a negative sign in front of entropy, the slope is negative and hence the inverse proportionality relation. The slope is not a constant because  $S$  itself is a function of temperature, and a plot of  $A$  vs  $T$  at constant  $V$  is shown in Figure 16.3. The magnitude of the slope is smaller at lower temperatures than at higher temperatures, because entropy itself increases with temperature. Thus, curve bends downwards as opposed to the plot in Figure 16.2, which indicated upward curvature.

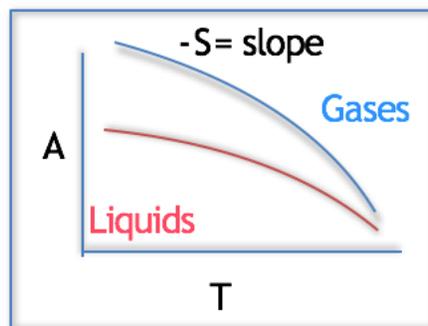


Figure 16.3 The decrease in Helmholtz free energy ( $A$ ) with increasing  $T$ , at a constant  $V$  (blue curve, gases). The plot is not linear, because  $S$  increases with increase in  $T$  at constant  $V$ . For the same reason the curve for liquids and solids will be less curved because entropy of gases increases with  $T$ , much faster than entropy increases for the condensed phases (red curve). This curve for the condensed phases is also lower than that of the gases for the same reason.

Thus, the Helmholtz free energy decreases with temperature, in an isochoric process and We know the plot is not linear because entropy is also a function of temperature, and increase in  $T$  at constant  $V$ , increases  $S$ , and hence, the curve will be downward. Even so, the plot must have a negative slope at every point on the curve and the slope keeps getting larger and larger with  $T$ .

We can distinguish between gases and the condensed phases, because gases have higher entropy than condensed phases (third law entropies) and the curve for gases at any temperature has higher curvature or negative slope than for condensed phases. (red curve). Slope at the beginning of the curve is smaller than the slope at the end of the curve, it decreases very rapidly for gases as compared to liquids.

Since the decrease in  $A$  is greater than or equal to  $w_{\text{total}}$ , less and less amount of work is extracted at higher and higher temperatures, an important insight.

#### 16.4.3 Pressure equilibrium

We will apply this understanding to mechanical equilibrium between two gas samples. Consider that there are two gas samples at different pressures that are separated by a movable wall, as in the steam box of a steam engine. Or, in the case of hurricane in the Atlantic where there is a pressure gradient with an imaginary wall separating the high-pressure and the low-pressure regions in the upper atmosphere.

Imagine that the gas is at higher pressure on left side of the wall (Figure 16.4) and lower pressure on the other side of the wall. Due to the pressure differential there will be a net force on the wall to move it from the high pressure side to the low pressure side, until the two pressures on either side of the wall are exactly the same. It achieves mechanical equilibrium and why does this process happen spontaneously?

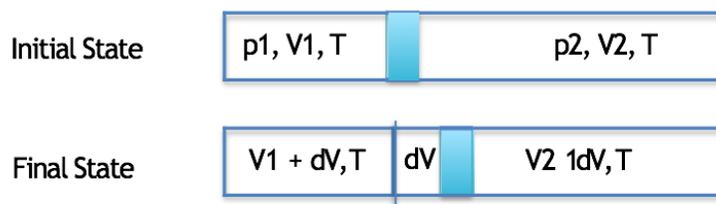


Figure 16.4 Mechanical equilibrium between two gas samples on either side of an imaginary wall separating two regions of a gas sample. If the pressure on the left is greater than the pressure on the right, then the gas at higher pressure will spontaneously expand and a decrease in Helmholtz free energy ( $A$ ) at constant  $T$ .

In the initial state ( $p_1$ ,  $V_1$ , and  $T$ , upper diagram, Figure 16.3) is converted to the final state ( $p_2$ ,  $V_2$ , and  $T$ ) at constant  $T$ , or isothermal expansion, and let  $p_1 > p_2$ . Let there be an infinitesimal expansion and the volume increase on the left side by  $dV$  inducing a decrease in pressure ( $- dp$ ).

On the right side of the wall the volume decreases ( $-dV$ ) and a final volume of  $V_2 - dV$  and a corresponding increase in pressure by  $dp$ . In the final state, the green separation has been moved to the right, so that volume on the left increases to  $V_1 + dV$  and there will be a corresponding drop in pressure,  $-dp$ . We will now analyze the change in  $A$  and decide if this process is spontaneous or not. If there is a decrease in  $A$ , then we know for sure that this is a spontaneous process and when the equilibrium is achieved,  $dA = 0$ .

Using the volume dependence of  $A$  at constant  $T$ , we write the following for the left side of the apparatus, where  $dA$  (left) is the change in  $A$  on the left side due to an infinitesimal change in volume as we expand.

$$dA (\text{left}) = -p_1 dV$$

Analogously, we write the change in Helmholtz free energy on the right due to compression, as the following.

$$dA (\text{right}) = -p_2 (-dV)$$

Therefore, total change in  $A$ , is the sum of the changes on the right and the left, and hence, we get the following (sign change due to parenthesis in the above expression).

$$dA (\text{total}) = (p_2 - p_1) dV$$

In the initial state,  $p_1 > p_2$ , the value in the parenthesis must be negative, and  $A$  must decrease as the expansion of the high-pressure region proceeds while compressing the low-pressure region. Thus, the expansion is a spontaneous process, and gases must flow from a high-pressure region to a low-pressure region, all by themselves. This is also our common observation in daily life. So, for a spontaneous process to occur  $dA < 0$  or  $-dA > 0$ , and hurricanes are driven by this change in the free energy of the system.

We can also predict when equilibrium will be achieved, that is  $A$  continues to decrease until there are no more changes in  $A$  or  $dA = 0$ . From the above equation, we predict that this will be the case when  $p_1 = p_2$  or when the two pressures on either side of the separation are equal. That is, hurricane ends when there is no detectable pressure gradient in the upper atmosphere. We also notice that blowing of the wind on the ground is due to the pressure gradient across the surface of the globe. This pressure gradient, in turn, is created by solar heating of the surface of the planet at the day-regions of the globe but not at night-regions. Similarly, there will be gradients across the equator to the poles as well caused by the seasons.

The above expression is also the condition for mechanical equilibrium, and is also the reason gases are uniformly distributed in a container. This was one of our assumptions in the Kinetic Theory of Gases as well, as we recall. Thus, we seem to have come a full circle but our analysis continues with Gibbs free energy, further. The latter is essential, because we want to keep both temperature and pressure constant in our experiments, for convenience, and test the conditions for spontaneity or equilibrium.

## 16.5 Properties of $G$

We will now examine the properties of Gibbs free energy and how  $G$  is related to important experimental variables such as volume, temperature, and pressure. This is important because it is convenient to hold  $T$  and  $p$  constant and measure  $G$  but  $G$  itself will a function of these variables. Thus, a full analysis of this important thermodynamic variable is in order, particularly because it can predict if a chemical reaction will occur or not, with certainty.

We use some calculus and common knowledge to pull this together. Using the definition of  $G$ , we first write it as a function of pressure, volume, and temperature in a rudimentary form. But this level of detail is not sufficient for further analysis. Thus, we write it in a differential form and then compare the terms with the exact differential of  $G$ , under specific sets of conditions. This way, we can readily obtain the various functions that we are interested in, as we did with the analysis of  $A$ , in the previous section. The details follow this strategy, as below.

$$G = U + pV - TS$$

In the differential form, we get multiple terms, two terms from each product, and write the following.

$$dG = dU + p dV + V dp - S dT - T dS$$

However, we recognize that we can replace  $U$  with  $q$  and  $pV$  terms (first law,  $pV$  work only) and test if we can simplify this long expression, a below.

$$dG = dQ_{Rev} - pdV + p dV + V dp - S dT - T dS \quad (dU = dq_{Rev} - pdV)$$

We use a reversible process, and use  $dq_{rev}$  and reversible  $pV$  work. This gives us a tidy relation, as following, after cancelling the  $pdV$  terms with opposite signs.

$$dG = dQ_{Rev} + Vdp - SdT - TdS$$

After a closer examination, we see recognize that second law tells us the  $dq_{rev} = T dS$ , and using this relation, we can simply cancel the first and the last terms on the right side to get the final expression.

$$dG = Vdp - SdT$$

$$-S = \left(\frac{\partial G}{\partial T}\right)_p$$

The last equation connects  $G$  with  $V$ ,  $p$ ,  $S$ , and  $T$  and this was obtained after substituting the first and the second law. We can now examine this in further detail, under constant pressure or constant temperature conditions, as in the case of  $A$ , for figure out how  $G$  depends on these two important experimental parameters, in the next section.

### 16.5.1 $G$ as a function of $p$ and $T$

To proceed further, we need tidy relations between  $G$  and  $T$ , and between  $G$  and  $p$ . This we achieve by comparing the above differential expressions with the exact differential of  $G$ . Because  $G$  is a state function we can write its exact differential in terms of changes in temperature and pressure, as following.

$$dG = \left(\frac{\partial G}{\partial T}\right)_p dT + \left(\frac{\partial G}{\partial p}\right)_T dp$$

The sum of the above two terms on the right give the total change in  $G$ . The first term is the contribution to  $G$  only due to the change in temperature, pressure being kept constant. As discussed earlier, this term is the rate of change of  $G$  with temperature multiplied by the change in temperature ( $dT$ ), at constant pressure.

The second term on the right is the change in  $G$  solely due to change in  $p$ , at constant temperature. This is the rate of change of  $G$  with respect to pressure multiplied by the change in pressure ( $dp$ ) at constant  $T$ . Thus, we split the total change in  $G$ , as equal to the sum of two different contributions, one from the temperature and the other due to pressure, for convenience. In the experiment also, it is convenient to vary one variable at a time to measure changes in the system.

We now compare the terms of the exact differential of  $G$  with the equation we got from the definition of  $G$  and the substitution of the first and the second laws. This is useful because the terms on the right of each equation have the  $dT$  term and then the  $dp$  term. Mathematically, their pre-terms must be identical, as we recognized before. That is the temperature term in both equations should be identical, so should the pressure terms. By this equality argument, we get the following two equations that we are after.

By comparing the temperature terms in both equations, we get the following, relating  $G$  with  $T$  at constant  $p$ .

$$\left(\frac{\partial G}{\partial T}\right)_p = -S$$

By comparing the pressure terms in both equations, similarly, we get the second equation, relating  $G$  with  $p$ , at constant  $T$ .

$$\left(\frac{\partial G}{\partial p}\right)_T = V$$

We will analyze these two new equations further, under more specific sets of conditions, in the next section.

### 16.5.2 G as a function of T, isobaric processes

Most of our transformations in the laboratory or in the environment around us take place under constant pressure conditions, and this is very convenient for evaluation. Thus, we ask how does G, the property that controls the spontaneity of chemical reactions or physical processes, depend on T at constant pressure (isobaric process). For example, we could change the temperature of our system to make the reaction go forward or make it go in the reverse direction. Thus, chemists rely on this property to adjust the propensity and the direction of chemical reaction at hand. Thus, a study of how G depends on T is of paramount importance.

The rate of change in G with temperature, at constant p, equals to -S, as given by the equation below.

$$\left(\frac{\partial G}{\partial T}\right)_p = -S$$

This immediately means that G decreases with temperature due to the negative sign on the right side of the equation and the slope of the plot of G vs T will be negative and equal to S (Figure 16.5).

#### Change in G with T, Constant p

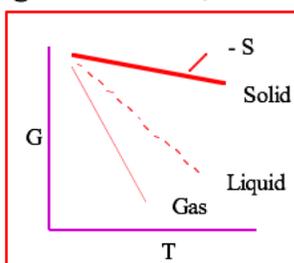


Figure 16.5 The decrease in Gibbs free energy (G) with increasing T, at a constant p (blue curve, gases). The plot is not linear, because S increases with increase in T at constant p. For the same reason, the curves for liquids and solids will be less curved, because entropy of gases increase with T, much faster than for the condensed phases (red curve). This curve for the condensed phases is also lower than that of the gases for the same reason. (replot, similar to 16.3)

### 16.5.3 Gibbs-Helmholtz Equation

Integration of the temperature dependence of G at constant pressure will give a function that will be useful to calculate value of G at any temperature, at constant pressure, but the integration is not straightforward. By examining the relation, we already obtained, below, we recognize that the slope of the rate of change of G with T involves entropy and entropy is a function of temperature itself. Thus, we need to write S in terms of variables that we could readily integrate and obtain G as a function of T.

$$\left(\frac{\partial G}{\partial T}\right)_p = -S$$

This path leads us to the famous Gibbs-Helmholtz equation and enthalpy is brought to rescue in this particular fashion. Using the relation  $G = H - TS$ , we replace S, as following.

$$G = U + pV - TS = H - TS$$

$$-S = (G - H)/T$$

$$\left(\frac{\partial G}{\partial T}\right)_p = -S = \frac{G - H}{T}$$

It is still not ready for integration and we simplify this further. We examine differential of G/T with respect to T at constant p, as following. We get two terms.

$$\left(\frac{\partial G/T}{\partial T}\right)_p = \frac{1}{T} \left(\frac{\partial G}{\partial T}\right)_p - \frac{G}{T^2}$$

Replacing the derivative of G with respect to T with (G-H)/T, we get the following simplified equation, after opening the brackets.

$$\left(\frac{\partial G/T}{\partial T}\right)_p = \frac{1}{T} \frac{(G-H)}{T} - \frac{G}{T^2} = -\frac{H}{T^2}$$

We recognize that  $d(1/T)$  is  $(-1/T^2)dT$ , and replacing  $dT$  with  $d(1/T)$  we get the final equation.

$$\left(\frac{\partial G/T}{\partial 1/T}\right)_p = H$$

So, we can treat G over T as a variable as a function of  $1/T$ , and if H is a constant, we can integrate this expression readily. We have seen that H is only weakly dependent on temperature and hence, this assumption is not difficult at all.

Plot of G/T vs  $1/T$  gives a straight line, over a short interval of temperature, with a positive slope equal to H (Figure 16.6). It gives us the rate of change of G/T with respect to  $1/T$ .

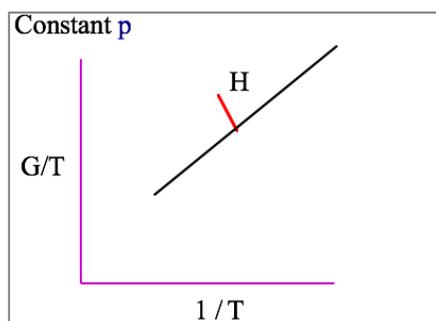


Figure 16.6 Plot of G/T as a function of  $1/T$ , at constant p (red line). The plot is linear over a short interval of time with slope equal to H. Thus, G/T increases with  $1/T$ .

Although this is not exactly what we wanted, this is a form to examine how G varies with temperature. We adopt this equation, measure  $\Delta H$  or  $\Delta G$  in the following form.

$$\left(\frac{\partial \Delta G/T}{\partial 1/T}\right)_p = \Delta H$$

By measuring  $\Delta G$  as a function of temperature, we can obtain  $\Delta H$  or by measuring  $\Delta H$  either by calorimetric measurements or by equilibrium measurements at a series of temperatures, we can determine  $\Delta G/T$ . Thus, we found a method to determine how G and  $\Delta G$  depend on temperature and this is a key relation in thermodynamic analysis of equilibria or chemical reactions of interest.

In summary, we looked at the temperature dependence of G. But it is complicated as it involves entropy and found an alternate route where we can examine G/T or  $\Delta G/T$  as a function of  $1/T$ . This relates free energy changes with enthalpy changes via temperature, at constant pressure, which turns out to be very useful.

#### 16.5.4 G as a function of p, ideal gas

Examining the expression below connecting G and p at constant T, indicates that the slope of the plot will be positive and equal to the volume of the ideal gas.

$$\left(\frac{\partial G}{\partial p}\right)_T = V$$

A plot of  $G$  vs  $p$  at constant  $T$ , should give a plot with a positive slope equal to  $V$  and since  $V$  is also a function of  $p$ , the plot will be non-linear but still the slope will be positive (Figure 16.7).

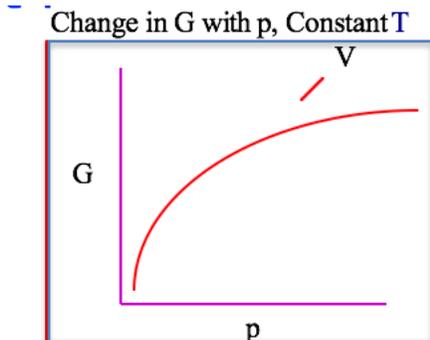


Figure 16.7 The increase in Gibbs free energy ( $G$ ) with increasing  $p$ , at a constant  $T$  (red curve, gas). The plot is not linear, because the slope is  $V$ , which also increases with increase in  $p$  at constant  $T$ . Integration of the expression for an ideal gas gives the logarithmic function shown here where the slope is still positive but equals to  $nRT$ .

We gain further insight into this expression by integrating it with appropriate limits so that we can calculate  $G$  at any pressure  $p$  (2) when we know its value at a standard pressure (1). Rearrangement of the above terms gives us the following integral.

$$\Delta G = \int_1^2 V dp$$

We attempt to integrate this equation, unlike the previous ones, and encounter that  $V$  itself is function of pressure for an ideal gas, not a constant. However, we can integrate this by replacing  $V$  with  $nRT/p$  where  $T$  is still a constant.

$$\Delta G = nRT \int_1^2 (1/p) dp$$

Instead of integrating between the two states 1 and 2, we will make it more relevant to our experimental conditions, where we start conveniently at atmospheric pressure ( $p_0$ ) and raise or lower the pressure to some other value,  $p$ . Integration with these new limits will appear as following.

$$\Delta G = nRT \int_{p_0}^p (1/p) dp$$

Upon integration, we get the logarithmic function because of  $p$  being in the denominator on the right, and it looks like this.

$$\Delta G = G_p - G_{(T)}^0 = n R T \ln(p/p_0)$$

### 16.5.5 Standard Gibbs free energy, ideal gas

We have written the limits  $G_p$  and  $G_o(T)$  corresponding to the limits  $p$  and  $p_0$  where  $p_0 = 1$  atm, at temperature  $T$ . A plot of  $G$  vs  $p$  shows a logarithmic growth with a positive slope of  $V$  at every point, and  $G$  increases with  $p$  (Figure 16.8) and the intercept is 0.

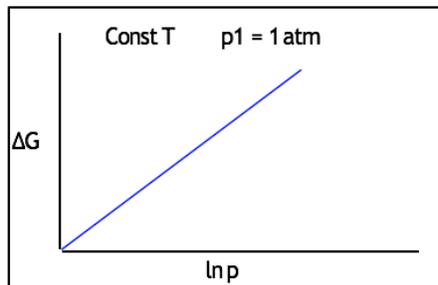


Figure 16.8 Plot of  $\Delta G$  vs  $\ln p$  for an ideal gas with a slope equal to  $nRT$ .

$$\Delta G = G_p - G_{(T)}^0 = n R T \ln(p/1 \text{ atm})$$

$$G_p = G_{(T)}^0 + n R T \ln(p/1 \text{ atm})$$

When the lower limit is 1 atm, then we have the ratio of the pressure at  $p$  to that of 1 atm, thus cancelling the units in the  $\ln$  term, which is required mathematically. The plot has an intercept of 0 because of this lower limit being 1 atm. Know  $G$  value at 1 atm and temperature  $T$ , we can calculate  $G$  at any other pressure and temperature  $T$ .

$$\Delta G = G_p - G_{(T)}^0 = n R T \ln(p_2/1 \text{ atm})$$

In the above equation  $G_{(T)}^0$  is the standard free energy at 1 atm pressure and it is a function of  $T$ .

For solids and liquids, we can ignore the change in the volume over a reasonable range of pressures because the coefficient of compressibility is too small, and we integrate the expression directly with limits  $p_0$  and  $p$ .

$$\Delta G = \int_{p_0}^p V dp$$

$$\Delta G = G_p - G_{(T)}^0 = V (p_0 - p)$$

### 16.5.6 Standard Gibbs free energy and fugacity

Because  $G$  is such an important property for us, we extend it to the discussion of real gases. Instead of worrying about which equation of state to use, we simplify the approach and introduce a new function called fugacity. Fugacity is to real gases as pressure is to the ideal gas. We simply replace pressure with fugacity and obtain expression for  $\Delta G$  for real gases, as below. Fugacity has units of atm, and we write the corresponding expression real gases, as below.

$$\Delta G = G_p - G_{(T)}^0 = n R T \ln(f/1 \text{ atm})$$

Here,  $f$  is the fugacity, and it simply includes all non-ideal behavior of the gas into this term. We can write  $\log$  of fugacity as equals to  $\log$  of pressure and the compressibility factor ( $Z$ ).

$$\ln f = \ln p + \int_0^p \left( \frac{Z-1}{p} \right) dp$$

$Z < 1$  below the Boyle temperature, then  $(Z-1)/p$  is negative, and fugacity is less than gas pressure. Above the Boyle temperature  $Z > 1$ , and fugacity is greater than gas pressure.

In summary, we looked at the pressure dependence of  $G$ . It involves  $V$  and integration of this expression is straight forward for an ideal gas or for condensed phases.  $G$  increases with  $p$ , and this is the reason gases expand spontaneously from high-pressure to low-pressure region. Accommodation is made for real gases by introducing fugacity, which is the equivalent to pressure of the ideal gas. Fugacity can be either greater than the gas pressure or less than the gas pressure, depending on the value of the compressibility factor. The latter depends on temperature, and hence, a thorough analysis is possible.

## 16.6 Equations of life

We write certain useful equations, as extensions of what we derived in this chapter, and these are useful for additional discussions of free energy terms. We begin with internal energy and write it under constant pressure conditions, when all work is only pV work.

$$U = q - pV$$

We then, express enthalpy in terms of internal energy, as following.

$$H = U + pV$$

From the definition of Helmholtz free energy, we write the following.

$$A = U - T S$$

From the definition of Gibbs free energy, we write the following, after substituting for A and then replacing U + pV with H.

$$G = A + p V = U - T S + p V$$

$$G = H - T S$$

$$G = U + pV - T S = A + pV$$

### 16.6.1 Combination of the first and the second laws

Substituting the second law into the first law, we get a very powerful relation which is often the starting point for the derivation of many thermodynamic relations (reversible process, pV work only, constant p).

$$dU = dq_{rev} - p dV$$

$$T dS = dq_{rev}$$

Combining the above two equations, we get the powerful relation, shown below.

$$dU = T dS - p dV$$

Complete differentiation of H and substituting dU, we get the expression below.

$$H = U + pV$$

$$dH = dU + p dV + V dp$$

Substituting for dU, we get a simpler relation.

$$dH = T dS - p dV + p dV + V dp$$

$$dH = T dS + V dp$$

Complete differentiation of A and substitution for dU, compact expression for dA is obtained.

$$A = U - T S \quad dA = dU - T dS - S dT$$

$$dA = T dS - p dV - T dS - S dT$$

$$dA = -p dV - S dT$$

Complete differential of G, and substitution for dU gives the following.

$$G = H - T S = U + p V - T S$$

$$dG = dU + p dV + V dp - T dS - S dT$$

$$dG = V dp - S dT.$$

In summary, we got the following equations that are useful for problem solving.

$$dU = dq + dW$$

$$dU = dQ_{rev} - p dV$$

$$\begin{aligned}
 dS &= dQ_{rev}/T \\
 dU &= T dS - p dV \\
 dH &= T dS + V dp \\
 dA &= -p dV - S dT \\
 dG &= V dp - S dT
 \end{aligned}$$

Finally, we write the exact differentials of the state functions to complement the above relations.

$$\begin{aligned}
 dU &= \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT \\
 dH &= \left(\frac{\partial H}{\partial p}\right)_T dp + \left(\frac{\partial H}{\partial T}\right)_p dT \\
 dS &= \left(\frac{\partial S}{\partial p}\right)_T dp + \left(\frac{\partial S}{\partial T}\right)_p dT \\
 dS &= \left(\frac{\partial S}{\partial V}\right)_T dV + \left(\frac{\partial S}{\partial T}\right)_V dT \\
 dA &= \left(\frac{\partial A}{\partial V}\right)_T dV + \left(\frac{\partial A}{\partial T}\right)_V dT \\
 dG &= \left(\frac{\partial G}{\partial T}\right)_p dT + \left(\frac{\partial G}{\partial p}\right)_T dp
 \end{aligned}$$

### 16.6.2 Cross Rule/Maxwell's Equations

The above thermodynamic relations are used with the cross rule to write additional equations (Maxwell's equations), shown below. Please consult your mathematics primer to learn about the cross rule. The fundamental equation and the corresponding result of applying the cross rule are demonstrated below.

$$\begin{aligned}
 dU = TdS - pdV &\rightarrow \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V \\
 dH = TdS + Vdp &\rightarrow \left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p \\
 dH = -pdV + SdT &\rightarrow -SdT - \left(\frac{\partial p}{\partial T}\right)_V = -\left(\frac{\partial S}{\partial V}\right)_T \\
 dG = Vdp - SdT &\rightarrow \left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T
 \end{aligned}$$

All the above equations are applicable to a variety of circumstances, their memorization is not recommended, they all can be derived from the first and second laws, and we must be careful to apply them but be aware of how we derived them.

### 16.7 Standard $\Delta G$ of Formation

The Gibbs free energy of formation is the difference in the free energies of the molecule and its corresponding elements. Standard free energy is measured at 1 atm, at a specified temperature.

$$\Delta G_f^0(\text{any compound}) = \Delta G_{products}^0 - \Delta G_{reactants}^0$$

### 16.8 Molecular interpretation and applications in daily life

#### Molecular interpretation

Gibbs free energy successfully predicts the direction of a process, under constant temperature and pressure conditions. The system likes to lose this kind of energy, and the products are more stable with respect to this kind of energy, compared to the reactants, when the reaction occurs in the forward direction. So, we ask what is this energy at the molecular level? This is the difference in energy between enthalpy and TS energy. We consider enthalpy as the total amount of energy a molecule and the energy needed to create the space for it to exist. TS is the energy related to the randomness of the system and hence, G is the intrinsic energy of making the system minus this penalty of energy associated with the randomness of the system. The energy associated with the randomness is a penalty because this term has the negative sign. Thus, we realize that when we take a certain molecule with all its potential and kinetic energy associated with its structure and motion, and convert one molecule to another molecule, we expend some of the intrinsic energy (H) but certain amount of penalty applies. This comes in the form of TS energy. It appears that all of enthalpy is not available for this conversion. That is the TS energy. Thus, simply decreasing the enthalpy of the molecule is not sufficient to drive a reaction, we must also pay a penalty in terms of the entropy change and when the sum of these two expenditures are met, the reaction can progress. Thus, the reactions can be enthalpy controlled ( $\Delta H$  over compensates for the penalty) or entropy controlled (entropy change dominates) or controlled by both or both contribute to the propensity of the chemical reaction. In simple terms, TS energy is very important for controlling the direction of the process, which is often not discussed in chemistry. Thus, when a chemical reaction or a physical process occurs spontaneously, the energy reserves of the molecule are used to some extent to lower its enthalpy sufficiently to overcome any unfavorable decreases in entropy.

### Applications in daily Life

The three laws are foundation stones for our discussions of thermodynamics and their applications in real life as well as in practical applications or fundamental arguments or gaining a better understanding of the world around us. The decrease in free energy (G or A) is essential to drive the natural processes occurring around us. Thus, when an apple falls from the tree, under constant p and T conditions), the Gibbs free energy is decreasing and the reverse process must increase this free energy which is not a spontaneous process. Thus, if we measure this change in this kind of energy which the enthalpy energy less the entropy energy, we can determine if the system will move forward or in the reverse direction. We designed several experimental methods to measure this energy directly without examining the surroundings.

When the stone rolls down the hill and reaches the valley below, it is lowering this kind of energy and the reverse process raises G. Thus, measurements of G or A are essential in our understanding of natural processes and this analysis explains why natural processes are natural!

#### 16.8.1 Units and worked out examples

##### Units

Both A and G have the units of energy, ergs, joules, calories etc.,.

##### Worked out example

1. Discuss the change in Gibbs free energy when gasoline burns in the cylinders of the car and the crank shaft turns propelling the car forward or in reverse.

We define the cylinder with fuel, before the spark plug ignites, as the system and the boundary of the gas separating the surroundings from the system. We choose this as an open system so that we can add the fuel, spark the plug and allow the work to appear at the boundary of the system as the piston moves to expand the burning gases. Some heat is transferred to the surroundings. The burning of the gases is spontaneous because the G of the products which is mostly carbon dioxide is lower than the G of the reactants, gasoline and oxygen. Thus, there is a decrease in the value of G, as this process occurs and the run of our car is also a spontaneous process. That is, when we remove the foot from the brake pedal and apply it to the accelerator, gas is pumped into the cylinders and work is produced to move the car forward or in reverse depending on the gear shift.

2. Calculate  $\Delta G$  when a gas of 1 mol expands from an initial pressure of 5 atm to a final pressure of 1 atm, at 300 K.

$$\Delta G = G_p - G_{(T)}^0 = n R T \ln(p_2/p_1)$$

$$= 1 \text{ mol } (8.3 \text{ J K}^{-1} \text{ mol}^{-1}) 300 \text{ K } \ln (1 \text{ atm} / 5 \text{ atm}) = - 1 \times 8.3 \times 300 \times 1.60 \text{ J}$$

### 16.8.2 Key points and terms

#### Key points

1. The free energy is an important concept in chemistry and Helmholtz free energy is a measure of all the work that can be extracted from a system under T conditions, while Gibbs free energy is a measure of all the work that can be extracted, other than pV work, under constant p and T conditions.
2. The natural processes that we witness around us driven by a decrease in G and they stop when no further decrease in G is possible.
3. Equilibrium is achieved when  $\Delta G = 0$ .
4. G decreases with decrease in p at constant temperature.
5. G depends on both H and S, as  $G = H - TS$  or  $\Delta G = \Delta H - T\Delta S$ .
6. G decreases with increase in volume at constant T.
7. The dependence of G on T is more complicated to study because this depends on entropy but a work around gives the Gibbs-Helmholtz equation.
8. We arrived at large number of key thermodynamic equations that originated by combining the first and the second laws of thermodynamics.

#### Key terms

Helmholtz free energy, Gibbs free energy

### 16.8.3 Graphing Assignment

Plot H vs U, H vs T, H vs p and H vs q for the Carnot cycle.

### 16.9 Further Reading

1. <https://ocw.mit.edu/courses/chemistry/5-60-thermodynamics-kinetics-spring-2008/video-lectures/lecture-13-gibbs-free-energy/>

2. <https://ocw.mit.edu/courses/chemistry/5-111-principles-of-chemical-science-fall-2008/video-lectures/lecture-18/13.6>

### 16.10 Self Tests

1. Gibbs energy of a liquid decreases with temperature, at constant pressure,  $(\partial G/\partial T)_p$  is  
a.  $>0$       b.  $<0$       c.  $=0$       d. None of these
2. Rate of change in Gibbs energy with pressure, at constant temperature, for a liquid is  
a. greater than that of the vapor   b. less than that of the vapor   c. about the same as the vapor   d. None of these
3. Standard state of a real gas is a  
a. hypothetical state      b. state when  $p \rightarrow 0$       c. non-equilibrium state   d. None of the above
4. Chemical potential of a solid, at constant pressure,  
a. increases with temperature      b. decreases with temperature      c. independent of temperature  
d. None of the above
5. Gibbs energy of a liquid, at constant temperature, increases with pressure. This statement is  
a. True      b. false      c. Can't say
6. Given  $(\partial G/\partial T)_p = G - H/T$ ,  $(\partial(G/T)/\partial T)_p$  is  
a.  $-H/T$       b.  $-H^2/T$       c.  $-H/T^2$       d.  $H/T^2$       e.  $T^2/G - H$

1b;2b;3d;4b;5a;6c;7c;8a;9b;10b

1. A given chemical reaction will be spontaneous if the change in the Gibbs energy accompanying the reaction is
- a. =0      b. >0      c. <0      d. none of the above
2. If  $df$  is the progress of the reaction, then the change in mole numbers of A in the following chemical reaction is
- $n_1 A + n_2 B \longrightarrow n_3 C + n_4 D$
- a.  $n_1 df$       b.  $-n_1 df$       c.  $n_2 df$       d.  $-df$       e. none of the above

**17 Chemical Potential**

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## Summary

The Gibbs free energy will be examined as a function of the mole numbers of the substance to obtain yet another state function, chemical potential ( $\mu$ ). Chemical potential of a substance in a mixture of substances provides a practical description of the Gibbs free energy changes for a chemical reaction. This is because chemical reaction is often times involves mixtures and the mole numbers of the reaction components change as the reaction takes place. Chemical potential will be examined as a function of concentration, pressure, and mole fraction. The entropies, enthalpies and volume of mixing will be examined along side the chemical potential of mixtures.

## Goals

Investigation of how  $G$  varies with composition is the main goal in this chapter. Since chemical reactions involve mixtures, even when a single reactant is considered the progress of the reaction produces a mixture of the reactant and at least one product, not in their pure forms. Thus, we will examine the rate of change of free energy with mole numbers for a given substance and examine how that varies as the composition of the mixture changes, or when there is a change in pressure. The changes in entropy, enthalpy, and volume for the mixture formation will be quantified.

### 17.1 Why Study this?

Most chemical reactions occur in finite proportions. Certain moles of  $A$  react completely with certain moles of  $B$  completely to give rise to exactly certain moles of products  $C$ ,  $D$  *et cetera*. Therefore, instead of using free energy per gram or per kilogram, it's more convenient for chemists to use free energy per mole. By this convention, we can measure  $\Delta G$  of the reaction by simply subtracting the molar free energies of reactants multiplied by their stoichiometries from the molar free energies of products multiplied by their respective stoichiometries. Thus, molar free energy is useful as another state function, and it has high significance, not just a mathematical convenience. We also recognize that while  $G$  is useful to study pure substances, chemical reactions require the analysis mixtures and hence, we need to examine how  $G$  varies with composition. Therefore, chemical potential is a key parameter that we use in determining the propensity of a chemical reaction and its direction.

Even when we start with single, pure, reactant the chemical reaction renders it impure as time progresses to make even a single product. AS the reaction progresses by an infinitesimal amount, we have a mixture of a small amount of product in a large amount of reactant and as the reaction continues, the composition of that mixture keeps changing till the reaction is complete, and in the end, we still have a mixture of products, or products and leftover reactants. Thus, we need to take into consideration that formation of a mixture is a fundamental process in the progress of a chemical reaction. Oftentimes you start the chemical reaction with a mixture of reactants and end up with a mixture of products and there may be some leftover reactants. So oftentimes we're dealing with mixtures of substances. Thus, we examine the thermodynamic parameters in the context of a mixture to accurately assess the spontaneity of a chemical reaction.

### 17.2 Chemical Potential

The rate of change of Gibbs free energy with composition is the chemical potential of the substance and it varies with the composition of the mixture. That is, we now examine  $G$  as a function of mole numbers and hence, we can immediately write the exact differential for  $G$  using the mole numbers of the various reaction components. These may be reactants or products or a mixture of them. Thus, change in  $G$  with respect to the changes in the mole numbers of the reaction components ( $n_1, n_2, n_3, \dots$ ) are written in the following manner.

$$dG = \left(\frac{\partial G}{\partial T}\right)_{p, n_1, n_2, \dots} dT + \left(\frac{\partial G}{\partial p}\right)_{T, n_1, n_2, \dots} dp + \left(\frac{\partial G}{\partial n_1}\right)_{p, T, n_2, n_3, \dots} dn_1 + \dots$$

By writing the above, we assume that all work is of  $pV$  work, as the reaction progresses, and we have already examined the first and the second terms in the previous sections. The remaining terms need explanation.

The third term is similar to the fourth and the rest of the terms in our sum and hence, a discussion of the third term can be applied with suitable changes to these other terms. It simply is the rate of change in the

free energy with respect to the mole numbers of component 1 when we keep  $p$ ,  $T$  and the mole numbers of all other components are kept constant, multiplied by the change in the mole numbers of component 1 ( $dn_1$ ). The next term involves the rate of change in  $G$  with respect to  $dn_2$  multiplied by  $dn_2$ , at constant  $p$ ,  $T$ , and when all the other mole numbers are kept constant. Thus, the exact differential is written as a rate of change with respect to the composition of the mixture,  $p$  and  $T$ . At constant  $p$  and  $T$ , the first two terms are reduced to zero and we get the following.

$$dG = \left( \frac{\partial G}{\partial n_1} \right)_{T,p,n_2,\dots} dn_1 + \left( \frac{\partial G}{\partial n_2} \right)_{T,p,n_1,\dots} dn_2 \dots$$

To simplify writing this long equation, we introduce the new state function ( $\mu$ ) as the rate of change in  $G$  with respect to the mole numbers of the substance of interest, while all other mole numbers,  $T$ , and  $p$  are kept constant.

$$\mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{T,p,n_1,\dots, \text{except } n_i}$$

Now, we immediately obtain the following sum.

$$dG = \mu_1 dn_1 + \mu_2 dn_2 + \mu_3 dn_3 \dots \sum \mu_i dn_i$$

In the above,  $\mu_i$  is the chemical potential of the  $i$ th term and change in  $G$  with respect to the change in the composition (mixture) is defined. Now, we examine the behavior of chemical potential. First, we examine a chemical potential and then the rates of changes of other thermodynamic properties with the composition of a mixture.

Plot of  $G$  vs  $n_i$  when all other variables are kept constant (Figure 17.1) provides us with the chemical potential of the  $i$ th component. The slope of the tangent drawn at any point corresponding to a given value of  $n_i$  is  $\mu_i$ . Since  $G$  or  $n_i$  can't be negative, we surmise that the slope of the tangent at any point will always be  $> 0$ . As  $\mu$  is the rate of change in  $G$  with respect to  $n_i$ , it is also the molar free energy or it is the change in the free energy of the mixture when one mole of component  $i$  is added to a large mixture such that the change in the mole numbers of the system is negligible. It is analogous to adding one mole of sodium chloride to an ocean of water and measuring the change in the free energy. Since the ocean has a large number moles of sodium chloride, the change in the concentration of salt in the ocean is negligible by this act but the change in the free energy of the ocean due to the addition of this additional sodium chloride is the chemical potential.

Change in  $G$  with  $n$ , Constant  $T, p$

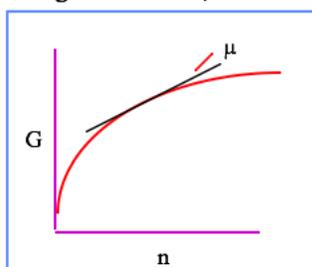


Figure 17.1 Change in the free energy as a function of the mole numbers, at constant  $T$ ,  $p$ , and  $V$  (red curve). The slope of the tangent (black line) at any point gives the corresponding chemical potential of the substance.

We arbitrarily chose a curve in the above plot, but it need not be a curve or a curve of this type but it should have positive slope at each point and  $G$  should vanish when  $n = 0$ . When  $\mu$  is independent of  $n$ , the plot will be linear with a positive slope. Plot of  $G$  for a mixture will be a multi-dimensional surface with variables of  $T$ ,  $p$ ,  $V$ , and all the mole numbers of the mixture.

In summary, we defined chemical potential as  $G$  over  $N$  or as the rate of change of free energy with mole numbers.

### 17.2.1 Gibbs free energy of a mixture

The above definition of chemical potential provides us with a unique opportunity to compute the total  $G$  of a mixture at constant  $T$ ,  $p$ , and  $V$  by simply integrating the above expression with appropriate limits. Let us assume that all the mixture of volume  $V$  is enclosed inside a sphere of finite diameter. The shape is chosen for convenience of integration, and final result will be independent of the shape of the container (Figure 17.2).

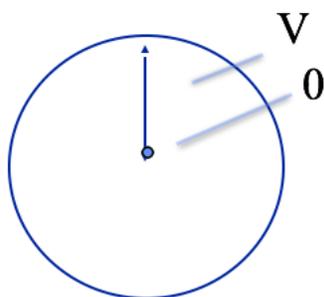


Figure 17.2 The integration sphere of volume  $V$  to obtain the  $G$  of the mixture. The lower limit of the integration is the point at the center with zero volume and the final limit is the total volume,  $V$ .

At constant temperature and pressure, we wrote the following for the change in  $G$  when the composition is changing. Now we integrate this expression with proper limits to get the free energy of the mixture.

$$\int dG = \int \sum \mu_i dn_i = \mu_i \int \sum dn_i$$

When the chemical potentials of all the components in the mixture are a constant then we can take that out of the integral. You have total volume  $V$ . and we start with zero volume and then increase the volume to  $V$ , so that we can enclose the entire mixture within this volume,  $V$  (Figure 17.2). The left side is  $G$  of the mixture minus  $G$  of 0 volume. Integration of  $dn_i$  from  $V = 0$  to  $V$  gives  $n_i$ , and  $\mu_i$  is a constant.

$$G_{mixture} - 0 = \int \sum \mu_i dn_i = \sum \mu_i n_i$$

$$G_{mixture} = \sum \mu_i n_i$$

Gibbs energy of a mixture is simply the sum of the products of the chemical potentials and their respective mole numbers. We recognize that the value of  $G$  depends on the mole numbers as well as the chemical potentials of the substances in the mixtures and we dig a bit deeper into the nature of the chemical potential. For example, we examine how the chemical potential of a pure substance depends on its concentration.

In summary, we showed that the chemical potential of the mixture is the sum of chemical potentials of individual components of the mixture weighted by their respective mole numbers.

### 17.2.2 Chemical potential as a function of pressure

As  $G$  is a function of pressure, at constant temperature, so will be chemical potential and as a chemical reaction progresses, there could be a change in the pressure of the system. We start with equation for  $G$  and work our way toward the chemical potential.

$$dG = V dp - S dT$$

$$dG = V dp$$

Integrating this expression with the limits of  $p$  and 1 atm, we get the following for an ideal gas.

$$\Delta G = n R T \ln(p/1 \text{ atm})$$

We recognize that  $\mu = (G/n)$  and use that to write the following relation between chemical potential and pressure.

$$\mu - \mu^0 = RT \ln(p/1 \text{ atm})$$

Here,  $\mu^0$  = chemical potential at 1 atm, and  $\mu - \mu^0$  is the change in the chemical potential as we change the pressure, and chemical potential increases as logarithm of pressure with a slope equal to  $RT$  (Figure 17.4), just as  $\Delta G$ .

$$\mu = \mu^0 + RT \ln p$$

A plot of  $\mu$  versus  $\ln p$  (Figure 17.3) has an intercept of  $\mu^0$  on the Y-axis, which corresponds to the chemical potential at 1 atm.

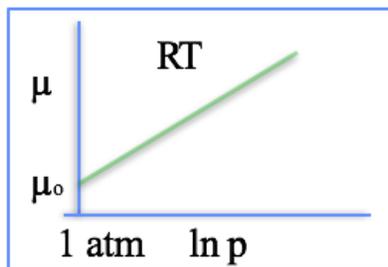


Figure 17.3 Chemical potential of an ideal gas as a function of pressure. The slope is equal to  $RT$  and the Y-intercept is the chemical potential at 1 atm.

For real gases, we simply replace pressure with fugacity, and get the following.

$$\mu = \mu^0 + RT \ln f$$

In summary, the chemical potential of a pure substance increases with pressure and hence, the reverse process (expansion) is spontaneous.

### 17.2.3 Chemical potential as a function of concentration

We ask what drives mass transport across a concentration gradient of a solute dissolved in a suitable solvent? These are gases but the topic will be useful later. Consider container A that has a concentrated solution of substance in container A and a dilute solution in container B. Let the two containers be connected with a stop cock and when it is open both solutions are mixed (Figure 17.4) and the solute will diffuse from higher concentration to low concentration spontaneously. We will analyze this using chemical potential.

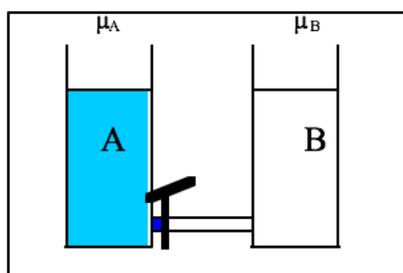


Figure 17.4 (modify) Container A (left) with a solution of higher concentration of a solute is brought in contact with another container B (right) that has a lower concentration of the same solute and both are connected but separated with a stop cock. When they are connected the solute moves from the high concentration region to the low concentration region, spontaneously.

Let  $\mu_A$  and  $\mu_B$  be the chemical potentials of the regions A and B, and let  $dn$  moles ( $> 0$ ) of the substance move from region A to region B when the stop cock is opened. Region A loses  $dn$  moles and region B gains  $dn$  moles. The change in the free energy of the system  $dG$ , is given by the following.

$$dG = \sum \mu_i dn_i = \mu_A (-dn) + \mu_B dn = (-\mu_A + \mu_B) dn$$

The first term in the sum has the negative sign for the mole numbers because region A is losing the material and the second term has a positive sign for change in mole numbers because the region B is gaining these mole numbers.

For the flow of the spontaneous transfer of the substance from left to right,  $dG$  must be less than zero. Then, we can write the following.

$$(-\mu_A + \mu_B) dn < 0$$

Since  $dn$  is not less than 0, we conclude that the chemical potential of region B should be less than that of region A.

$$(-\mu_A + \mu_B) < 0$$

$$\mu_B < \mu_A$$

Therefore, we conclude that substances move from a region of higher chemical potential to region of lower chemical potential. The transfer will continue till the chemical potentials of the two regions are the same, then  $dG = 0$ , and equilibrium is achieved.

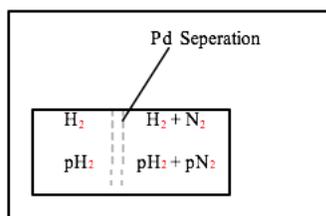
$$\mu_B = \mu_A (\text{equilibrium})$$

In summary, we showed that the chemical potentials of any two phases in equilibrium are equal and that substances are more uniformly distributed in the medium over time. Components move from high concentration regions to low concentration regions spontaneously, the same way as gases move from high pressure to low pressure regions spontaneously.

#### 17.2.4 Chemical potential of an ideal gas in a mixture of ideal gases

From above we recognize that when two phases are in equilibrium their chemical potentials are equal. This condition is exploited to determine the chemical potential of an ideal gas in a mixture of ideal gases, in terms of the chemical potential of the pure ideal gas and the partial pressure of that gas in the mixture. For this purpose, we need to set up an experiment where the pure gas is in equilibrium with its component in the mixture.

Consider pure hydrogen in a container separated from nitrogen gas separated by a Pd membrane. Initially, the two gases are in pure state, and let them be at 1 atm pressure (Figure 17.5). As time progresses, some of the hydrogen gas dissolves in the Pd membrane forming a solid-gas solution. This happens as the chemical potential of the hydrogen gas lowers due to its dissolution in Pd and reduction in pressure. The chemical potential of Pd also lowers due to the formation of the solid-gas solution. But the hydrogen gas on the left soon forms an equilibrium with the gas dissolved in the Pd membrane. Now, the hydrogen gas in the Pd membrane can escape into the nitrogen gas on the other side and occupy additional volume. This process continues till the chemical potential of the hydrogen gas mixed with the nitrogen gas is the same as that of the hydrogen-saturated Pd-hydrogen solid solution.



**Figure 17.5** Pure hydrogen gas in equilibrium with a mixture of hydrogen and nitrogen separated by Pd membrane which is permeable to hydrogen but not to nitrogen. The two hydrogen samples have the same chemical potential at equilibrium.

The pressure of pure hydrogen would have decreased by this equilibration, and the partial pressure of hydrogen in the mixture increased from zero to certain value, proportional to its mole fraction in the mixture. When the system reaches equilibrium, the chemical potential of the pure hydrogen gas on the left is equal to that of the solid solution which is also equal to the chemical potential of the hydrogen present in the nitrogen. Therefore, chemical potential of pure hydrogen on the left is equal to the chemical potential of hydrogen on the right, in the mixture, then we write the following.

$$\mu_{(\text{hydrogen, mix})} = \mu_{(\text{hydrogen, pure})}$$

We write  $\mu$  of pure hydrogen in terms of its value at one atmosphere and its pressure  $p$ .

$$\mu_{(\text{hydrogen, pure})} = \mu_{(\text{hydrogen, pure})}^0 + R T \ln p$$

Then, we can write the chemical potential of the hydrogen in the mixture in terms of the chemical potential of the pure hydrogen and its pressure ( $p_{\text{hydrogen,pure}}$ ), as following.

$$\mu_{(\text{hydrogen,mixture})} = \mu_{(\text{hydrogen, pure})}^0 + R T \ln p_{(\text{hydrogen, pure})}$$

At equilibrium, the pressure of pure hydrogen ( $p_{\text{hydrogen, pure}}$ ) on left side of the membrane should be the same as the partial pressure of hydrogen on the right side of the membrane ( $p_{\text{hydrogen, mixture}}$ ), the mixture. The partial pressure is then write in terms of its mole fraction and total pressure of the mixture, as below.

$$p_{(\text{hydrogen,pure})} = p_{(\text{hydrogen,mix.})} = X_{\text{H}_2} p_{\text{total}}$$

The chemical potential of the hydrogen in the mixture is then written in terms of the chemical potential of hydrogen in the pure state, total pressure ( $p_{\text{total}}$ ) of the gas mixture and the mole fraction of hydrogen in the mixture, as following.

$$\mu_{\text{H}_2(\text{mixture},T,p)} = \mu_{\text{H}_2(\text{pure})}^0 + R T \ln p_{\text{total}} + R T \ln X_{\text{H}_2}$$

One final adjustment is to recognize that the first two terms on the right can be replaced by chemical potential of pure hydrogen when kept under the total pressure and the mole fraction of hydrogen in the mixture.

$$\mu_{\text{H}_2(\text{mixture},T,p)} = \mu_{\text{H}_2(\text{pure},p,\text{total})} + R T \ln X_{\text{H}_2}$$

We immediately recognize that the second term on the right side is less than zero, because mole fraction of hydrogen is less than 1, and hence, chemical potential decreases when a mixture is formed. Thus, formation of a mixture of ideal gases is facilitated by decrease in chemical potential.

For simplicity, we write  $\mu^*$  for the chemical potential of the pure substance while  $\mu$  is used to denote that of a component in a mixture.

$$\mu_i = \mu_i^* + R T \ln X_i$$

$$\mu^* = \mu_{\text{pure}}$$

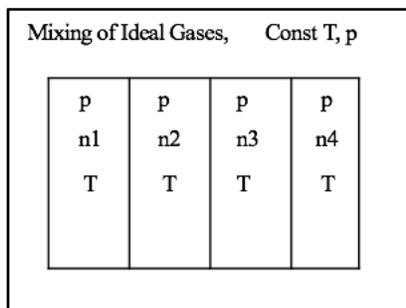
We remind ourselves that  $\mu_i$  and  $\mu_i^*$  are under the same pressure, total pressure, chemical potential of the mixture is less than the chemical potential of the pure substance. So, substances spontaneously mix, making it a natural process.

In summary, we showed that the chemical potential of an ideal gas in the mixture is less than that of its pure form, under the same  $p$ ,  $T$ , and  $V$  conditions.

### 17.2.5 Chemical potential of mixing

We now use the above expression connecting the free energy of a component in a mixture with free energy of the corresponding pure component and compute the free energy change when gases are mixed. This is different from the free energy of the mixture, which we discussed earlier. Chemical potential of mixing is required for our discussions of chemical reactions, because reactions are always accompanied by mixing, either before (multiple reactants) or during the reaction (single reactant). Thus, progress of the chemical reaction could have free energy changes due to the chemical reaction as well as the ensuing mixing.

Consider several ideal gases of mole numbers  $n_1, n_2, n_3, \dots$  in a container, separated from each other by imaginary walls, each component at pressure  $p$ , and constant temperature ( $T$ ) (Figure 17.6). By moving the walls, the gases mix spontaneously, and equilibrate. We compute the change in the chemical potential of the system due to this process, while we assume that the gases are unreactive.



**Figure 17.6** Mixing of several ideal gases separated by imaginary walls which are removed and the gases are to mix and equilibrate. The change in the Gibbs free energy accompanying this spontaneous process is the free energy of mixing. All gases mix with all other gases, spontaneously.

The free energy of the initial state consisting of the pure gases is simply the sum of all the free energies and each free energy term is the product of the number of moles of that component ( $n_i$ ) and the chemical potential of the pure substance ( $\mu_i^*$ ). Thus, we can write the following.

$$G(\text{pure}) = n_1 \mu_1^* + n_2 \mu_2^* + n_3 \mu_3^* + \dots = \sum \mu_i^* n_i$$

The  $G$  of the mixture on the other hand is given by the sum of the product of the mole numbers and their corresponding chemical potentials in the mixture ( $\mu_i$ ) that we already worked out, earlier.

$$G(\text{mixture}) = \sum \mu_i n_i$$

The free energy of mixing is equal to those of the mixture minus the pure components, as below.

$$\Delta G_{\text{mixing}} = \sum \mu_i n_i - \sum \mu_i^* n_i$$

Opening the sums and grouping the terms of the same components together, we get a more compact sum.

$$\Delta G_{\text{mixing}} = \sum n_i (\mu_i - \mu_i^*)$$

However, we already showed that the chemical potentials of the pure substance and that of the corresponding mixture are related as following.

$$\mu_i = \mu_i^* + R T \ln X_i$$

The mixing free energy is given by the following.

$$\Delta G_{\text{mixing}} = \sum n_i (\mu_i^* + R T \ln X_i - \mu_i^*)$$

By cancelling the terms and taking  $RT$  out of the sum, at constant  $T$ , we simplify the sum.

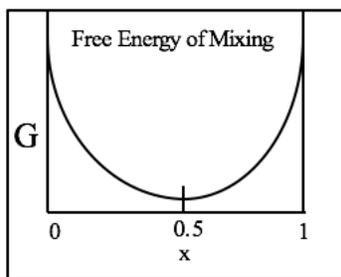
$$\Delta G_{\text{mixing}} = R T \sum n_i \ln X_i$$

Recognizing that the mole fraction equals to  $n_i/n$ , where  $n$  is the total mole numbers, we multiply and divide the sum with  $n$  and write the final expression for mixing free energy.

$$\Delta G_{\text{mixing}} = n R T \sum (n_i/n) \ln X_i$$

$$\Delta G_{\text{mixing}} = n R T \sum X_i \ln X_i$$

Thus, the free energy of mixing depends on the mole fractions of each of the components of the mixture in an interesting manner and a plot of the function for a two component system is shown in **Figure 17.7**.



2 component system

**Figure 17.7** Plot of the  $\Delta G$  of mixing of two ideal gases (non-reactive) as a function of the mole fraction. When  $X = 0$  or when  $X = 1$ , only pure components exist and hence, mixing free energy is zero, the highest value. When  $X = 0.5$ , the function has the minimum value, on either side the mixing free energy is  $< 0$ . (indicate zero on Y axis, change G to  $\Delta G$ )

A plot of the free energy of mixing vs mole fraction is an inverted bell-shaped curve. When mole fraction is 1 or 0, only pure components exist and hence, the mixing free energy is zero. When it is a 1:1 molar mixture, the mixing free energy is the lowest value.

In summary, free energy of mixing of ideal gases is less than zero and depends on the mole fractions of the components. Since we computed the free energy of mixing, we can readily write entropy of mixing, enthalpy of mixing and energy of mixing and complete the discussion.

### 17.3 Entropy of mixing

Entropy of mixing is important because the initial chemical reaction produces a mixture, and there could be substantial role for entropy of mixing in driving the reaction at least initially. Toward the end of the reaction, the entropy of mixing may be unfavorable, because enriching the concentrations of the products in the reaction lowers entropy and a penalty will be applied. Thus, this topic is of importance not only for forming physical mixtures but also for chemical reactions. From free energy of mixing, we can arrive at entropy of mixing in two steps. We use the relation that connects G, T and S, and replace G.

$$\left(\frac{\partial G}{\partial T}\right)_{p,n_1,n_2,\dots} = -S$$

Replacing G by  $\Delta G$  and S by  $\Delta S$ , we get the following.

$$\left(\frac{\partial \Delta G}{\partial T}\right)_{p,n_1,n_2,\dots} = -\Delta S$$

We write corresponding delta S equation, as following.

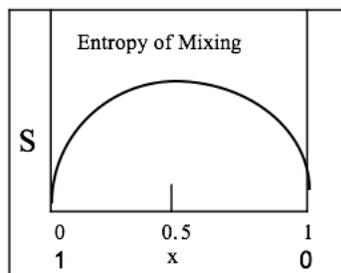
$$\Delta S_{mix} = -\left(\frac{\partial \Delta G_{mix}}{\partial T}\right)_{p,n_1,n_2,\dots}$$

But we know  $\Delta G_{mix}$ , and we differentiate with temperature at constant p and mole numbers.

$$\begin{aligned}\Delta S_{mix} &= \frac{d}{dT} \left( -n R T \sum X_i \ln X_i \right) \\ \Delta S_{mix} &= -n R \sum X_i \ln X_i\end{aligned}$$

The above expression shows that  $\Delta S_{mix} > 0$  because n, R, and X are positive, and log of  $X_i$  is negative. Then, the entire sum is negative, therefore entropy of mixing is positive. Plot of  $\Delta S_{mix}$  vs mole fraction for a two-component system is a bell-shaped curve (**Figure 17.8**), with entropy of mixing being zero at  $X = 1$  and

0. At these points we only have one pure component. When we have a 1:1 mixture, then entropy of mixing is maximized and the most favorable value is 1:1 mixture.



**Figure 17. 8** Plot of the  $\Delta S$  of mixing of a two-component system (non-reactive) as a function of the mole fraction. When  $X = 0$  or when  $X = 1$ , only pure components exist and hence, entropy of mixing zero, the lowest value. When  $X = 0.5$ , the function has the minimum value, on either side the value is less than this. (indicate zero on Y axis, change S to  $\Delta S$ )

In summary, we related  $\Delta G$  in the expression for free energy of mixing with  $\Delta S_{mix}$  and obtained the needed expression, in a two-step derivation. The entropy of mixing is always greater than zero, when there is a mixture and for a 1:1 mixture, it has the highest value. Next, we will examine enthalpy of mixing.

### 17.4 Enthalpy of mixing

Since we know  $\Delta G_{mix}$  and  $\Delta S_{mix}$ , we can readily obtain  $\Delta H_{mix}$  using the fundamental thermodynamic relation, shown below.

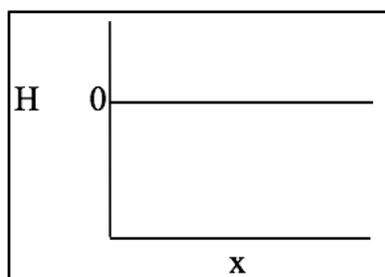
$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

Substituting these known values in the above, we get  $\Delta H_{mix}$  as below.

$$\Delta H_{mix} = \Delta G_{mix} + T\Delta S_{mix}$$

$$\Delta H_{mix} = nRT \sum X_i \ln X_i - T(nR \sum X_i \ln X_i) = 0$$

Thus,  $\Delta H_{mix}$  is 0 for ideal mixtures and this is essentially because the substances have no interactions between each other. In other words, each gas molecule doesn't experience the presence of another gas molecule. Plot of  $\Delta H_{mix}$  vs mole fraction for a two-component system (Figure 17.9 is a flat line parallel to the X-axis.



**Figure 17. 9** Plot of the  $\Delta H$  of mixing of a two-component system (non-reactive) as a function of the mole fraction. The enthalpy for mixtures of ideal gases as these have no interactions among them. This is an excellent criterion to decide if a mixture is ideal or non-ideal. (indicate zero on Y axis, change H to  $\Delta H$ ).

In summary, we have shown that enthalpy of mixing of ideal gases is zero, from expression of the free energy of mixing and entropy of mixing. This is an important criterion to determine if a given mixture is ideal or not. One last remaining topic is the volume of mixing, as discussed below.

## 17.5 Volume of mixing

The volume of mixing is obtained readily by examining the relation between  $G$ ,  $V$ ,  $p$  and  $T$ , as follows. We start with the fundamental equation and constrain  $dT = 0$ .

$$dG = V dp - S dT$$

$$d\Delta G = \Delta V dp$$

We rearrange, impose constant  $p$ , and mole numbers to get  $\Delta V$ ,

$$\left(\frac{\partial \Delta G}{\partial p}\right)_{T, n_1, n_2, \dots} = \Delta V$$

But the free energy of mixing is given below which upon differentiation with pressure gives the desired relation.

$$\Delta G_{mix} = n R T \sum X_i \ln X_i$$

$$\Delta V_{mix} = \frac{d}{dp} (\Delta G_{mix})$$

$$\Delta V_{mix} = \frac{d}{dp} (n R T \sum X_i \ln X_i) = 0$$

Thus, volume of mixing is zero for all values of the mole fraction, just like the enthalpy of mixing. Yet, another condition for ideal behavior is obtained.

$$\Delta V_{mix} = 0$$

In summary, we have deduced volume of mixing to be zero for ideal gases by simply starting from one of the basic equations of thermodynamics and substituting for free energy of mixing.

## 17.6 Chemical Potential in Terms of Other Variables

We can write chemical potential as a function of Helmholtz free energy or enthalpy or internal energy and these relations are useful for thermodynamic analysis of chemical systems. Chemical potential, for example, is defined in terms of Helmholtz free energy as a function of mole numbers as following.

$$G = U + pV - T S = A + pV$$

$$dG = dA + d(pV)$$

Under constant  $T$ ,  $V$  and  $p$  conditions, we can write the following.

$$\mu_i = \left(\frac{\partial A}{\partial n_i}\right)_{T, V, n_{j \neq i}}$$

We also define chemical potential in terms of enthalpy. Since  $G = H - TS$ , at constant  $T$ ,  $p$  and  $V$ , conditions, we can write the following, at constant  $T$  and  $S$ .

$$G = H - T S$$

$$dG = -SdT + Vdp$$

$$dG = dH - TdS$$

Under constant  $S$  conditions, we can define chemical potential as following.

$$\mu_i = \left(\frac{\partial H}{\partial n_i}\right)_{S, P, n_{j \neq i}}$$

We write chemical potential as a function of the internal energy at constant  $T$ , and  $p$  as following.

$$H = U + pV$$

$$\mu_i = \left( \frac{\partial(U + pV)}{\partial n_i} \right)$$

Under constant T, p and V conditions, we get the desired expression.

$$\mu_i = \left( \frac{\partial U}{\partial n_i} \right)_{T,p,V,n_{j \neq i}}$$

Chemical potential is related to the fundamental thermodynamic properties with the above restrictions, and the chemical potential is the underlying potential and kinetic energy changes when a process occurs.

## 17.7 Molecular Interpretation and Applications in Daily Life

### Molecular interpretation

Chemical potential successfully predicts the direction of a process, under constant temperature and pressure conditions. Here, we connected it with mole numbers and gained insight into how ideal gases and real gases mix spontaneously. Mixtures are formed spontaneously when there are no intermolecular interactions or when these interactions do occur, they should be favorable or decrease the chemical potential of the system. Substances do not mix when the molecular interactions between one component and the other are unfavorable. Unfavorable interactions raise the chemical potential and hence, this not a spontaneous process.

The chemical potential is intimately related to the entropy and enthalpy changes occurring during a process and when molecular interactions are unfavorable, then  $\Delta H > 0$  while  $\Delta S$  is still favorable for mixing. Thus, the interactions at the molecular level are responsible for the macroscopic observations. Chemical potential is the total molar potential and kinetic energies of a substance and it is the ultimate thermodynamic property that drives chemical reactions or physical processes around us.

### Applications in daily Life

Chemical potential is the foundation for our discussions of thermodynamics and its applications in real life as well as in practical applications of processes occurring in the world around us. The decrease in chemical potential is the single most important criterion essential to drive the natural processes. Thus, when an apple falls from the tree, under constant p and T conditions, the chemical potential is decreasing and the reverse process is not a spontaneous process. We will be switching between G and  $\mu$  when we discuss chemical reactions and physical processes, as needed.

#### 17.7.1 Units and worked out examples

##### Units

Chemical potential has the units of energy per mole.

##### Worked out example

1. Discuss the change in chemical potential when gasoline burns in the cylinders of the car and the crank shaft turns propelling the car forward or in reverse.

We define the cylinder with fuel and air mix, before the spark plug ignites, as the system and the boundary of the gas separating the surroundings from the system. We choose this as an open system so that we can add the fuel, spark the plug and allow the work to appear at the boundary of the system as the piston moves to expand burning gases. Some heat is transferred to the surroundings during this expansion but not much due to the short time interval of expansion (thousands of rpm of the crank shaft). The burning of the gases is spontaneous because  $\mu$  of the products carbon dioxide and water is lower than  $\mu$  gasoline and oxygen. Thus, there is a decrease in the value of  $\mu$ , as this process occurs This example illustrates the advantage of  $\mu$  over G, because the mole numbers are no longer required. That is, when we remove the foot from the brake pedal and apply it to the accelerator, gas is pumped into the cylinders and work is produced to move the car forward or in reverse depending on the gear shift while decreasing the  $\mu$  of the system.

3. Calculate  $\Delta\mu$  when a gas of 1 mol expands from an initial pressure of 5 atm to a final pressure of 1 atm, at 300 K.

$$\Delta\mu = \Delta G/n = (G_p - G_{(T)}^0)/n = RT \ln(p_2/p_1)$$

$$\Delta\mu = (8.3 \text{ J K}^{-1} \text{ mol}^{-1}) 300 \text{ K} \ln (1 \text{ atm} / 5 \text{ atm}) = -1 \times 8.3 \times 300 \times 1.60 \text{ J/mol}$$

### 17.7.2 Key points and terms

#### Key points

1. Chemical potential is the rate of change of Gibbs free energy and is equal to the molar free energy or the slope of the tangent of the function  $G(n)$ .

$$\mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{T,p,n_{j \neq i}}$$

2. The  $G$  of a mixture is simply the sum of the chemical potentials of the components in the mixture.

$$G_{mixture} = \sum \mu_i n_i$$

3. The chemical potential of an ideal gas increases with pressure, logarithmically, just as  $G$ .

$$\mu = \mu^\circ + RT \ln p_i$$

4. The chemical potential of a gas in a mixture of gases is less than the chemical potential of the corresponding pure component.

$$\mu_i = \mu_i^* + RT \ln X_i$$

5. A gradient of concentration drives the uniform distribution of material, and at equilibrium, the chemical potential at any region A will be the same as at any other region, B.

6. The free energy of mixing is dependent on the composition of the mixture and given by the following.

$$\Delta G_{mix} = RT \sum n_i \ln X_i$$

$$\Delta G_{mix} = n R T \sum X_i \ln X_i$$

7. Entropy of mixing is always negative and depends on the composition, as given by the following.

$$\Delta S_{mix} = -n R \sum X_i \ln X_i$$

8. The enthalpy of mixing and volume of mixing are zero, for ideal mixtures due to the absence of any interactions between the gas particles. Thus, mixing is entirely driven by entropy changes and enthalpy changes do not contribute.

#### Key terms

Chemical potential, mixing free energy, enthalpy, volume, and entropy

### 17.7.3 Graphing Assignment

Plot  $\mu$  vs  $U$ ,  $\mu$  vs  $T$ ,  $\mu$  vs  $p$  and  $\mu$  vs  $S$  for a spontaneous process.

### 17.8 Further Reading

1. [https://ocw.mit.edu/courses/materials-science-and-engineering/3-00-thermodynamics-of-materials-fall-2002/lecture-notes/lecture\\_20\\_oneside.PDF](https://ocw.mit.edu/courses/materials-science-and-engineering/3-00-thermodynamics-of-materials-fall-2002/lecture-notes/lecture_20_oneside.PDF)

2. <https://ocw.mit.edu/courses/chemistry/5-60-thermodynamics-kinetics-spring-2008/video-lectures/lecture-14-multicomponent-systems-chemical-potential/>

### 17.9 Self Tests





**Chapter 18 Gibbs Free Energy of a Reaction and Equilibrium**

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## Summary

Free energy changes that occur during a chemical reaction are of two kinds. One is the intrinsic change in the Gibbs free energy of the reaction mixture as the reaction progresses while the other is the Gibbs free energy of mixing. Thus, these two parameters control the extent to which a chemical reaction will progress and in what direction. We examine the chemical equilibrium, the change in the Gibbs free energy and its relation to the equilibrium constant. The thermodynamic equilibrium constant is predictable, precisely, from the Gibbs free energy changes, alone. Due to this strong connection between free energy and the equilibrium constant, there are systematic ways we can control the equilibrium constant and the degree of completion of a chemical reaction. For example, pressure and temperature control the magnitude of the equilibrium constant.

## Goals

Our focus here will be the evaluation of the connection between the Gibbs free energy and the progress of the chemical reaction. First, we will examine the relation between the reaction free energy and the progress of a chemical reaction. Then, we will factor out the contributions of the mixing free energy to the reaction progress. After that, we will explore equilibrium and derive expression connecting the reaction free energy and the thermodynamic equilibrium constant. Finally, we will examine specific factors that control the equilibrium constant and how to control it, as desired.

### 18.1 Why Study this?

Study of chemistry requires the study of chemical reactions, inevitably. Reaction free energy ( $\Delta G_{\text{reaction}}$ ) is of importance to predict if a given chemical reaction will move forward, if it is in equilibrium or if it will move in the reverse direction. This is of paramount importance, therefore, for our investigation of why do chemical reactions occur? A more detailed understanding of the free energy transactions of a chemical reaction will provide better clues and handles for controlling the chemical reactions, the main task of a chemist. Chemical potential, in this context, provides a practical means to control the position of equilibrium as well as the direction of a chemical reaction. Thus, this chapter is a mile stone in our discussion of thermodynamics of chemical reactions.

We recognize that number of chemical reactions are of importance in our daily lives, in the body, in the environment and in industry. Thermodynamic control over them is of convenience for improving our productivity while caring for the environment. Many biochemical reactions taking place in our bodies are controlled by the same principles and hence, they are of immense importance. Chemical reactions are utilized for the manufacturing of most of the industrial goods, pharmaceuticals, agro chemicals and food. Thus, the role of chemical potential in controlling the chemical reactions, as well as the equilibria, are of immediate concern to us.

### 18.2 Free energy of a Chemical reaction

We looked at the free energy of a mixture and free energy of mixing, in the previous chapter, and this is of significance in the discussions of controlling a chemical reaction. For example, even if we start with a single reactant for our reaction, a mixture is created when the chemical reaction begins. That is, a small amount of product formed, even at the beginning of the reaction, creates a mixture of the reactant and the product. As the reaction progresses, a mixture of reactants and products continues to form till the reaction is complete. Only when the reaction complete and results in only one product, we achieve a pure product. Under all other conditions, we end up with a mixture and hence, mixing continues during the chemical reaction. If we start with multiple reactants, then we need to mix them before the reaction can commence. Therefore,  $\Delta G_{\text{mixing}}$  contributes to the reaction free energy, not only at the beginning but also throughout the reaction course. This is a powerful recognition because this insight provides another handle to control the progress of a chemical reaction. However, the mixing free energy is negative, for all ideal gases but the mixing enthalpy and mixing volume are zero. The increase in entropy due to mixing of the ideal gases, the spontaneous formation of mixture and this is a pre-requisite for most chemical reactions that involve more than one reagent.

The criterion that we obtained for a chemical reaction to proceed forward under constant T and p conditions is  $\Delta G < 0$ , or  $\Delta G > 0$  to proceed in the reverse direction, or  $\Delta G = 0$  for achieving equilibrium. We ask the question, how does free energy of the system change as the chemical reaction progresses, along the way? We keep in mind that, this is likely to involve the reaction free energy and the mixing free energy.

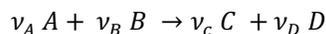
Obviously, the reaction progress is zero when we have only pure reactants. The very next thing is mixing of the reactants to induce chemistry, this itself lowers the free energy of the system, because mixing of ideal gases is a spontaneous process. As the reaction kicks in, sooner or later, products are created. The Gibbs free energy decreases further just because of mixing of the newly produced products with existing reaction mixture but there is also the effect of the chemical reaction buried in that free energy change of the system. Thus, the total change in G is the sum of mixing free energy and the reaction free energy for the conversion of pure reactants to pure products. At the end of the chemical reaction, when the progress is complete, the reactants are completely consumed while the products fully are produced. Normally, these appear as a mixture in our reaction vessel, and not in their pure states, unless the reaction is specific or gives only one product. Most reactions do not go to completion even when stoichiometric amounts of the reactants are used.

$$\Delta G = \Delta G_{\text{reaction}} + \Delta G_{\text{mixing}}$$

Even when the reaction is 100% complete and reactants are chosen in their corresponding stoichiometric amounts, there is still the possibility that the reaction generates more than one product. Then, we still have a mixture. If one of the reagents is used in excess, then we will have a mixture, even if the reaction is complete. Thus, most chemical reactions fall under the category that a mixture is produced at the end of the day, with few exceptions. Therefore, we consider two separate contributions to the chemical reaction, reaction free energy and mixing free energy, and we need to look at both parameters to examine the chemical reaction and its progress.

### 18.2.1 Stoichiometric coefficients and the reaction free energy

Consider a chemical reaction where the reactants A and B produce products C and D, with their corresponding stoichiometric coefficients,  $\nu_i$ .



The stoichiometric coefficient of A is  $\nu_A$ , that of B is  $\nu_B$ , and so on. As the chemical reaction progresses, A and B will be consumed in proportion to their stoichiometric coefficients and produce C and D in proportions of their respective stoichiometric coefficients. Initially, when the reaction progress is zero, we have only pure reactants no products. And in the end, when the reaction progress is 100%, we have pure products, and no reactants, and all substances are in their pure states, not as mixtures. When we write a reaction in the above manner, this is what a chemical reaction represents. Pure reactants giving rise to pure products, with 100% conversion of reactants in finite proportions to the corresponding products.

We assign the stoichiometry coefficient of reactants to have a negative sign, because their mole numbers diminish with reaction progress. The stoichiometric coefficients of the products, in contrast, are given positive sign because their mole numbers increase as the reaction progresses. Thus, we write the corresponding mathematical equation representing a chemical reaction, as following.

$$-\nu_A A - \nu_B B + \nu_C C + \nu_D D = 0$$

We write a general equation involving i-components for the chemical reaction as follows, where the stoichiometric coefficient of the ith component is  $\nu_i$  and the corresponding chemical component is  $A_i$ , as follows.

$$\sum \nu_i A_i = 0$$

In the above equation, stoichiometric coefficients of the products, by definition, are positive and the stoichiometric coefficients of the reactants are negative. This is the mathematical equivalent of the chemical reaction under consideration.

### 18.2.2 Exoergonic, endoergonic and Isoergonic reactions

We divide our discussion of reactions into those that are exoergonic ( $\Delta G < 0$ , Figure 18.1, left), isoergonic ( $\Delta G = 0$ ) and endoergonic ( $\Delta G > 0$ , Figure 18.1, right).

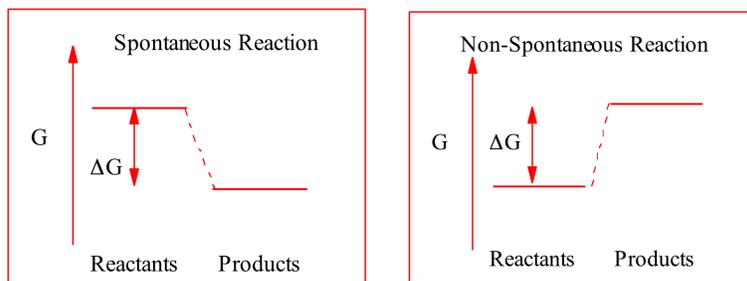


Figure 18.1 Gibbs free energy changes of the system when  $\Delta G < 0$ , the process is spontaneous and the reaction progresses forward (left), and when  $\Delta G > 0$ , the reverse reaction occurs spontaneously (right). (label exoergonic and endoergonic reactions, draw dotted lines parallel to the X-axis to show the relative energies of the reactants/products and move the  $\Delta G$  double headed arrow).

The change in Gibbs free energy of the exoergonic reaction is negative, meaning that the products are more stable than the reactants. Thus, the reaction progresses in the forward direction to minimize the Gibbs free energy of the system, not internal energy or enthalpy. Similarly, the reverse reaction occurs when the reactants are more stable than the products and the system moves spontaneously in the reverse direction to minimize the Gibbs free energy. Thus, chemical reactions spontaneously occur to minimize the Gibbs free energy of the system and produce more stable products.

When  $G$  does not decrease any more or  $\Delta G$  equals to zero, then the system is at equilibrium and the sum of Gibbs free energies of the reactants is exactly equal to the sum of the Gibbs free energies of the products, and the system reaches the lowest Gibbs free energy state. No more changes will occur under these conditions, and we say that the system has attained equilibrium. We recognize that the reactants continue to form products, and products continue to form reactants but the two rates are exactly matched in Gibbs free energy, when the equilibrium is achieved.

### 18.3 G and Reaction Progress

The change in the Gibbs free energy of the system, as the mole numbers of the system are changing due to the chemical reaction, is simply equal to the sum of the chemical potentials of the reactants and products ( $\mu_i$ ) multiplied by the changes in their respective mole numbers ( $dn_i$ ). For a generic reaction consisting of  $i$  reaction components (see above), where  $A_i$  is the  $i$ th chemical component and  $\nu_i$  is its stoichiometric coefficient, we can write the corresponding change in  $G$ , as following.

$$dG = \sum \mu_i dn_i$$

As before,  $\mu_i$  is the chemical potential of the  $i$ th component in the reaction mixture and  $dn_i$  is the change in the mole numbers of that component at any given time. We recognize that we have used the chemical potentials of the substances in the mixture, not in their pure states and hence, intrinsically we included the mixing free energy into the change in the Gibbs free energy of the system. We also recognize that  $dG$  is changing as a function of time, as long as the reaction is progressing or  $dn_i$  is changing, because the composition of the system is changing. Therefore,  $dG$  is a function of the reaction progress.

Since  $dG$  is a function of the reaction progress, we first define this quantity. The progress of a chemical reaction ( $\xi_i$ ) is zero at the beginning of the reaction, equals to 1 when the reaction is complete, and when the reaction is halfway done, it equals to 0.5. Thus, the progress of the chemical reaction, which defines the value of  $dG$  is important for our discussions.

$\xi = 0$  at the beginning of the reaction

$\xi = 1$  when the reaction is complete.

Let  $n_i$  be the mole numbers of the  $i$ th component at any time when the reaction is in progress is  $\xi$  and  $n_i^0$  be the number of moles of that substance at the beginning of the reaction. As the reaction progresses,  $\nu_i^* \xi$  moles of the reactant are consumed, and the mole numbers at this progress is given as below.

$$n_i = n_i^0 + \nu_i \xi$$

However, we need  $dn_i$  and relate reaction progress to  $dG$ . By differentiating the above expression, we get the infinitesimal change in the mole numbers as a function of the infinitesimal change in the reaction progress, as follows, which can be readily related to  $dG$  of the reaction.

$$dn_i = \nu_i d\xi$$

We recognize that the stoichiometric coefficients are independent of the reaction progress, and hence, not variables in our equation. We write  $dG$  by replacing  $dn_i$  with the  $d\xi$  term, as following.

$$dG = \sum \nu_i \mu_i d\xi$$

Therefore, the rate of change of Gibbs free energy with progress is given by the sum of the chemical potentials of the reactants and products, as we discussed earlier.

$$dG/d\xi = \sum \nu_i \mu_i$$

A plot of  $G$  vs  $\xi$  would give us a function which will have a slope of the tangent defined by the chemical potentials of the reactants and products, as the reaction composition is changing. We recognize that  $d\xi$  is always positive (0 to 1), and hence, when the slope is negative, the reaction will move forward because  $dG$  will be negative. When the slope is positive,  $dG$  will be positive and the reverse reaction will be spontaneous, and when the slope is zero, the system is at equilibrium. These details are further discussed in the following section.

A plot of  $G$  of our reaction mixture as a function of the reaction progress is shown in Figure 18.2. Initially, when the reaction is about to start,  $\xi = 0$  and  $G$  is the Gibbs free energy of the reactants. As the reaction progresses,  $dG < 0$  (blue curve) because the sum of the Gibbs free energies of the products is less than those of the reactants, and  $dG$  is further decreased by the contributions of  $\Delta G_{\text{mix}}$ . The dark blue curve represents the reaction free energy + the mixing free energy while the blue straight line corresponds to the changes in  $G$  due to the chemical reaction only.

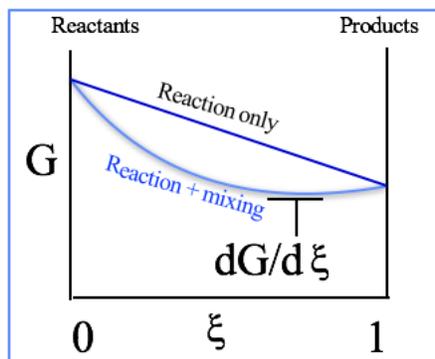


Figure 18.2 Plot of the Gibbs free energy of the reaction mixture of a two-component system, as a function of the reaction progress for an exoergonic reaction. When the progress is 0 (left Y-axis),  $G$  is the sum of the Gibbs free energies of the reactants and when progress is complete (1, right Y-axis). At all other compositions,  $G$  is the sum of the Gibbs free energies of the products and reactants in their corresponding mixtures. The plot is shown for an exoergonic reaction, where the Gibbs free energies of the products is less than the Gibbs free energies of the reactants. The linear plot represents the contribution to  $G$  from the chemical reaction, while the blue concave curve represents the contribution to  $G$  due to mixing and the chemical reaction, combined.

Due to the mixing of the reactants with the products, the blue curve is lower than the linear plot, at any given point other than when  $\xi = 0$  or 1. As the plot shows, the slope of the curve decreases as the reaction

progresses, and  $dG/d\xi = 0$ , at some point before the end of the reaction. At this composition and progress, the reaction is at equilibrium and further progress will not take place. This is because, at progress greater than the equilibrium point, the slope of the blue curve is positive, and hence  $dG > 0$ , and the forward reaction is no longer spontaneous. The system reaches equilibrium. Thus, even when the reaction is favorable, there could be certain amounts of reactants will be left over due to the equilibrium point before the completion of the reaction. Theoretically speaking it is almost impossible to get 100 percent yield for a chemical reaction, at least from these rudimentary arguments. We now separate mixing free energy from the reaction free energy.

### 18.4 $\Delta G$ mixing and $\Delta G$ reaction

The  $G$  of the reaction mixture is given by the following, where the reaction is treated as a mixture. This is just free energy of a mixture, as derived in the previous chapter.

$$G(\text{total}) = \sum n_i \mu_i$$

But to get the reaction free energy, we need to introduce the chemical potentials of the pure reactants and pure products. These we represent as  $\mu_i^*$  where the star represents that the substance is in its pure form. We add and subtract the chemical potentials of the pure substances on the right of the above equation.

$$G = \sum n_i (\mu_i - \mu_i^* + \mu_i^*) = \sum n_i (\mu_i - \mu_i^*) + \sum n_i \mu_i^*$$

We recognize that the first sum on the right is the difference in the free energy of the pure components and the components in the mixture, and the second sum is that of the free energies of all the pure components, where it represents the reaction free energy where the pure reactants produce pure products. So, we replace the two sums with these corresponding terms to get the following equation.

$$G = \Delta G_{\text{mix}} + G_{\text{pure substances}}$$

Differentiating the above with respect to reaction progress, on both sides, we get the following.

$$(dG/d\xi) = d(\Delta G_{\text{mix}})/d\xi + d(G_{\text{pure substances}})/d\xi$$

Thus, the slope of the plot of  $G$  vs reaction progress will be the sum of the derivatives of  $\Delta G_{\text{mix}}$  and  $G_{\text{reaction}}$ . But the Gibbs free energy of mixing is  $< 0$ , for all reactions and hence, the net slope depends on the changes in both the terms.

#### 18.4.1 Endoergic reactions

Now, we can consider endoergic reactions and ask, will it be possible for these reactions to occur? Since the  $\Delta G > 0$ , we would predict that the reaction should not proceed but examining the plot of  $G$  vs reaction progress (Figure 18.3) reveals that the reaction could be driven, at least to some extent, by the Gibbs free energy of mixing.

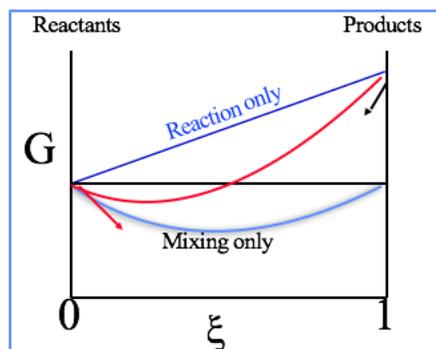


Figure 18.3 Plot of the Gibbs free energy of the reaction mixture of a two-component system as a function of the reaction progress for an endoergic reaction. When the progress is 0 (left Y-axis),  $G$  is the Gibbs free energy of the pure reactant, and when progress is complete (1, right Y-axis)  $G$  is the Gibbs free energy

of the pure product. At all other compositions,  $G$  is the sum of the Gibbs free energies of the product and reactant in their corresponding mixtures. The linear plot represents the contribution to  $G$  from the chemical reaction, while the blue concave curve represents the contribution to  $G$  due to mixing only.

The plot of  $G$  vs  $\xi$  for the endoergic reaction (Figure 18.3) for a two-component system has pure reactant on the left Y-axis, and pure product at the right Y-axis. At any point in between, Gibbs free energy of the reaction mixture is the sum of the free energies of the pure reactant and pure product, at that composition. When the reaction proceeds by an infinitesimal amount, we make a mixture and it will have lower free energy than the corresponding pure components.

The red line is the Gibbs free energy of the reaction mixture, the linear purple plot is that of the pure reactants and pure products while the blue concave line is that due to mixing alone. The sum of the values of the blue and purple lines at any composition produces the corresponding value on the red line and the reaction proceeds initially. The reaction could proceed, initially, and this is because the slope of the red line at  $\xi = 0$  is  $< 0$ . As the reaction progresses, the system reaches equilibrium  $dG = 0$ , and any further change in composition only raises the Gibbs free energy, and hence, it is not spontaneous but the reverse reaction is. Thus, the mixing free energy can drive the reaction forward, even if the reaction free energy is not favorable, at least initially. The equilibrium point depends on the slope of the purple curve, and the depth of the blue curve. Finally, we recognize that endoergic reactions can occur and reach equilibrium, and no reaction can be 100% unreactive, at least theoretically.

## 18.5 Gibbs Free Energy and the Equilibrium Constant

From the above discussions, one would expect that the Gibbs free energy of the reaction is related to the equilibrium constant. The position of equilibrium, for example, depends on the slopes of the plots of the reaction free energy of the pure reactants and their free energy of mixing. The following provides an important insight into this relationship.

### 18.5.1 Chemical potential and chemical equilibrium

Consider a reaction where all the reactants and products are ideal gases and we assume that the ideal gases do react to produce products but otherwise have no interactions. The Gibbs free energy of the reaction is simply the difference in the Gibbs free energies of the products and the reactants, written as below.

$$\Delta G_{reaction} = \sum G_{products} - G_{reactants}$$

The terms can be written in terms of the chemical potentials and the stoichiometric coefficients as below.

$$\Delta G_{reaction} = \sum v_i \mu_i$$

Substituting the chemical potentials of the pure substances ( $\mu_i^*$ ) for the chemical potentials of the components in the mixture ( $\mu_i$ ), as discussed in the previous chapter, where  $p_i$  is the pressure of the  $i$ th component in the reaction mixture.

$$\mu_i = \mu_i^* + R T \ln p_i$$

We substitute the above to get two separate terms for the Gibbs free energy of the reaction.

$$\begin{aligned} \Delta G &= \sum v_i (\mu_i^* + R T \ln p_i) \\ \Delta G &= \sum v_i \mu_i^* + \sum v_i R T \ln p_i \end{aligned}$$

Recognizing that the first sum on the right is the sum of the free energies of pure reactants and pure products, we can replace with the symbol,  $\Delta G^\circ$ , as follows.

$$\Delta G^\circ = \sum v_i (\mu_i^*)$$

Therefore, the total free energy of the reaction is written as follows.

$$\Delta G = \Delta G^0 + R T \sum v_i \ln p_i$$

### 18.5.2 Equilibrium constant and $\Delta G^0$

At equilibrium, we notice that  $\Delta G = 0$ , and hence, we write  $\Delta G^0$  in terms of partial pressures of reactants and products at equilibrium, as follows.

$$\Delta G^0 = -R T \sum v_i (\ln p_i)_{\text{equilibrium}}$$

We recognize that the stoichiometric coefficients of the reactants have negative and stoichiometric coefficients of the products are positive, and we can write these explicitly, as follows.

$$\Delta G^0 = -R T \sum [v_i \ln p_i]_{\text{equilibrium,products}} - [v_i \ln p_i]_{\text{equilibrium,reactants}}$$

Taking advantage of the  $\ln$  functions with opposite signs, we can write the summation, as the ratio, and since  $x \ln x$  is  $\ln x^x$ , each pressure term is raised to the power of its stoichiometric coefficient.

$$\Delta G^0 = -R T \left\{ \ln \frac{[p_i]_{\text{equilibrium,reactants}}^{v_i}}{[v_i \ln p_i]_{\text{equilibrium,reactants}}} \right\}$$

The ratio of pressure terms raised to the powers of the stoichiometric coefficients at equilibrium is exactly the equilibrium constant, and we write the final expression, as follows.

$$\Delta G^0 = -R T \ln K_p$$

For the chemical reaction at equilibrium, the change in the Gibbs free energy of the pure reactants and pure products is directly related to the equilibrium constant, and hence, we can predict this value from knowing the Gibbs free energies of chemical substances. Thus, the equilibrium constant changes very rapidly with  $\Delta G^0$  and lower its value (more negative), greater the equilibrium constant (Figure 18.4). The  $\ln$  function indicates that small decreases in the  $\Delta G^0$  causes large changes in the value of  $K_p$  and the slope of the line is  $-RT$ , depends directly on the temperature of the system.

Figure 18.4 Plot of  $\Delta G^0$  vs  $K_p$  for a chemical reaction involving ideal gases. The negative slope indicating inverse relation, lesser the value of  $\Delta G^0$ , larger the equilibrium constant. The slope is given by  $-RT$ , and directly depends on the temperature of the system.

From a different view point, taking anti-logs on both sides of the above relation, we can write  $K_p$  as an exponential function of Gibbs free energy of reaction.

$$K_p = e^{(-\Delta G^0/R T)}$$

For a simple reaction,  $A + B$  going to products  $C + D$  with their corresponding stoichiometric coefficients, the equilibrium constant, for example, is written in terms of their corresponding equilibrium partial pressures raised to their corresponding stoichiometric coefficients, as follows.

$$K_p = (p_D^{v_D} p_C^{v_C}) / (p_A^{v_A} p_B^{v_B})$$

### 18.5.3 Equilibrium constant for real gases and $\Delta G^0$

The partial pressures of the ideal gas are replaced with fugacities to accommodate the non-ideal behavior of real gases. The equilibrium constant for real gases ( $K_f$ ) in terms of their fugacities, at equilibrium, is given below.

$$K_f = (f_D^{v_D} f_C^{v_C}) / (f_A^{v_A} f_B^{v_B})$$

Then, the  $\Delta G^\circ$  for real gases is written in terms of the ratio of equilibrium fugacities, and the dependence of the equilibrium constant as well.

$$\Delta G^\circ = -R T \ln K_f$$

$$K_f = e^{(-\Delta G^\circ / R T)}$$

Again, if we know the free energies of the pure substances we can calculate the equilibrium constant, without doing an experiment, and this is the power of this approach of thermodynamics.

In summary, the overall Gibbs free energy change accompanying a chemical reaction is factored out into the mixing free energy and the reaction free energy. We found the relation between the equilibrium constant and the decrease in the free energy of the system in terms of pure products and pure reactants. The composition of the equilibrium is precisely defined by the differences in the Gibbs free energies of the pure products and pure reactants.

## 18.6 Equilibrium and Temperature

We will examine the equilibrium constant as a function of temperature so that, by knowing its value at one temperature we may be able to calculate the equilibrium constant at any other temperature. In the process, we will relate the equilibrium constant to enthalpy and entropy changes of the pure reactants and pure products, at the equilibrium composition of the reaction. Thus, one can obtain the equilibrium constant at one temperature and estimate the reaction enthalpies and entropies. Thus, the study of temperature dependence of the equilibrium (chemical or physical) is of immense importance in thermodynamics.

### 18.6.1 Temperature dependence of $K_p$

Starting with the central relation connecting the equilibrium constant and the Gibbs free energy difference of pure products and reactants.

$$\Delta G^\circ = -R T \ln K_p$$

We re-write the above with temperature and the equilibrium constant on opposite sides of the equation in preparation to differentiate the above expression with respect to temperature.

$$\ln K_p = -\frac{\Delta G^\circ}{R T}$$

Since  $\Delta G^\circ$  depends on temperature, we will write it in terms of temperature, explicitly, prior to differentiation using the fundamental equation involving  $\Delta H^\circ$  and  $\Delta S^\circ$ .

$$\ln K_p = -\frac{\Delta H^\circ - T \Delta S^\circ}{R T}$$

The enthalpy and entropy changes are those of the pure substances, at equilibrium composition. Differentiating the above on both sides with respect to temperature, we get the following.

$$\frac{d}{dT} (\ln K_p) = -\frac{d}{dT} \left( \frac{\Delta H^\circ - T \Delta S^\circ}{R T} \right)$$

We open the fraction in the parenthesis to cancel the temperature term in the numerator, as following.

$$\frac{d}{dT} (\ln K_p) = -\frac{d}{dT} \left( \frac{\Delta H^\circ}{R T} - \frac{T \Delta S^\circ}{R T} \right)$$

$$\frac{d}{dT} (\ln K_p) = -\frac{d}{dT} \frac{1}{R} \left( \frac{\Delta H^\circ}{T} - \Delta S^\circ \right)$$

When we consider a small temperature interval, and given the shallow T-dependence of  $\Delta H^\circ$  and  $\Delta S^\circ$ , we can simplify the operand, even further as following.

$$\frac{d}{dT} (\ln K_p) = -\frac{\Delta H^\circ}{R} \frac{d}{dT} \left( \frac{1}{T} \right)$$

Differentiating the expression followed by integration with limits  $T$  and  $T_0$  corresponding to the equilibrium constant,  $K_p$  and  $K_p^{T_0}$ , we get the following.

$$\ln K_p = \ln K_p^{T_0} - \frac{\Delta H^0}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right)$$

Thus,  $\ln K_p$  at any temperature  $T$  is related to at a standard temperature  $T_0$  and  $\Delta H^0$ , not a new relation but seen before in a slightly different form. When  $T > T_0$ , then the parenthesis is negative and  $\ln K_p$  increases or decreases depending in the sign of  $\Delta H^0$ . A plot of  $\ln K_p$  vs  $1/T$  (Figure 18.5) indicates a line with slope equal to....

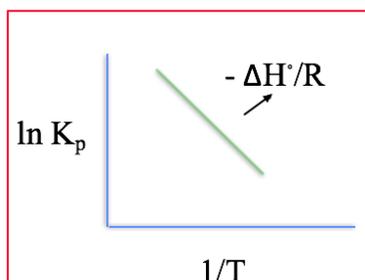


Figure 18.5 Plot of  $\ln K_p$  vs  $1/T$  for an equilibrium, involving ideal gases. The negative slope indicating inverse relation with  $1/T$ . When the reaction is endothermic ( $\Delta H^0 > 0$ ), the slope is negative, and the equilibrium constant increases with increase in  $T$ . The slope will be positive when  $\Delta H^0 < 0$  or exothermic, and the equilibrium constant decreases with increase in temperature.

We summarize our discussion of the temperature dependence as following.

$$\ln K_p \uparrow \text{ when } T \uparrow \text{ and } \Delta H^0 > 0, \text{ or endothermic}$$

$$\ln K_p \downarrow \text{ when } T \uparrow \text{ and } \Delta H^0 < 0, \text{ or exothermic}$$

### 18.6.1 van 't Hoff equation and $\Delta H^0$

We re-write the above equation in the original differential form and assume that both  $\Delta H^0$  and  $\Delta S^0$  are independent of temperature, and obtain the following equation.

$$\frac{d}{dT}(\ln K_p) = \frac{\Delta H^0}{RT^2}$$

This is the van 't Hoff equation which related the equilibrium constant with the enthalpy changes of the pure products and reactants, at equilibrium. One powerful application of the above equation is to obtain the enthalpy change by simply measuring the equilibrium constant at few temperatures, by a non-calorimetric method. We already discussed this approach under the heat of vaporization studies, earlier. The enthalpy obtained this way is the van 't Hoff enthalpy of the reaction (Figure 18.5).

The van 't Hoff equation is exactly valid when both  $\Delta H^0$  and  $\Delta S^0$  are independent of temperature and the equilibrium is established. Over short ranges of temperature, the assumption is reasonably valid and provides an approximate value for  $\Delta H^0$ , the standard enthalpy of the reaction when measured at 1 atm and when pure substances are considered.

### 18.6.1 Temperature dependence and $\Delta S^0$

From the equilibrium constant  $K_p$  and by measuring  $\Delta H^0$ , we can obtain  $\Delta S^0$  by a non-calorimetric method by simple manipulation of thermodynamic quantities.

$$\Delta G^0 = (\Delta H^0 - T \Delta S^0) = -R T \ln K_p$$

By rearranging, the terms we get the relation with enthalpy and entropy changes, as following.

$$\ln K_p = - \left( \frac{\Delta H^0 - T \Delta S^0}{RT} \right)$$

Expanding the fraction, we obtain a clearer expression for the entropy change.

$$\ln K_p = -\left(\frac{\Delta H^\circ}{RT}\right) + \left(\frac{\Delta S^\circ}{R}\right)$$

Plot of  $\ln K_p$  vs  $1/T$  will have a slope of  $-\Delta H^\circ/R$  and an intercept of  $\Delta S^\circ/R$  (Figure 18.5). These plots are referred to as the van 't Hoff plots and entropy can be measured. While the slope of the plot is more reliable, the intercepts have larger errors, we note.

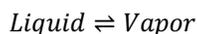
In summary, enquiry into the Gibbs free energy changes of a chemical reaction led us to connect it with the equilibrium constant, which in turn led us to predicting the equilibrium constant from the Gibbs free energy changes. Temperature dependence of the equilibrium constant led us to the reaction enthalpies and reaction entropies which are valid for equilibrium conditions. Thus, the entire thermodynamic picture of equilibrium is obtained by a systematic thermodynamic analysis.

## 18.8 Effect of Pressure on the Equilibrium Constant

Using liquid-vapor equilibrium in a previous snippet we looked the heat of vaporization, and we applied the barometric law to obtain the relation but now we will achieve a direct derivation of this important equation.

### 18.8.1 The liquid-vapor equilibrium.

Let the liquid be in equilibrium with its vapor and as we change the temperature the vapor pressure will change above the liquid will also change. As we heat the sample, some liquid molecules gain a certain amount of excess energy and escape into the gas phase. Thus, the vapor pressure will increase as we increase the temperature and when we cool the sample, some gas molecules will condense into the liquid phase and the vapor pressure will drop. Thus, the system is at equilibrium between the liquid phase and the gas phase at any given temperature, after some time.



Since the vapor pressure changes with temperature but the concentration of the liquid does not change, and hence, we can write the following, for the equilibrium constant of the liquid-vapor equilibrium.

$$K_p = p$$

At equilibrium, the chemical potential of the gas molecules exactly equal to the chemical potential of the liquid molecules and it is a reversible process. We will ignore the change in the volume of the liquid with temperature because the change in the pressure of the vapor will be much greater than the change in the liquid volume, and write the following equation to account for the temperature effect on the equilibrium constant, from the previous section.

$$\ln(K_p / K_p^{T_0}) = -\frac{\Delta H^0}{R} \left(\frac{1}{T} - \frac{1}{T_0}\right)$$

However, for the liquid-vapor equilibrium we showed approximated that  $K_p$  can be replace by  $p$  itself, and we recognize that the  $\ln$  of the ratio of vapor pressures at any two temperatures are related by the heat of vaporization  $\Delta H^\circ_{\text{vapor}}$ , as following.

$$\ln(p/p_{at \tau_0}) = -\frac{\Delta H^\circ_{\text{vapor}}}{R} \left(\frac{1}{T} - \frac{1}{T_0}\right)$$

A plot of logarithm of vapor pressure measured in the experiment versus one over temperature, get a straight line with slope and intercept as by defined by the above equation (Figure 18.6). Since heat of vaporization of most liquids is positive, the slope will be negative and numerical value equals to  $\Delta H^\circ_{\text{vapor}}/R$ . The heat of vaporization can be measured by a non-calorimetric method by monitoring the vapor pressure as a function of temperature.

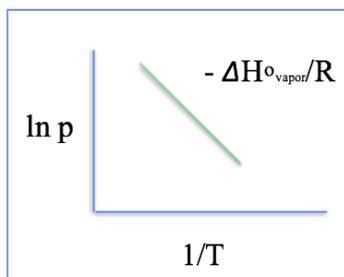


Figure 18.5 Plot of  $\ln K_p$  vs  $1/T$  for an equilibrium, involving ideal gases. The negative slope indicating inverse relation with  $1/T$ . When the reaction is endothermic ( $\Delta H^\circ > 0$ ), the slope is negative, and the equilibrium constant increases with increase in  $T$ . The slope will be positive when  $\Delta H^\circ < 0$  or exothermic, and the equilibrium constant decreases with increase in temperature.

Taking anti-logs on both sides, writing  $p_{at T_0}$  as  $p_0$ , we get heat of vaporization as following. Thus, vapor pressure decreases with increase in the heat of vaporization but increases with increase in temperature and it is similar to what we deduced in module 1.

$$p = p_0 e^{-\frac{\Delta H_{vapor}^\circ}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right)}$$

**In summary**,  $\Delta H^\circ$  can be measured by a non-calorimetric method, and an expensive calorimeter is not required. However, some limitations of the method are that we assume that the liquid volume does not change during the heating and that the vapor behaves ideally but corrections can be introduced for these approximations, when more precise values are necessary.

## 18.9 Controlling the Equilibrium Position

Next, we use the above assets to control the position of the equilibrium of a chemical reaction. This is what a chemist does for a living, and the chemist is asked to control the direction of a chemical reaction as well as the position of the equilibrium. Although the effect of temperature and effect of pressure on equilibrium constant are examined earlier, there are still other aspects to be discussed, as demonstrated below. We investigate these possibilities by writing the exact differential of  $\Delta G$  as a function of  $T$ ,  $p$  and reaction progress ( $\xi$ ), as following.

$$d(\Delta G) = \left( \frac{\partial \Delta G}{\partial T} \right)_{p,\xi} dT + \left( \frac{\partial \Delta G}{\partial p} \right)_{T,\xi} dp + \left( \frac{\partial \Delta G}{\partial \xi} \right)_{T,p} d\xi$$

The net change in  $\Delta G$  is due to changes in its value due to each of the three variables,  $T$ ,  $p$ , and  $\xi$ , and we previously showed the following expression connecting reaction progress and reaction free energy.

$$dG/d\xi = \sum \nu_i \mu_i = \Delta G$$

Under constant  $T$ , and  $p$  conditions, we can write the above equation, as the following.

$$\left( \frac{\partial G}{\partial \xi} \right)_{T,p} = \Delta G$$

We replace  $\Delta G$  in the last term of the exact differential of  $\Delta G$  with  $(dG/d\xi)_{T,p}$ , as below.

$$d(\Delta G) = \left( \frac{\partial \Delta G}{\partial T} \right)_{p,\xi} dT + \left( \frac{\partial \Delta G}{\partial p} \right)_{T,\xi} dp + \frac{d}{d\xi} \left( \frac{\partial G}{\partial \xi} \right) d\xi$$

The third term is simply the second derivative of  $G$  with respect to reaction progress and indicate it as  $G''$  for simplicity.

$$d(\Delta G) = \left( \frac{\partial \Delta G}{\partial T} \right)_{p,\xi} dT + \left( \frac{\partial \Delta G}{\partial p} \right)_{T,\xi} dp + G'' d\xi$$

This equation describes how the reaction free energy is controlled by the variables T, p and reaction progress, and we will examine these specifics for a chemical equilibrium, in the subsequent sections.

### 18.9.1 Effect of pressure on the equilibrium position

Imposing constant composition conditions ( $\xi = \text{constant}$ ) on the above equation, we obtain the following.

$$d(\Delta G) = \left(\frac{\partial \Delta G}{\partial T}\right)_{p,\xi} dT + \left(\frac{\partial \Delta G}{\partial p}\right)_{T,\xi} dp + 0$$

But the differential of  $\Delta G$  with respect to T and p, from previous sections, is as below.

$$d(\Delta G) = -\Delta S dT + \Delta V dp$$

For exact differential of  $\Delta G$  given above, we can now replace the first and the second terms with  $\Delta S$  and  $\Delta V$  terms, as following.

$$d(\Delta G) = -\Delta S dT + \Delta V dp + G'' d\xi$$

At constant T, we set  $d\Delta G = 0$  at equilibrium.

$$d(\Delta G) = 0 = \Delta V dp + G'' d\xi$$

By rearranging, we see that the change in the progress with pressure at constant T is given in terms of the volume change,  $\Delta V$ .

$$G'' d\xi = -\Delta V dp$$

$$\left(\frac{d\xi}{dp}\right)_T = -\frac{\Delta V}{G''}$$

The second derivative of G with respect to reaction progress ( $G''$ ) is  $>0$  because the plot of G vs reaction progress is concave upward (Figure 18.2, 18.3).

$$G'' > 0 \text{ for upward concave functions}$$

Therefore, plot of  $\xi$  versus p should be linear with positive slope, when  $\Delta V < 0$  (Figure 18.6, left) or a negative slope when  $\Delta V > 0$  (right).

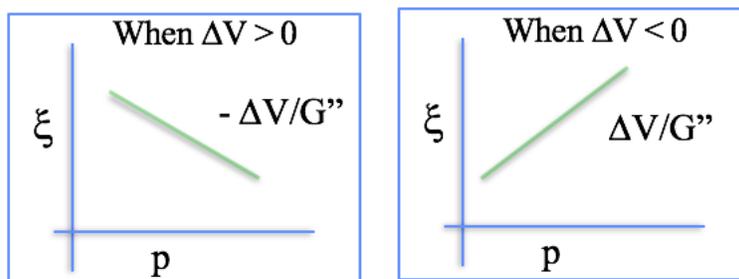


Figure 18.6 Plot of reaction progress vs pressure for an equilibrium, involving ideal gases. Because  $G''$  is  $>0$ , the slope of the plot will be negative when  $\Delta V > 0$  (left). The equilibrium will move in the reverse when pressure increases. The opposite is predicted when  $\Delta V < 0$  and the equilibrium will move forward (right). Thus, the system will move to compensate for the external influences.

When volume increases during a reaction, increase of pressure will move the equilibrium in the reverse direction to offset the increase of pressure. Conversely, when the volume decreases during a reaction, the increase of pressure moves the equilibrium in the forward direction. Thus, the system tends to compensate for the external effects applied. These can be summarized by the following.

$$\xi \downarrow \text{ when } p \uparrow \text{ and } \Delta V > 0$$

$$\xi \uparrow \text{ when } p \uparrow \text{ and } \Delta V < 0$$

### 18.9.2 Effect of temperature on the equilibrium position

The effect of T on the reaction progress for an equilibrium is analyzed in a similar manner. We write the exact differential of  $\Delta G$  as a function of T, p, and reaction progress, and then impose the constant pressure conditions.

$$d(\Delta G) = -\Delta S dT + \Delta V dp + G'' d\xi$$

Imposing the equilibrium conditions, we set  $\Delta G = 0$  and we get the following.

$$\Delta G = 0 = -\Delta S dT + G'' d\xi$$

The negative sign is absorbed by shifting the  $\Delta S$  term to the other side of the equality.

$$G'' d\xi = \Delta S dT$$

Rearranging the terms, we get the partial derivative with respect to T at constant pressure, and we replace  $\Delta S$  with  $\Delta H/T$ , since  $\Delta G = 0$ , as following.

$$\left(\frac{d\xi}{dT}\right)_p = \frac{\Delta S}{G''} = \frac{\Delta H}{T G''}$$

Plot of reaction progress as a function of T at constant p gives a linear plot with slope equal to  $\Delta H/G''$ . The slope will be positive or negative based on the sign of  $\Delta H$  term (Figure 18.7).

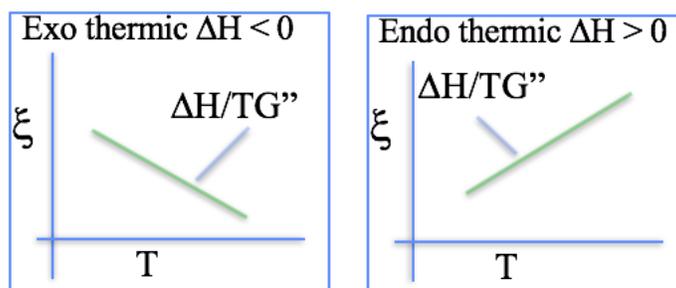


Figure 18.7 Plot of reaction progress vs temperature for an equilibrium process, involving ideal gases. Because  $G''$  is  $>0$ , the slope of the plot will be negative when  $\Delta H < 0$  (left). The equilibrium will move in the reverse for exothermic reactions, when temperature increases. The opposite is predicted when  $\Delta H > 0$  and the equilibrium will move forward with increase in temperature for endothermic reactions (right). Thus, the system will move to compensate for the external influences.

When heat is released during the reaction (exothermic,  $\Delta H < 0$ ), then increase of temperature will move the equilibrium in the reverse direction. Conversely, when heat is absorbed (endothermic,  $\Delta H > 0$ ), increase of temperature moves equilibrium in the forward direction. Thus, the system tends to compensate for the external effects applied to the system. These can be summarized by the following.

$$\xi \downarrow \text{ when } T \uparrow \text{ and } \Delta H < 0$$

$$\xi \uparrow \text{ when } T \uparrow \text{ and } \Delta H > 0$$

**In summary**, we looked at the effect of pressure and temperature on the reaction progress for an equilibrium. The position of the equilibrium will move in such a manner as to compensate for the external influence.

### 18.9 Kp and Calorimetry

In this episode, we will look at experimental measurements of equilibrium constants using calorimetry. Calorimetry we already encountered in the second module. We write the fundamental equation and get the following equations.

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

$$-R T \ln K_p = \Delta G^0 = \Delta H^0 - T \Delta S^0$$

Rearranging the terms, we get the equilibrium constant in terms of enthalpy and entropy changes.

$$\ln K_p = -(\Delta H^\circ/R T) + (\Delta S^\circ/R)$$

We measure enthalpy changes directly with a calorimeter and estimate  $\Delta S^\circ$  from third law entropies. By definition,  $\Delta S^\circ$  is written in terms of the entropies of pure products at T and the entropies of pure reactants at T.

$$\Delta S^\circ = \Delta S_{\text{products}}^\circ - \Delta S_{\text{reactants}}^\circ$$

$$\Delta S^\circ = \Delta S_0^\circ + \Delta S_{0 \text{ to } T}^\circ$$

Here,  $\Delta S_0^\circ$  is the reaction entropy 0 K, and then we apply the third law to calculate the entropy increase when the temperature increases to T K. Thus, substances that follow the third law are then straightforward to obtain the reaction entropies. The equilibrium constant is then obtained using the following equation.

$$\ln K_p = -(\Delta H^\circ/R T) + (\Delta S_{0 \text{ to } T}^\circ/R)$$

In modern calorimetry,  $\Delta H$  is measured as a function of the concentration of one of the reactants while the other reactants are held constant. At low concentrations of the limiting reagent, the  $\Delta H$  is approximately equal to the reaction enthalpy. A plot of  $\Delta H$  as a function of the concentration of the limiting reagent gives an isotherm. By fitting the isotherm with specific equilibrium models, one obtains the equilibrium constant, and the corresponding  $\Delta G^\circ$ . From these, then one obtains the  $\Delta S^\circ$  or one studies the variation of  $\Delta H^\circ$  as a function of temperature and obtains  $\Delta S^\circ$  using the fundamental equation. Thus,  $\Delta S^\circ$  can be obtained experimentally, without the third law application.

### 18.7 Solid-Gas Equilibrium: Limestone Decomposition

An example of industrial significance is the decomposition of a solid calcium carbonate (solid) to give calcium oxide (solid) and carbon dioxide (gas). Since the partial pressure of carbon dioxide increases as the reaction progresses, and all other components are solids, the equilibrium constant is dictated solely by the pressure of carbon dioxide. The concentrations of other substances do not change during the reaction.



The value of  $K_p$  equals to the partial pressure of carbon dioxide raised to the power 1, and we use the previous discussion to calculate  $\ln K_p$  and get  $\Delta G^\circ$  as well as all the other good things from it.

### 18.10 Molecular interpretation and applications in daily life

#### Molecular interpretation

Chemical reactions occur because of a decrease in Gibbs free energy but this decrease could be due to the chemical reaction as well as the mixing that occurs as the reaction begins to progress. Thus, the chemical reaction might be just due to mixing free energy alone, when the chemical reaction is endoergonic. However, equilibrium is established when there is no further change in the Gibbs free energy, and the equilibrium constant is related exponentially to the decrease in the reaction free energy. At the molecular level, these discussions point out that as the electronic distribution and nuclear coordinates change during the chemical reaction, the changes are favored as long as the net value of the Gibbs free energy is reduced or this could also be due to the entropy gains resulting from the mixing of the reactants and products or both. Thus, mixing of the reaction mixture and the resulting Gibbs free energy changes could facilitate the chemical reaction or the changes in the coordinates of the electrons and nuclei in the reactants. Thus, the popular argument that the chemical reactions occur because products are of lower Gibbs free energy than the reactants is not entirely correct. The decrease in the potential and kinetic energies of the nuclei and electrons in molecules accounts for only a part of the reaction free energy.

The same arguments apply for the establishment of equilibrium. At equilibrium, the reaction mixture has electrons and nuclei with the lowest possible kinetic and potential energies under the conditions of pressure, temperature and composition. Any further decrease is not possible unless the equilibrium conditions are changed, such as raising or lowering temperature, pressure or changing the concentrations of the reactants or products. These changes, in turn, trigger further changes in Gibbs free energy until there are no more changes, and the equilibrium is established under a new set of conditions.

Increase of temperature, for example, raises the kinetic energy of the molecules and in case of an exothermic reaction this excess heat energy is utilized to make reactants, shifting the equilibrium to the reactants' side. The equilibrium moves in the reverse direction to store that extra energy in the potential and kinetic energies of the reactants, and new equilibrium position is established. The argument is reversed for endothermic reactions. Thus, molecular level descriptions aid in the understanding of the effect of temperature on the equilibrium.

Similarly, the effect of pressure on equilibrium can be examined at the molecular level. For a reaction that undergoes expansion of volume as it proceeds, the application of pressure will reverse it. This is because the products occupy more volume than the reactants, usually due to the increase in the mole numbers as the reaction moves forward. As increase in pressure increases the Gibbs free energy, the system moves to lower free energy by converting some of the products to reactants, thereby reducing the volume of the system. Again, the nuclei and electrons are involved in the production of reactants and the excess energy is stored in the system as potential and kinetic energies of these particles. The reverse is true for reactions with  $\Delta V < 0$ . In all situations, the kinetic and potential energies of the fundamental particles of atoms and molecules changes to accommodate the external stimulus that is applied to the system.

### Applications in daily Life

Equilibria are everywhere in our daily lives and they are constantly being shifted by either pressure or temperature or other stimuli. The cloud formation in the upper atmosphere, for example, is due to a change in the mole numbers of water molecules coupled with changes in the temperature. The equilibrium between water vapor and water droplets is influenced by these changes. When these droplets grow to large enough size that earth's gravity can pull them down, we experience rain.

All distillations are at equilibria and this is a major industrial method to fractionate petroleum and numerous other substances such as alcohol. Crystallization is another equilibrium process that is shifted toward the solid phase in many industrial processes. Human body is maintained at 37 °C and this requires a constant supply of enthalpy to keep it away from equilibrium with room temperature. Most biochemical process occur away from the equilibrium but that requires constant production of enthalpy and continuous decrease in the Gibbs free energy. Thus, shifting the equilibrium is the constant struggle of life.

Oceans at thermal equilibrium with the atmosphere above, and the liquid water is in equilibrium with the humidity in the air above it. When there is a change in the temperature of water or the pressure of the atmosphere, storms can develop and utilize the excess Gibbs energy that is made available due to these temperature and/or pressure changes. Some of these free energy is utilized, in turn, by the gusting winds to topple trees or lift boats out of docks and onto the streets.

### 18.10.1 Units and worked out examples

#### Units

The thermodynamic equilibrium constant  $K_p$  is dimensionless, contrary to the popular misconception. Logarithmic function can't be applied if  $K_p$  has units and the equilibrium constant is to be written in terms of standard concentrations, moles per cubic meter, of reactants and products. For example, the reactant and product concentrations are to be divided by their respective standard concentrations, so that the ratio of their concentrations is dimensionless. For gaseous products and reactants, their partial pressures are divided with the standard pressure of 1 atm, so that the equilibrium constant is dimensionless.

#### Worked out example

1. Calculate the equilibrium constant for the decomposition of lime stone to calcium oxide and carbon dioxide when the partial pressure of  $\text{CO}_2$  is 0.01 atm and 1.1 atm at 100 and 500 K.

The balanced chemical equation for the above reaction is as follows.



Since limestone and CaO are in the solid phase, their concentrations do not change as we heat the reaction mixture. Thus,  $K_p = p(\text{CO}_2)/1 \text{ atm}$ .  $K_p$  at 100 K is 0.01 and  $K_p$  at 500 K is 1.1.

2. Calculate  $\Delta G$  for the above example at 500 K.

$$\Delta G = -R \ln(1.1 \text{ atm}/1 \text{ atm})$$

$$= - (8.3 \text{ J K}^{-1} \text{ mol}^{-1}) 500 \text{ K} \ln (1.1) = - 395 \text{ J/mol}$$

3. Calculate the change in the equilibrium constant when the reaction free energy increased from RT to 3RT.

$$K_p = e^{(-RT/RT)}, K_p' = e^{(-3RT/RT)}; \Delta K_p = 0.05 - 0.37 = -0.32$$

4. Calculate the change in the equilibrium constant when the reaction free energy decreased from - RT to -3RT.

$$K_p = e^{(RT/RT)}, K_p' = e^{(3RT/RT)}; \Delta K_p = 20.09 - 2.72 = 17.37, \text{ almost an order of magnitude for a decrease of standard reaction free energy by } 2RT \text{ or } \sim 5 \text{ kcal/mol!}$$

### 18.10.2 Key points and terms

#### Key points

1. The concepts of chemical potential and reaction progress are important in chemistry and in the study of chemical kinetics. The progress of the reaction defines the rate of a chemical reaction and the rate of change of chemical potential defines the direction of the reaction.
2. The progress of a chemical reaction is zero when the reaction is about to begin ( $t = 0$ ) and it is unity when the reaction is complete. Thus, the progress defines the degree of completion.
3. The endoergonic reactions are not favorable but sufficient amount of mixing free energy can move the reaction forward and establish the equilibrium and by removing one of the products from the reaction mixture, the equilibrium can be re-established forming more product. Thus, even endoergonic reactions can be driven toward completion by combining the above two strategies.
4. The standard free energy of the reaction is related to the equilibrium constant, exponentially. Hence, small decreases in the reaction free energy can shift the equilibrium constant by a large amount.
5. The equilibrium shifts in such manner to offset the stimulus applied on the system. For example, for example for reactions where the volume increases, decrease of pressure moves the equilibrium shifts to the products' side. Addition of products to the reaction mixture shifts the equilibrium toward the reactants and so on. This is the famous LeChatelier's principle.
  4. G depends on both H and S, as  $G = H - TS$  or  $\Delta G = \Delta H - T\Delta S$ .
  5. G decreases with increase in volume at constant T.
  6. The dependence of G on T is more complicated to study because this depends on entropy but a work around gives the Gibbs-Helmholtz equation.
  7. We arrived at large number of key thermodynamic equations that originated by combining the first and the second laws of thermodynamics.

#### Key terms

Equilibrium constant, chemical potential, enthalpies and entropies of reactions

### 18.10.3 Graphing Assignment

Plot H vs  $\xi$ , H vs G, S vs  $\xi$  and  $\mu$  vs  $\xi$  for an endothermic reaction and for an exothermic reaction.

### 18.11 Further Reading

1. [https://ocw.mit.edu/courses/chemistry/5-60-thermodynamics-kinetics-spring-2008/lecture-notes/5\\_60\\_lecture16.pdf](https://ocw.mit.edu/courses/chemistry/5-60-thermodynamics-kinetics-spring-2008/lecture-notes/5_60_lecture16.pdf)
2. <https://ocw.mit.edu/courses/chemistry/5-60-thermodynamics-kinetics-spring-2008/video-lectures/lecture-15-chemical-equilibrium/>
3. <https://ocw.mit.edu/courses/chemistry/5-60-thermodynamics-kinetics-spring-2008/video-lectures/lecture-16-temperature-pressure-and-kp/>
4. [https://en.wikipedia.org/wiki/Le\\_Chatelier%27s\\_principle](https://en.wikipedia.org/wiki/Le_Chatelier%27s_principle)

## **18.12 Self Tests**