Where chemical reactions come to equilibrium:

We begin with $G(T,P)$ at fixed $T$, and $P$, for processes in which a single chemical reaction occurs. The only expressions we really need are:

$$dG = -SdT + VdP + \sum_{i=1}^{N} \mu_i dn_i$$

$$dG = \sum_{i=1}^{N} \mu_i dn_i$$

$$G = \sum_{i=1}^{N} \mu_i n_i$$

We need the relation of the chemical potential to the system variables; we use the ideal relation we developed by thinking about the mixing of gasses:

$$\mu_i = \mu_i^0 + RT \ln \frac{P_i}{P_o}$$

From here, all else that we need to do for mixtures and gasses and chemical reactions follows. Consider the chemical reaction. There are $N$ species involved in the reaction, each species is labeled $\Phi_i$, and the signed stoichiometric coefficient of that species is $\nu_i$

$$0 \Leftrightarrow \sum_{i=1}^{N} \nu_i \Phi_i$$

The number of moles is controlled by a single parameter, $X$, called the advancement parameter. $X$ can be either positive or negative.

$$n_i = n_i^{init} + \nu_i X$$

$$dn_i = \nu_i dX$$

Combining the parameters of advancement with the free energy, then for a chemical reaction or for any combination of gasses we have:

$$G = \sum_{i=1}^{N} \mu_i n_i$$

$$dG = \sum_{i=1}^{N} \mu_i dn_i = \sum_{i=1}^{N} \mu_i \nu_i dX = \Delta G_{rxn} dX$$

$$\Delta G_{rxn} = \sum_{i=1}^{N} \mu_i \nu_i = \left( \frac{dG}{dX} \right)_{T,P,\{\mu_i\}}$$

The reason we wanted $G$ or $dG$ in the first place was that for processes at constant $T$ and $P$, $dG$ was the criterion of how much work we could get from the system: $dG \leq dw_{non-PdV}$. DG was the criterion for the maximum amount of extra, non-PdV work we can get from the system. So this describes batteries and biology.

If you plot $dG$ as a function of $X$, you get work out the system if $dG$ is negative. The work that you can get from a chemical system is $dG$ and it must be negative. If a small reaction takes place, then $dX$ will be positive and $\Delta G_{rxn}$ must be negative. $\Delta G_{rxn}$ is the
slope of the plot of $G$ vs. $X$. Therefore the total work one can get from a chemical system is the total of all the dG’s for all different changes of the system by dX:

$$w_{\text{total}}^{\text{max-rev-non-PV}} = \Delta G = \int_{X=0}^{X_{\text{eq}}} \left( \frac{dG}{dX} \right)_{T,P,\mu_i} dX = \int_{X=0}^{X_{\text{eq}}} \Delta G_{\text{rxn}} dX$$

Notice that this is just the same type of integral as we always do for calculating the change of any property.

We can write the reaction Gibbs energy in terms of $X$:

$$\Delta G_{\text{rxn}} = \sum_{i=1}^{N} \mu_i v_i = \sum_{i=1}^{N} \mu_i^o v_i + RT \sum_{i=1}^{N} v_i \ln \left( \frac{P_i}{P_o} \right)$$

We take the chemical potentials at standard state to be the molar free energies of formation: $\mu_i^o = \Delta G_f^o (i)$.

$$\sum_{i=1}^{N} \mu_i v_i = \sum_{i=1}^{N} \Delta G_f^o (i) v_i = \Delta G_{\text{rxn}}^o$$

The reaction Gibbs energy at standard state is a number. You know how to compute this number from the numbers in the tables in the Appendix, as Table 4.2. So you know it is just a number, which depends on $T$ but not on $P$. Therefore we can equate it to another number $K_p$: $\Delta G_{\text{rxn}}^o = -RT \ln K_p$

This is useful because the sum of the partial pressures can be written as the proper reaction quotient:

$$\sum_{i=1}^{N} v_i \ln \left( \frac{P_i}{P_o} \right) = \ln \prod_{i=1}^{N} \left( \frac{P_i}{P_o} \right)^{v_i} = \ln Q_p$$

$$Q_p = Q_p (X) \equiv \prod_{i=1}^{N} \left( \frac{P_i}{P_o} \right)^{v_i}$$

The reason for the definition of $K_p$ rather than using $\Delta G_{\text{rxn}}^o$ is that now:

$$\Delta G_{\text{rxn}} = \sum_{i=1}^{N} \mu_i^o v_i + RT \sum_{i=1}^{N} v_i \ln \frac{P_i}{P_o} = \Delta G_{\text{rxn}}^o + RT \ln Q_p = RT \ln Q_p - RT \ln K_p = RT \ln \left( \frac{Q_p}{K_p} \right)$$

The criterion for equilibrium then is that $\Delta G_{\text{rxn}} = 0$, this is equivalent then to setting

$$\left( \frac{Q_p}{K_p} \right) = 1 \text{ or } Q_p = K_p$$

Because $Q_p = Q_p (X)$, it is a function of $X$, and this defines $X$ at equilibrium. You must solve the equation $Q_p (X_{eq}) = K_p$, for $X = X_{eq}$.

However, when not at equilibrium we can get work out of the system:
\[ w_{\text{max-non-PdY}}^{\text{total}} = \int_{X=0}^{X=X_0} \Delta G_{\text{rxn}} dX = RT \int_{X=0}^{X=X_0} \ln \left( \frac{Q_p(X)}{K_p} \right) dX, \] 
and the system comes to equilibrium as the integral reaches its upper limit. The plot of \( \Delta G_{\text{rxn}} \) vs. \( X \) is useful because the area under the curve, on either side of equilibrium is the total energy generated to do productive work. For the case where \( X \) goes from left to right the area is negative, so work comes from the system. However, for the cases where the area is positive, work comes from the system by going toward equilibrium from the right so that \( dX \) is negative, so the integral is done in the other direction and that area is also negative.

Let’s do a couple of examples. The first is that of mixing. If we just mix different amounts of stuff together, how does the energy change from having each substance pure and unmixed but at the same pressure? Well, from the entropy idea by mixing gasses we give each gas a chance to have more places to be, because the container is bigger. So we expect the basic entropy to go up so the Gibbs energy should go down. Let’s see how this happens:

\[ G = \sum_{i=1}^{N} \mu_i^0 n_i + RT \sum_{i=1}^{N} n_i \ln \frac{P_i}{P_o} \]

From this expression, we use Dalton’s law to allow the gasses to mix. The standard state chemical potentials are independent of mixing, and the total pressure is the same before and after the mixing:

\[ G^o = \sum_{i=1}^{N} \mu_i^0 n_i \]

\[ P_i = \chi_i P_o = \frac{n_i}{n_{\text{tot}}} P_o \]

\[ \Delta G_{\text{mixing}} = G - G^o = RT \sum_{i=1}^{N} n_i \ln \frac{P_i}{P_o} \]

\[ = RT n_{\text{tot}} \sum_{i=1}^{N} \chi_i \ln \chi_i \]

Now, we used the same formula for the chemical potential but we did not have the number of moles linked by a reaction. We just threw them together and find that the mixing energy is negative, because the mole fractions must be less than one, so the log terms are all negative. Therefore the mixing lowers the free energy. Moreover it is purely entropic, because

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

\[ \Delta S = -\left( \frac{\partial \Delta G}{\partial T} \right)_{P,[n]} \]
And so we have: \( \Delta G_{\text{mixing}} = -T \Delta S_{\text{mixing}} \) The maximum amount of mixing entropy occurs when each term contributes the same amount so \( \chi_i = \frac{1}{N} \), and therefore:

\[
\Delta G_{\text{mixing}} = -RTn_{\text{tot}} \ln N = -2.48 \cdot n_{\text{tot}} \ln N \quad kJ
\]

Now let’s consider a chemical reaction. Now the number of moles of each species is tied to all the other species, and we use \( X \) to keep track of all the different species. Let’s find the equilibrium for the reaction of two reactant molecules to form a product, or dimer.

\[
2\text{NO}_2 \rightleftharpoons N_2\text{O}_4
\]

\( 2A \rightleftharpoons B \)

\( 0 \rightleftharpoons B - 2A \)

Here are the different ways to write the reaction using \( B \) and \( A \) as symbols for the product and reactant respectively. We put the reactants on the r.h.s. in the last expression to show the stoichiometric coefficients with the signs. From the free energy changes of the reaction we can get the \( K_p \):

\[
\ln K_p = -\frac{\Delta G^o_{\text{rxn}}}{RT} = -\frac{\Delta G^o_f(B) - 2\Delta G^o_f(A)}{RT} = -\frac{99.8 - 2 \cdot 51.3}{2.48} = 1.13
\]

\[
K_p = 3.1
\]

There are various ways to write out \( Q_p \): It can be written in terms of the partial pressures of the gases, and it can be written in terms of the mole fractions of the species, or it can be written in terms of the number of moles of each of the species, and finally it can be written in terms of the concentrations of each of the species. Your text illustrates how it can be solved in terms of the mole fractions, so let’s look at a different approach. Let’s solve for the concentrations of the two species at equilibrium (or any other place) as a function of \( X \).

\[
\frac{P_i}{P_o} = \frac{n_i}{n_o} \frac{RT}{V} = \frac{c_i}{c_o} \frac{RTc_o}{P_o}
\]

\[
Q_p = Q_p(X) = \prod_{i=1}^N \left( \frac{P_i}{P_o} \right)^{v_i} = \left( \frac{RTc_o}{P_o} \right)^{\Delta v} \prod_{i=1}^N \left( \frac{c_i}{c_o} \right)^{v_i}
\]

\[
\frac{c_i}{c_o} = \frac{n_i}{c_o V} = \frac{n_i^{\text{init}}}{c_o V} + v_i \frac{X}{c_o V}
\]

\[
Q_p = \left( \frac{RTc_o}{P_o} \right)^{\Delta v} \prod_{i=1}^N \left( \frac{c_i^{\text{init}}}{c_o} + v_i \frac{X}{c_o V} \right)^{v_i}
\]

Finally we have \( Q_p \) actually written as a function of \( X \). We take the reference pressure to be 1 Atm, and the reference concentration to be 1 mole/liter, so the concentrations are in moles per liter, and there are no terms, which have dimensions. While it may not be as obvious as it is when using mole fractions and pressure, the \( Q_p \) does depend on pressure because the volume must respond to pressure changes. Recall that all of our chemical
reactions are going on at constant pressure, which means that as our monomers (A molecules) are forming dimers the total number of molecules is disappearing, which means that the volume is decreasing because P and T are fixed during the chemical reaction.

Applying the general formula for $Q_p$ to our specific case, we understand that the concentrations are written in terms of mole/liter so we will not keep putting in the

\[ \Delta v = 1 - 2 = -1 \]

c_o = 1 mol / liter, and define \( x = \frac{X}{c_o V} \), and \[ \left( \frac{RT c_o}{P_o} \right)^{\Delta v} = 24.8^{-1} = 0.0403 \]

Then applying the general formula of $Q_p$ to the problem at hand we find:

\[ Q_c = Q_p 24.8 = \prod_{i=1}^{N} (c_i + v_i x)^{v_i} = (c_B^{init} + x)^i (c_A^{init} - 2x)^{-2} = \frac{(c_B^{init} + x)^{\frac{1}{i}}}{(c_A^{init} - 2x)^{\frac{2}{i}}} \]

This gives us the expression for $Q_p$ for any advancement we choose. The one of interest is equilibrium. Then we solve this by setting: $K_p = Q_p$ or $K_c = Q_c$:

\[ K_p = Q_p = 0.0403 \frac{(c_B^{init} + x)^{\frac{1}{i}}}{(c_A^{init} - 2x)^{\frac{2}{i}}} \]

\[ K_c = \frac{K_p}{\left( \frac{RT c_o}{P_o} \right)^{\Delta v}} = \frac{3.1}{0.0403} = 77 = \frac{(c_B^{init} + x_{eq})^{\frac{1}{i}}}{(c_A^{init} - 2x_{eq})^{\frac{2}{i}}} \]

This leads to a second order polynomial problem, for which the general form of the solution is known. We can compare with the general solution to this problem done in example 6.9 by realizing that this reaction is the reaction in 6.9 run in the reverse direction. Therefore our $x$ will be a negative number. So let’s assume that $c_A^{init} = 0$ and express the equilibrium advancement in terms of $K_c$ and the initial amount of B. Realize our $K_c$ is the inverse of the one needed for the reaction run in the other direction.

\[ 4K_c x_{eq}^2 - \left( c_B^{init} + x_{eq} \right) = 0 \]

The general answer is:

\[ x_{eq} = \frac{1 \pm \sqrt{1 + 4 \cdot 4K_c c_B^{init}}}{8K_c} \]

And we much choose the sign in front of the square root so that $x$ is negative. So the – sign gives:
\[-x_{eq} = \frac{\sqrt{1 + 4 \cdot 4K_c c_{B, init}} - 1}{8K_c}.\] In terms then of the fraction amount of \( c_B \) left:

\[
\frac{c_B}{c_{B, init}} = 1 + \frac{x_{eq}}{c_{B, init}} = 1 + \frac{1 - \sqrt{1 + 16K_cc_{B, init}}}{8K_c c_{B, init}}
\]

\[y = 8K_cc_{B, init}\]

\[
\frac{c_B}{c_{B, init}} = 1 + \frac{1 - \sqrt{1 + 2y}}{y}
\]

The above is a plot of the final function in terms of the single parameter, \( y \), which is the product of the equilibrium constant and the initial concentration of B (the dimer). Notice that at low values of \( K_c \) there is no dimer left, as the value of the equilibrium constant goes to infinity the concentration is that of pure dimer. Notice in this example \( K_c = 77 \), so if we start with 0.1M dimer, we will end up with half dimer half monomer, or 0.05M dimer.

Now, lets consider a very important problem that illustrates one of the principles of LeChatellier. Consider the monomer and dimer in equilibrium initially, and then we change the pressure. For illustrative purposes lets assume we double the pressure. Now how will the system respond, and what will the new concentrations be and what will the new volume be?

The system is in equilibrium initially that means that \( C(A) \) and \( C(B) \) are connected as:
\[ K_c = \frac{c_B'}{(c_A')}^2 \]. We have omitted the reference concentration and understand these concentrations must be in moles per liter. This brings up an interesting question: Does \( K_c \) have units?

We now double the pressure. To first order this halves the volume or doubles the concentrations. If that is the case the new concentrations are out of balance because now they are off by a factor of 2 from the equilibrium constant, \( K_c \). So we must shift the equilibrium to bring the system back into balance. This means more \( B \) needs to be made at the expense of \( A \). Doing so shifts the equilibrium toward dimer, which now reduces the number of molecules in the container, this then causes a further reduction in the volume of the contain. As LeChatellier put it, the system responded to the external change by yielding to it. So lets see if we can show that the total number of molecules, or moles of gas must drop and that the volume at the end is even smaller than half the original volume.

There are two approaches. Let’s see how the concentrations must change using the ideal gas law, and knowing that the compression is done isothermally so \( T \) does not change:

\[
\frac{PV}{n_{\text{tot}}} = RT = \frac{P'V'}{n_{\text{tot}}'}
\]

\[
n_{\text{tot}} = n_A + n_B \neq n_{\text{tot}}'
\]

\[
\frac{n_{\text{tot}}}{V'} = c_B' + c_A'
\]

\[
\frac{n_{\text{tot}}}{V} = \frac{n_A}{V} + \frac{n_B}{V} = c_B + c_A
\]

\[
\left(\frac{c_B'}{c_A'}\right)\frac{P}{P'} = c_B + c_A
\]

Therefore the sums of the concentrations are related to one another before and after compression by the compression ratio, but this no longer applies to each species individually because of the equilibrium. We require the system to come to equilibrium after compression, just as it was at equilibrium before compression and the equilibrium constant does not depend on pressure.

\[ K_c = \frac{c_B'}{(c_A')}^2 = \frac{c_B}{(c_A)^2} \]

At this point we do not know \( C(A) \) and \( C(B) \) but we have two equations and two unknowns. We can solve for them.

To illustrate how this works lets assume \( c_A' = 0.1M; c_B' = 0.77M; \frac{P}{P'} = 2 \). Then we can solve for the two unknowns:
This is a pretty dramatic deviation from what we would have gotten had there been no chemical reaction going on. We would have expected $C(A) = 0.2\text{M}$, or the concentration to have doubled, so we find that it moved less than half way. It should have doubled but many monomers were used to make dimers. This is a basic principle of LeChatellier. If you stress the system, as here to go from $C(A,\text{Initially}) = 0.1$ to a final value of $0.2\text{M}$ but it can respond, and it will respond to absorb the effect, and so the final concentration here lies intermediate between the initial value and the expected-if-no-reaction final value. So $C(B)$ absorbed all of the doubling and then some.

We have solved the problem for the concentrations, but unless we go further we cannot solve for the number of moles or the volume. We now must use the advancement to determine the number of moles that shifted. From above we know that $n_A' = 7.7n_A$ and that $n_B = 11.02\cdot n_A$. To use these values to find the total we need to follow the number of moles that change and obtain the advancement parameter, then we can compute the new total number of moles.

This brings up the second method. We must use the reaction advancement, $X$, to find how many moles changed from monomer to dimer. Because we want the extensive quantities we need to compute the actual number of moles that change from $A$ to $B$. That is the only way we will get the change in volume:

$$V = \frac{n_{\text{tot}}P^i}{n^i_P}V^i$$

$$n_A = n_A' - 2X$$

$$n_B = n_B' + X$$

$$n_{\text{tot}} = n_A + n_B = (n_A' + n_B') - X = n_{\text{tot}}' - X$$

From here we can directly compute the degree of advancement because we know the molar ratio from the concentrations of $A$ and $B$: 

$$77c_A^2 = c_B$$

$$2 \cdot 0.87 = c_B + c_A = 77c_A^2 + c_A$$

$$c_A = \frac{-1 + \sqrt{1 + 4 \cdot 77 \cdot 2 \cdot 0.87}}{2 \cdot 77} = 0.144\text{M}$$

$$c_b = 1.74 - 0.144 = 1.6\text{M}$$
\[ \frac{V}{V^I} = \frac{1}{2} \frac{n_{\text{tot}}}{n_A^I} \]
\[ z = \frac{X}{n_A^I} \]
\[ \frac{n_B}{n_A} = \frac{n_B^I + X}{n_A^I - 2X} = \frac{n_B^I + z}{1 - 2z} \]
\[ 11.02 = \frac{7.7 + z}{1 - 2z} \]
\[ z = 0.144 \]
\[ \frac{n_{\text{tot}}}{n_I} = 1 - \frac{n_A^I}{n_{\text{tot}}} = 1 - \frac{0.144 \cdot n_A^I}{8.7 \cdot n_A^I} = 0.98 \]

This shows that there is a small shift of the total number of moles, so that the new volume is a bit less than \( \frac{1}{2} \), which illustrates that the volume indeed decreases more than it would if the system were not dynamic with a reaction going on. The new volume then was initially expected to be \( \frac{1}{2} \) the original volume, but the shift in the number of moles of A to B reduced the number of moles and this reduced the volume by 98%, not a big change, after all this work to compute it. But then, knowing you know how to do a problem is worth more than the answer.

The problem is finished but it can be interesting to try to obtain the same result using the mole fraction method and computing the shift or advancement parameter directly from the \( K_p \) equations. You may want to compare the methods, and decide if one is easier than the other. The equilibrium part can be written in terms of the pressures and the mole fractions or number of moles of the two gasses:

\[ K_P = 3.1 = \left( \frac{P_A}{P_o} \right)^2 \left( \frac{P_B}{P_o} \right)^4 = \frac{P_A}{P} \cdot \frac{\chi_B^I}{\chi_A^I} \]
\[ K_P = \frac{P_A}{P} \cdot \frac{\chi_B^I}{\chi_A^I} = \frac{P_A}{P} \cdot \frac{n_B^I}{n_A^I} \cdot \frac{(n_A^I + n_B^I)}{(n_A^I)^2} \]
\[ K_P = \frac{P_A}{P} \cdot \frac{\chi_B^I}{\chi_A^I} = \frac{P_A}{P} \cdot \frac{(n_B^I + X)}{(n_A^I)^2} \cdot \frac{(n_A^I + n_B^I - X)}{(n_A^I - 2X)^2} \]

We now use that \( n_B^I = 7.7n_A^I \) which we specified initially in the problem above.
\[ K_p = 3.1 = \left( \frac{P_A}{P_o} \right)^{-2} \left( \frac{P_B}{P_o} \right)^{1} = \frac{P_A}{P} \cdot \chi_B \]

\[ \frac{P}{P_o} = \frac{7.7 \cdot 8.7}{3.1} = 21.6 \]

\[ 3.1 = \frac{P_o}{P} \cdot \left( \frac{7.7 + \frac{X}{n'_A}}{8.7 - \frac{X}{n'_A}} \right) \left( 1 - \frac{2 \cdot X}{n'_A} \right) \]

\[ \frac{P}{P'} = \frac{7.7 \cdot 8.7}{8.7} = \frac{8.7 + \frac{X}{n'_A}}{8.7 - \frac{X}{n'_A}} \left( 1 - \frac{2 \cdot X}{n'_A} \right) \]

We can now solve for \( z = \frac{X}{n'_A} \). Notice that \( z=0 \) if the new pressure is the same as the initial pressure. But now the new pressure is twice the initial pressure:

\[ 2 \cdot 7.7 \cdot 8.7 (1 - 2z)^2 = (7.7 + z) \cdot (8.7 - z) \]

\[ 8z^2 - 8z + 1 = 0 \]

\[ z = \frac{\sqrt{8 \cdot 8 - 4 \cdot 8}}{2 \cdot 8} = \frac{1 - \sqrt{1 - \frac{1}{2}}}{2} = \frac{1 - .707}{2} = 0.1464 \]

This shows us how the number of moles shifted:

\[ n_A = n'_A \left(1 - 2z\right) = \frac{n'_A}{2} = 0.71 \cdot n'_A \]

The number of moles of A dropped by 70%. Using the ideal gas relations above:

\[ \frac{V}{V_i} = \frac{1}{2} \cdot \left( 1 - \frac{z}{8.7} \right) = \frac{1}{2} \cdot 0.98 \]

Could we have gotten some insight: Yes, we know the number of moles of A was 15% of that of B, and so we knew the concentration of A dropped by 50% from what we expected, so about 1/3 of the A molecules moved to B, so only half of them are the net less, so this give about a 2% change, which is about what we saw.

We would find a more dramatic effect if we were to reduce the pressure by two fold rather than increase it. In that case we have a lot of dimer molecules that can dissociate to make monomers, so the change in volume should be more dramatic than the factor of 2 increase we would expect. Perhaps as practice you might compute the new volume ratio if the pressure is reduced by two fold.