

6.4: Chemical reactions and chemical potential

In the preceding section we calculated $\Delta_r G^\circ$ of a reaction at the standard state (or $\Delta_r G$ at a non-standard temperature) assuming that the reaction went to completion. In a mathematical sense, what we were doing is integrating the partial change of Gibbs energy ∂G with the lower limit representing the initial reactant state and the upper limit defined as the product state as shown in Equation 6.9:

$$\int_{\sum_{\text{reactants}} \epsilon \Delta_r G}^{\sum_{\text{products}} \epsilon \Delta_r G} dG = \sum_{\text{products}} \epsilon \Delta_r G - \sum_{\text{reactants}} \epsilon \Delta_r G$$

This is depicted graphically in Figure 6.4A, in which a negative $\Delta_r G^\circ$ implies that a reaction will go to completion. This is because a process that exudes Gibbs energy is also creating a net gain in total entropy which the 2nd Law allows.

However, the idea that chemical reaction yields are either 0% or 100% clearly isn't correct. After all, if this is true then why are synthetic chemists working hard to optimize reaction conditions? The problem is that we didn't consider how $\Delta_r G$ changes as a function of the extent of reaction " ϵ ", which is a unitless parameter that varies from $\epsilon = 0$ (all reactants) to $\epsilon = 1$ (all products). As shown in Figure 6.4B, if there is a minimum in the Gibbs energy below either product or reactant at point $\epsilon = \alpha$, then the reaction will stop there as the most total entropy is generated at that point. The reaction yield is thus determined by the value of α .

We can use chemical thermodynamics to determine the yield of a reaction. What we know is that $\Delta_r G = \frac{\partial G}{\partial \epsilon} = 0$ J when the reaction stops and the system has reached equilibrium. To go forward we need to know the mechanism by which $\Delta_r G$ changes as a spontaneous reaction proceeds forward after initiation. This will also allow us to calculate the reaction yield. As usual, we will start with a simple example.

6.4.1 Phase Changes. We will start analyzing chemical reactions using the example of ice melting. Although boring, it has the benefit of being very simple to analyze. First, we need to realize that a reaction yield is a percentage, and thus independent of how many moles of reactants initiate the reaction. This points towards the thermodynamic drive being an intensive variable. In fact, it's the energy per mole, which must change throughout a reaction as there must be an energetic consequence to chemicals being *removed from* or *added into* a system. Note that the addition of chemicals into a system represents the creation of products, while the reactants are removed.

In our previous derivations of U, H, A and G we never considered that the moles could change. As this is unavoidable in a chemical reaction, we have to revisit our equations for energy starting with internal energy U, the change of which is:

$$\partial U = -P\partial V + T\partial S + \left(\frac{\partial U}{\partial n}\right)_{V,S} \partial n \quad (6.10)$$

Likewise:

$$\partial H = V\partial P + T\partial S + \left(\frac{\partial H}{\partial n}\right)_{P,S} \partial n \quad (6.11)$$

$$\partial A = -P\partial V - S\partial T + \left(\frac{\partial A}{\partial n}\right)_{V,T} \partial n \quad (6.12)$$

$$\partial G = V\partial P - S\partial T + \left(\frac{\partial G}{\partial n}\right)_{P,T} \partial n \quad (6.13)$$

This is all rather unfortunate, because it appears that all four of our energy equations just became more complicated with the addition of new terms! However, this is in fact not quite the case. For example, we know that $H = U + PV$, for which the change in enthalpy is:

$$\partial H = \partial U + \partial(PV)$$

Substituting in Equation 6.11 for ∂H and Equation 6.10 for ∂U :

$$V\partial P + T\partial S + \left(\frac{\partial H}{\partial n}\right)_{P,S} \partial n = -P\partial V + T\partial S + \left(\frac{\partial U}{\partial n}\right)_{V,S} \partial n + \partial(PV)$$

which can be simplified:

$$V\partial P + T\partial S + \left(\frac{\partial H}{\partial n}\right)_{P,S} \partial n = -P\partial V + T\partial S + \left(\frac{\partial U}{\partial n}\right)_{V,S} \partial n + P\partial V + V\partial P$$

After doing some cancellation and taking like terms to one side: $V\partial P - V\partial P + T\partial S - T\partial S + \left(\frac{\partial H}{\partial n}\right)_{P,S} \partial n = \left(\frac{\partial U}{\partial n}\right)_{V,S} \partial n$ which further simplifies to:

$$\left(\frac{\partial H}{\partial n}\right)_{P,S} \partial n = \left(\frac{\partial U}{\partial n}\right)_{V,S} \partial n$$

Division by ∂n leads to $\left(\frac{\partial H}{\partial n}\right)_{P,S} = \left(\frac{\partial U}{\partial n}\right)_{V,S}$. Similar derivations reveal that:

$$\left(\frac{\partial G}{\partial n}\right)_{P,T} = \left(\frac{\partial A}{\partial n}\right)_{V,T} = \left(\frac{\partial H}{\partial n}\right)_{P,S} = \left(\frac{\partial U}{\partial n}\right)_{V,S} = \mu \quad (6.4.1)$$

Equation 6.4.1 demonstrates that, however we express the change in energy per mole and whatever conditions are held constant, we are dealing with the same thermodynamic quantity. We will call it the chemical potential μ , which can be used to calculate the change in energy with increasing / decreasing moles of a substance in a system as $\mu \cdot \partial n$. For the purposes of this chapter and later ones, we will assume conditions of constant temperature and pressure for all reactions.

6.4.1.1 Ice melting. We will study the melting of an ice cube into liquid water as characterized by the chemical potentials μ_{ice} and μ_{water} . Let us first assume that the ice and water are in equilibrium, which requires that change in Gibbs energy is 0 J if any of the ice melts (or water freezes). Mathematically this is expressed as:

$$\partial(\Delta_r G) = \mu_{\text{water}} \partial n_{\text{water}} + \mu_{\text{ice}} \partial n_{\text{ice}} = 0 \text{ J}$$

where we have added the change in Gibbs energy in each phase to represent the total. Since the ice and water are both H₂O, then it must be true that $\partial n_{\text{ice}} = -\partial n_{\text{water}}$, which we can insert into the above as: $\mu_{\text{water}} \partial n_{\text{water}} - \mu_{\text{ice}} \partial n_{\text{water}} = 0 \text{ J}$. Rearranging terms:

$$(\mu_{\text{water}} - \mu_{\text{ice}}) \partial n_{\text{water}} = 0 \text{ J}$$

Here, we have to figure out whether $(\mu_{\text{water}} - \mu_{\text{ice}})$ or $\partial n_{\text{water}}$ is 0. To resolve we can perform the following experiment- put an ice cube into water at 0 °C. If you wait long enough, the cube will transform into a sphere, which means that it is possible to have microscopic mass transfer even at equilibrium which implies $|\partial n_{\text{water}}|$ doesn't have to be 0, even at equilibrium. Therefore, it must be true that $\mu_{\text{water}} - \mu_{\text{ice}} = 0 \text{ J/mol}$, and thus $\mu_{\text{water}} = \mu_{\text{ice}}$ at equilibrium. We just proved that the chemical potentials of things at equilibrium are equal!

Let's now raise the temperature of the ice / water system so the ice melts. The system is no longer at equilibrium, and the irreversible melting of ice increases the total entropy of the Universe. Under conditions of constant temperature and pressure this requires a negative change in Gibbs energy: $\Delta_r G = \mu_{\text{water}} \Delta n_{\text{water}} + \mu_{\text{ice}} \Delta n_{\text{ice}} < 0 \text{ J}$

which trickles down to $(\mu_{\text{water}} - \mu_{\text{ice}}) \Delta n_{\text{water}} < 0 \text{ J}$ for the same reasons as above. Now since $\Delta n_{\text{water}} > 0 \text{ mol}$ because the ice is melting, then it must be true that $\mu_{\text{water}} - \mu_{\text{ice}} < 0 \text{ J/mol}$, requiring $\mu_{\text{water}} < \mu_{\text{ice}}$. Consequently, when a reaction occurs, mass transfers from the high chemical potential to the lower chemical potential state. While this is true for ice melting, it's also true for any chemical reaction including the ones where actual chemical bonds are broken and formed.

6.4.2 Real Chemical Reactions: Changing chemical potential. Based on the discussion above it is clear that the net change of the chemical potential of a spontaneous reaction ($\Delta_r\mu$) is negative. Of course, all reactions eventually stop at which time the chemical potentials of reactants and products must be equal and $\Delta_r\mu = 0 \text{ J/mol}$. Thus, there must be some mechanism for the potentials of reactants and products to change though the course of the reaction. Let's study a reaction in the gas phase, starting with 1 mole of a reactant at the standard state. The chemical potential will decrease as the reaction progresses, but the question is how do we measure this change in μ ? Here is a simple observation- as the reactant is consumed, its partial pressure decreases. This is akin to performing work (see Sec. 2.2):

$$\Delta w = -nRT \cdot \ln\left(\frac{V_f}{V_i}\right)$$

We insert the perfect gas relationship to modify the work equation for pressure:

$$\Delta w = -nRT \cdot \ln\left(\frac{V_f}{V_i}\right) = -nRT \cdot \ln\left(\frac{nRT/P_f}{nRT/P_i}\right) = -nRT \cdot \ln\left(\frac{P_i}{P_f}\right) = nRT \cdot \ln\left(\frac{P_f}{P_i}\right)$$

We stipulated that the initial pressure P_i is the standard state pressure $P^\circ = 1 \text{ bar}$ (recall that the $^\circ$ symbol refers to the standard state, which is 298.15 K and 1 bar pressure). Furthermore, the pressure is actually the reactant's partial pressure, not total pressure, since the product(s) will also contribute to the total pressure. Next we divide by n to calculate the work energy per mole of reactant:

$$\frac{\Delta w}{n} = RT \cdot \ln\left(\frac{P_f}{P^\circ}\right)$$

This should be added to the initial energy per mole (μ° , the chemical potential at the standard state) to represent the change in the chemical potential of the reactant as it is depleted during the course of the reaction:

$$mu = \mu^\circ + RT \cdot \ln\left(\frac{P_f}{P^\circ}\right) \quad (6.4.2)$$

We can make another modification using Dalton's Law, which states that the partial pressure of a gas can be expressed as the total pressure times the mole fraction of that gas. In other words, $P_f = \chi \cdot P$, and thus:

$$mu = \mu^\circ + RT \cdot \ln\left(\frac{\chi \cdot P}{P^\circ}\right) \quad (6.4.3)$$

where χ is the mole fraction of the gas which changes through the course of the reaction. Initially $\chi=1$, and if the reactant is totally consumed then $\chi=0$ in the final state.

Equation 6.4.3 allows us to connect the changing mole fraction's effect on a reaction's partial ($\Delta_r G$) via the chemical potential. To this end recall: $\partial G = V\partial P - S\partial T + \left(\frac{\partial G}{\partial n}\right)_{P,T} \partial n$, which we simplify for constant pressure and temperature conditions ($\partial P = \partial T = 0$) and for the fact that multiple species (reactants and products) exist:

$$\partial G = \sum \left(\frac{\partial G}{\partial n}\right)_i \cdot \partial n_i = \sum \mu_i \cdot \partial n_i$$

where we used $\left(\frac{\partial G}{\partial n}\right)_i = \mu_i$ and inserted an index "i" to delineate the various chemical participants (the reactants and products). We will analyze the energies further using the extent of the reaction " ϵ " that was introduced earlier. Recall that ϵ varies from 0 \rightarrow 1, where $\epsilon = 0$ represents the initial reactant state and $\epsilon = 1$ is for an all product state. A graph of G vs. ϵ is shown in Fig. 6.5A, where we can see that $\frac{\partial G}{\partial \epsilon}$ is the quantity of interest. Initially, $\frac{\partial G}{\partial \epsilon}$ is negative near $\epsilon = 0$. Does this make the reaction spontaneous? To answer, we assume that $\partial \epsilon$ is positive (the reaction goes forward) and as a result ∂G must be negative which is the definition of a spontaneous reaction. At some point $\frac{\partial G}{\partial \epsilon} = 0 \text{ J}$ and the reaction stops. It is here that the most negative reaction $\Delta_r G$ is realized as determined using:

$$\Delta_r G = \int_0^\alpha \frac{\partial G}{\partial \epsilon} \partial \epsilon$$

which is also where the most total entropy is generated. We see this more clearly in Figure 6.5B, which is a plot of the derivative $\frac{\partial G}{\partial \epsilon}$ vs. ϵ . The negative area (shaded red) starting from the reactant side to point $\epsilon = \alpha$ generates the most negative net $\Delta_r G$ possible. Further progression of the reaction past point α diminishes the net $\Delta_r G$ as the additional Gibbs energy contribution is positive (blue shaded area), which consumes the net entropy and is thus not allowed.

The extent of the reaction ϵ is related to the changes in the moles of products and reactants by the simple relationship: $\partial n = v \cdot \partial \epsilon$, where v represents the stoichiometric coefficient of a reactant or product. As such, v is positive for products, because these "appear" during the reaction, whereas v is negative for reactants since they "disappear". We insert these ideas into the change of Gibbs energy:

$$\partial G = \sum \mu_i \cdot \partial n = \sum_{\text{products}} v_i \cdot \mu_i \cdot \partial \epsilon - \sum_{\text{reactants}} v_i \cdot \mu_i \cdot \partial \epsilon = \left(\sum_{\text{products}} v_i \cdot \mu_i - \sum_{\text{reactants}} v_i \cdot \mu_i \right) \cdot \partial \epsilon$$

Division of $\partial \epsilon$ on both sides reveals:

$$\frac{\partial G}{\partial \epsilon} = \sum_{\text{products}} v_i \cdot \mu_i - \sum_{\text{reactants}} v_i \cdot \mu_i$$

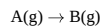
Using this relationship with the mole fraction (χ)-dependent chemical potentials $\mu_i = \mu_i^\circ + RT \cdot \ln\left(\frac{\chi \cdot P}{P^\circ}\right)$ allow us to find the composition of a reactive system when the reaction reaches equilibrium as defined by $\frac{\partial G}{\partial \epsilon} = 0 \text{ J}$. In other words, we can determine the reaction yield.

For any of this to practically work, we must insert real data into the thermochemical relationship above. The chemical potential of a reacting entity is its per molar Gibbs energy due to the fact that: $\mu = \frac{\partial G}{\partial n} = \frac{G}{n} = G_m$, which is true because energy and moles are extensive quantities and can be integrated as:

$$\mu = \frac{\int_0^G \partial G}{\int_0^n \partial n} = \frac{G}{n} = G_m$$

Due to the relative nature of energy, we use the standard state per molar Gibbs energy of formation from a data table to represent the chemical potential, i.e. $\mu^\circ = G_m^\circ = \Delta_f G_m^\circ$. When we put this all together, we see that $\mu = \mu^\circ + RT \cdot \ln\left(\frac{\chi \cdot P}{P^\circ}\right)$ is equivalent to $\Delta_f G_m = \Delta_f G_m^\circ + RT \cdot \ln\left(\frac{\chi \cdot P}{P^\circ}\right)$. This also means that $\frac{\partial G}{\partial \epsilon}$ is the "instantaneous" $\Delta_r G$ at point ϵ along the reaction.

At this point you may be overwhelmed with the complexity of composition-dependent chemical potentials derived above. We will stop and work some examples that will hopefully make all of this much more clear. First, we will determine the reaction yield for something simple:



Each species has its own chemical potential and mole fraction. Starting with $\Delta_r G$:

$$\Delta_r G = \nu_B \cdot \mu_B - \nu_A \cdot \mu_A$$

$$= \nu_B \cdot \mu_B^\circ + \nu_B \cdot RT \cdot \ln\left(\frac{\chi_B \cdot P}{P^\circ}\right) - \nu_A \cdot \mu_A^\circ - \nu_A \cdot RT \cdot \ln\left(\frac{\chi_A \cdot P}{P^\circ}\right)$$

$$= (\nu_B \cdot \mu_B^\circ - \nu_A \cdot \mu_A^\circ) + RT \cdot \left(\nu_B \cdot \ln\left(\frac{\chi_B \cdot P}{P^\circ}\right) - \nu_A \cdot \ln\left(\frac{\chi_A \cdot P}{P^\circ}\right) \right)$$

Applying the identities: $y \cdot \ln(x) = \ln(x^y)$; $\ln(x) - \ln(y) = \ln(x \cdot y^{-1})$; and $x^A \cdot x^{-B} = x^{A-B}$:

$$\Delta_r G = \left(\nu_B \mu_B^\circ - \nu_A \mu_A^\circ \right) + RT \ln \left(\frac{\chi_B^{\nu_B} \chi_A^{-\nu_A}}{P^{\nu_B - \nu_A}} \right)$$

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$$\Delta_r G = \left(\nu_B \mu_B^\circ - \nu_A \mu_A^\circ \right) + RT \ln \left(\frac{\chi_B^{\nu_B} \chi_A^{-\nu_A}}{P^{\nu_B - \nu_A}} \right)$$

The stoichiometric coefficients ($\nu_{A,B}$) are equal to 1 mol due to the 1:1 stoichiometry of A and B in this example. This allows us to remove the pressure term: $\left(\frac{P}{P^\circ}\right)^{\nu_B - \nu_A} = \left(\frac{P}{P^\circ}\right)^0 = 1$. We can also insert the definition of the initial chemical potentials as the formation Gibbs energy: $\mu^\circ = \Delta_f G_m^\circ$; thus, we can simplify $\Delta_r G$ as:

$$\Delta_r G = \Delta_f G_{B,m}^\circ - \Delta_f G_{A,m}^\circ + RT \ln \left(\frac{\chi_B}{\chi_A} \right)$$

What is the above relationship good for? We assume that most chemical reactions will occur, but we just don't know how far, so we use the above relationship to determine χ_B and χ_A at equilibrium, which will give us the reaction yield. And at the end of a reaction $\Delta_r G = \nu_B \cdot \mu_B - \nu_A \cdot \mu_A = 0$, which means that:

$$0 = \Delta_f G_{B,m}^\circ - \Delta_f G_{A,m}^\circ + RT \ln \left(\frac{\chi_B}{\chi_A} \right)$$

allowing us to simplify the above to:

$$\Delta_f G_{B,m}^\circ - \Delta_f G_{A,m}^\circ = -RT \ln \left(\frac{\chi_B}{\chi_A} \right) \quad (6.4.4)$$

Note that $\Delta_f G_{B,m}^\circ - \Delta_f G_{A,m}^\circ = \Delta_r G^\circ$ is what you calculate from a standard Hess's Law question. This quantity is *not* the same as $\Delta_r G$, which accounts for the changing chemical potential as the reaction occurs due to the $RT \cdot \ln\left(\frac{\chi_B}{\chi_A}\right)$ term.

With equation 6.17 we can calculate χ_B and χ_A at equilibrium to determine the reaction yield. First, we must account for the fact that the mole fractions are not independent of each other because $\chi_A + \chi_B = 1$. Let's make a table that details the stoichiometries of the product and reactants before and after the reaction, as well as the resulting mole fractions. We initially begin with "n" moles of A. At the end of the reaction a certain fraction of A has reacted, which we will call α . As a result, there are $n - n\alpha$ moles of A and $n\alpha$ moles of B at the end:

	A	B
Initial	n	0
Equilibrium	n - n·α	n · α
Mole fraction	1 - α	α

Here you can see that, if $\alpha=0$, then no reaction has taken place. If $\alpha=1$ then all the A reacted to become B giving a 100% yield. The mole fractions of products and reactants at equilibrium are determined by adding up the total number of moles at equilibrium: $n_A + n_B = n - n\alpha + n\alpha = n$. Thus, the mole fraction of A at equilibrium is $\chi_A = \frac{n - n\alpha}{n} = 1 - \alpha$ and $\chi_B = \frac{n\alpha}{n} = \alpha$. Plug these into the preceding relationship for the chemical potential and mole fractions, Equation 6.17:

$$\Delta_r G^\circ = -RT \ln \left(\frac{\alpha}{1 - \alpha} \right)$$

With a numerical value for $\Delta_r G^\circ$ from a Hess's Law calculation, we can thus determine α which is the reaction yield. To demonstrate, we will apply some limiting scenarios; let's say that the difference in Gibbs formation energies of A and B is 0 J. In this case, we are solving:

$$0 = -RT \ln \left(\frac{\alpha}{1 - \alpha} \right)$$

which simplifies to: $\ln\left(\frac{\alpha}{1 - \alpha}\right) = 0$. Taking the exponential of both sides: $\exp\left(\ln\left(\frac{\alpha}{1 - \alpha}\right)\right) = \exp(0)$. The result is: $\frac{\alpha}{1 - \alpha} = 1$, and thus $\alpha=0.5$. The result is sensible- if there is no driving force to form either products or reactants, then the reaction goes to 1/2 completion! This is graphically illustrated in Figure 6.6, along with scenarios of $\Delta_r G^\circ = 2$ J, $\Delta_r G^\circ = -2$ J, and finally $\Delta_r G^\circ = -10$ J. The way that the G vs. ϵ curve bends downwards is due to the entropy of mixing between the product and reactant as discussed below.

6.4.3 Entropic Contribution. Here we will examine why a reaction with a $\Delta_r G^\circ = 0$ J, technically non-spontaneous, has a product yield of 50%. While we could simply say "because the math worked out that way" as shown in the previous section, there is a more fundamental reason. It is due to that fact that changes in Gibbs energy is derived from enthalpy and entropy, and it is entropy that can drive a reaction forward even when it is not spontaneous. To understand, recall that the change in a system entropy per mole is: $\Delta S_m = -R \cdot \ln\left(\frac{P_f}{P_i}\right)$ at constant temperature, which when multiplied by -T gives us:

$$-T \cdot \Delta S_m = RT \ln \left(\frac{P_f}{P_i} \right) = RT \ln \left(\frac{\chi \cdot P}{P^\circ} \right)$$

where $P_f = \chi \cdot P$ from Dalton's Law and $P_i = P^\circ$ due to standard state conditions. This is the same composition-adjustment factor that was applied to the chemical potential, Equation 6.16: $\mu = \mu^\circ + RT \cdot \ln\left(\frac{\chi \cdot P}{P^\circ}\right)$. The way to understand the result is the fact that it is entropically favorable

for chemical "A" to mix with "B", but the only way to do so is for some of "A" to react to become "B"! This is why most of the G vs. ϵ curves in Figure 6.5 bow downwards near the middle of the graph, where mixing is greatest. We see that more products form in the case of

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 $\Delta_r G^\circ = -10$ kJ due to the generation of greater total entropy near the ~100% reaction yield point. In this situation, the reaction likely produces a lot of heat (i.e. has a large negative enthalpy), which adds significant exterior entropy. Hence, it is this extra generation of exterior entropy due to a near-completion of the reaction that overwhelms the entropic effects of mixing in the system that wants to stop at the 1/2 way point.

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