

3.10: Thermodynamics Applied to Chemical Reactions

3.10.1 Thermodynamics of mixtures

So far in this book we have considered mostly pure substances. What happens if we have a mixture of several chemical species, say the four substances A, B, C, and D? In this case the mechanical parameters will include the numbers N_A , N_B , N_C , and N_D , and the entropy

$$S(E, V, N_A, N_B, N_C, N_D) \quad (3.10.1)$$

will have the total differential

$$dS = \frac{1}{T} dE + \frac{p}{T} dV - \sum_{i=A}^D \frac{\mu_i}{T} dN_i. \quad (3.10.2)$$

The differential above defines the quantity

$$\mu_A(E, V, N_A, N_B, N_C, N_D) = -T(E, V, N_A, N_B, N_C, N_D) \left(\frac{\partial S}{\partial N_A} \right)_{E, V, N_B, N_C, N_D}. \quad (3.10.3)$$

Notice that the chemical potential of substance A can depend upon the number of molecules of B, C, and D present, so it is not necessarily the same as the chemical potential of pure A. (For example, the chemical potential of sugar dissolved in a cup of water is not equal to the chemical potential of pure sugar, unless the solution is saturated and there is undissolved sugar at the bottom of the cup.)

It is convenient to define the total number of molecules

$$N = N_A + N_B + N_C + N_D \quad (3.10.4)$$

and the (intensive) fractional amounts

$$f_A = \frac{N_A}{N}, \text{ etc.} \quad (3.10.5)$$

The thermodynamic dance can be followed for mixtures just as well as it can be for pure substances. One noteworthy result is

$$\begin{aligned} G(T, p, N_A, N_B, N_C, N_D) &\equiv E - TS + pV \\ &= \sum_{i=A}^D \mu_i(T, p, f_A, f_B, f_C, f_D) N_i \end{aligned}$$

3.10.2 Equilibrium condition for a chemical reaction

Suppose that α molecules of substance A can combine with β molecules of substance B to produce γ molecules of substance C and δ molecules of substance D. If this can happen, then of course the reverse can also occur: γ molecules of substance C may combine with δ molecules of substance D to produce α molecules of substance A and β molecules of substance B. The first action is called a “forward step” of the chemical reaction, and the second is called a “backward step”. This chemical reaction is symbolized by



Thus if we mix together a certain number of molecules each of A, B, C, and D, there can be a reaction and we might not end up with the same distribution of molecules that we started off with. It is possible that there will be more forward than backwards steps, in which case we will end up with more C’s and D’s and fewer A’s and B’s than we had at the start, or it could go predominantly the other way. It is allowable for the system to exist in a wide range of conditions, varying from “mostly reactants” to “mostly products”, but experience teaches us that the overwhelmingly likely condition is one with some of each are present. In this condition reactions still proceed, in both the forward and backward directions, but steps in both directions proceed at the same rate so there is no net change in the number of molecules of any species. This condition is called “chemical equilibrium”.

The above paragraph precisely parallels the discussion in section 2.7, “Using entropy to find (define) temperature and pressure”. In that section we saw that if, for example, two systems could exchange volume, it was possible for all the volume to go to one system or for all of it to go to the other system, but that the overwhelmingly likely possibility was the “equilibrium condition” in which the

two systems shared volume in such a way that each had the same pressure. The equilibrium condition was the one with a maximum number of microstates (or, equivalently, a maximum entropy) with respect to the distribution of volume.

Precisely the same effect is at work in chemical equilibrium. The equilibrium state is characterized by a maximum in the entropy with respect to the number of number of reaction steps taken. At this equilibrium point the entropy doesn't change when the chemical reaction proceeds by one step in either direction. The change in entropy through a forward step is of course

$$-\alpha \frac{\partial S}{\partial N_A} - \beta \frac{\partial S}{\partial N_B} + \gamma \frac{\partial S}{\partial N_C} + \delta \frac{\partial S}{\partial N_D}, \quad (3.10.7)$$

and the change in entropy through a backward step is the negative of this. In either case, the equilibrium condition is that this change in entropy vanish, i.e. that

$$\alpha \mu_A + \beta \mu_B = \gamma \mu_C + \delta \mu_D. \quad (3.10.8)$$

Interpretation in terms of “escaping tendency”.

If we specialize to the case of liquid-gas phase equilibrium, this equation is just equation (3.162).

We cannot go further without formulas for the chemical potentials μ . Complete formulas are not available within the realm of thermodynamics, but the next section shows that thermodynamics can put severe constraints on the permissible functional forms for μ .

3.10.3 Chemical potential of an ideal gas

I emphasized on page 69 that the equation of state did not contain full thermodynamic information. Thus, for example, knowledge of the equation of state $V(T, p, N)$ is not sufficient to uncover the master function $G(T, p, N)$. On the other hand, that knowledge is sufficient to restrict the functional form of the Gibbs potential, which in turn restricts the possible functional forms of the chemical potential. In this subsection we uncover that restriction.

Our strategy is to recognize that volume is the derivative of $G(T, p, N)$ with respect to p , and chemical potential is the derivative of $G(T, p, N)$ with respect to N . Given $V(T, p, N)$, we can integrate with respect to p to find $G(T, p, N)$, and then differentiate with respect to N to find $\mu(T, p)$. This process does not completely determine the Gibbs potential or the chemical potential, because a constant of integration is involved. But it does restrict the permissible functional forms of $G(T, p, N)$ and $\mu(T, p)$. The master thermodynamic equation for variables (T, p, N) is

$$dG = -SdT + Vdp + \mu dN \quad (3.10.9)$$

whence

$$V(T, p, N) = \left(\frac{\partial G}{\partial p} \right)_{T, N}. \quad (3.10.10)$$

Thus for a substance obeying the ideal gas equation of state, we have

$$\frac{Nk_B T}{p} = \left(\frac{\partial G}{\partial p} \right)_{T, N}. \quad (3.10.11)$$

Integrating both sides with respect to p gives

$$Nk_B T \int \frac{dp}{p} = \int \left(\frac{\partial G}{\partial p} \right)_{T, N} dp \quad (3.10.12)$$

or

$$Nk_B T \ln \left(\frac{p}{\tilde{p}(T, N)} \right) = G(T, p, N) \quad (3.10.13)$$

The role of “constant of integration” is played by $\tilde{p}(T, N)$, which must be constant with respect to p but which may vary with T and N .

In fact, careful examination of the above equation shows what the dependence of $\tilde{p}(T, N)$ on N must be. The quantities G and N above are extensive, while T and p are intensive, so \tilde{p} must be intensive so that both sides will depend linearly on system size. Thus \tilde{p} is independent of N , and we have

$$G(T, p, N) = Nk_B T \ln \left(\frac{p}{\tilde{p}(T)} \right) \quad (3.10.14)$$

whence

$$\mu(T, p) = \frac{G(T, p, N)}{N} = k_B T \ln \left(\frac{p}{\tilde{p}(T)} \right). \quad (3.10.15)$$

This is the form of the Gibbs potential and of the chemical potential for any ideal gas. The function $\tilde{p}(T)$ is undetermined, and it is through differences in $\tilde{p}(T)$ that one ideal gas differs from another. But the dependence on p and on N are completely pinned down by the above results.

This result is frequently written in terms of the number density $\rho = N/V$. For an ideal gas $p = k_B T \rho$, and we can define the function $\tilde{\rho}(T)$ through $\tilde{p}(T) = k_B T \tilde{\rho}(T)$. Then we can write

$$\mu(T, \rho) = k_B T \ln \left(\frac{\rho}{\tilde{\rho}(T)} \right). \quad (3.10.16)$$

What if the ideal gas is a mixture of, say, the four chemical species A, B, C, and D? Exactly the same result applies for each species:

$$\mu_A(T, \rho_A) = k_B T \ln \left(\frac{\rho_A}{\tilde{\rho}_A(T)} \right) \quad (3.10.17)$$

where the function $\tilde{\rho}_A(T)$ is the same for a pure ideal gas of A and for an ideal gas mixture. The chemical potential μ_A is independent of the densities ρ_B , ρ_C , and ρ_D . I am looking for a purely thermodynamic argument to prove this result, but until I find it you'll have to accept this statistical argument: In an ideal gas the molecules of A don't interact with the molecules of B, C, and D, so they don't know whether or not such molecules are even present. The behavior of A thus can't depend upon the number of B, C, and D molecules present, and it will be the same even if there are 0 molecules of B, C, and D, that is if the gas is pure.

3.10.4 The equilibrium condition for ideal gas reactions

[Before plunging in, I want to point out that there's a contradiction embodied in the term "ideal gas chemical reaction". In an ideal gas, molecules do not interact. . . when two molecules approach, they just pass right through each other. But a chemical reaction is a form of interaction! Clearly, in this section we are thinking of molecules that interact weakly unless they are very close to each other, but once they approach they interact strongly and react quickly.]

Putting together the general equilibrium condition for chemical reactions

$$\alpha \mu_A + \beta \mu_B = \gamma \mu_C + \delta \mu_D \quad (3.10.18)$$

with expression (3.183) for the chemical potential of an ideal gas gives the equilibrium condition

$$\alpha k_B T \ln \left(\frac{\rho_A}{\tilde{\rho}_A(T)} \right) + \beta k_B T \ln \left(\frac{\rho_B}{\tilde{\rho}_B(T)} \right) = \gamma k_B T \ln \left(\frac{\rho_C}{\tilde{\rho}_C(T)} \right) + \delta k_B T \ln \left(\frac{\rho_D}{\tilde{\rho}_D(T)} \right) \quad (3.10.19)$$

Using the properties of logarithms, this can be rewritten as

$$\left(\frac{\rho_A}{\tilde{\rho}_A(T)} \right)^\alpha \left(\frac{\rho_B}{\tilde{\rho}_B(T)} \right)^\beta = \left(\frac{\rho_C}{\tilde{\rho}_C(T)} \right)^\gamma \left(\frac{\rho_D}{\tilde{\rho}_D(T)} \right)^\delta, \quad (3.10.20)$$

or, after minor rearrangement, as

$$\frac{\rho_C^\gamma \rho_D^\delta}{\rho_A^\alpha \rho_B^\beta} = \frac{\tilde{\rho}_C^\gamma(T) \tilde{\rho}_D^\delta(T)}{\tilde{\rho}_A^\alpha(T) \tilde{\rho}_B^\beta(T)}. \quad (3.10.21)$$

Chemists like to write this equation in terms of "the concentration of A", written as $[A]$, namely as

$$\frac{[C]^\gamma [D]^\delta}{[A]^\alpha [B]^\beta} = K(T), \quad (3.10.22)$$

where $K(T)$ is called the “equilibrium constant” (despite the fact that it is a function of temperature). This result is called the “law of mass action” despite the fact that it is not a fundamental law (we have just derived it) and even despite the fact that (because it holds only for ideal gases) it’s not precisely true for any real substance! (And also, I might add, despite the fact that the “law” has nothing to do with “mass” or with “action”.) Even though the result is poorly named, it shows just how valuable thermodynamics is in connecting disparate areas of research. Who would have guessed that the law of mass action follows from only thermodynamics and the ideal gas equation of state? We have proven the result without once doing a chemical experiment!

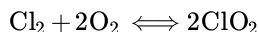
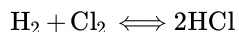
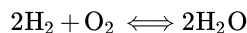
Problems

3.40 Chemical potential for ideal gas mixtures

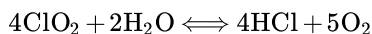
The entropy $S(E, V, N_A, N_B)$ of a classical monatomic ideal gas mixture was uncovered using statistical mechanics in problem 2.16. Invert the result of that problem to find $E(S, V, N_A, N_B)$, then show that the temperature and pressure of an ideal gas mixture obey familiar results for pure ideal gases. Show that

$$\mu_A(T, p, f_A, f_B) = k_B T \ln \left[\left(\frac{h_0^2}{2\pi m_A (k_B T)^{5/3}} \right)^{3/2} p f_A \right], \quad (3.10.23)$$

and relate this expression to the form (3.183). Verify relation (3.172). 3.41 Relations between equilibrium constants You measure the equilibrium constants for these three chemical reactions:



(Call those constants K_A , K_B , and K_C .) Find an expression for the equilibrium constant for the reaction



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