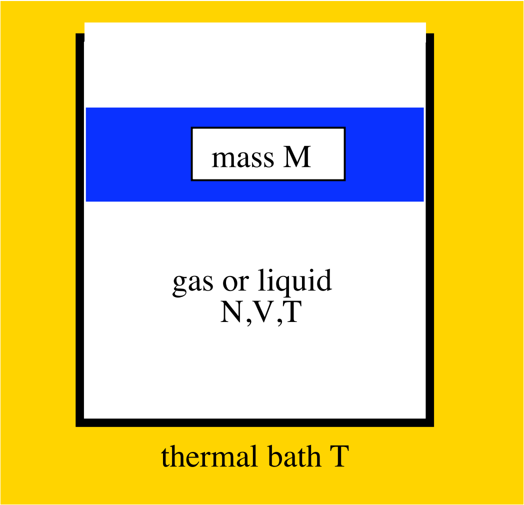
Lecture 19: Chemical Equilibrium and the Mass-Action Law

Midterm coming up Friday, Oct 29.
Problem Set 3 due Oct. 22 (accepted up thru Oct. 25) now available at the website.

But, first, a comment: Constant-pressure ensemble and the Gibbs free energy:

I am having you do some of this in Problem 11. Let me sketch another part of it here.

The significance of this ensemble and of the Gibbs free energy is that biology/chemistry occurs in the lab at fixed T and P.



How to visualize a constant pressure ensemble?
The piston of (macroscopic mass) M moves freely in the cylinder. Note that it is held up by the pressure of the fluid below, so $Mg = PA$, i.e., the mass of the piston fixes the pressure below.

If something happens in the system (e.g., heat fed in, T increases) the position H of the piston readjusts but the pressure P remains fixed.

Consider a larger "SYSTEM" including both the fluid and the piston. A "microstate" of this larger SYSTEM consists of a state n of the original system and a designation H for the height of the piston.

Why not the momentum of the piston?
It is only a single degree of freedom and will be irrelevant.

The energy of the SYSTEM is $E_n + MgH$, so its partition function is:

$$\mathcal{Z}(T,P,N) = \int_0^\infty dH e^{-\frac{MgH}{k_BT}} \sum_n e^{-\frac{E_n}{k_BT}} = \int_0^\infty dH e^{-\frac{MgH}{k_BT}} Z(T,V,N).$$

But, $MgH = \frac{Mg}{A} \cdot HA = PV$, so $\mathcal{Z}(T,P,N) = \frac{1}{A}\int_0^\infty dV\, e^{-\frac{PV}{k_BT}} Z(T,V,N)$.

In the thermodynamic limit the overall 1/A factor is irrelevant (gives term O(lnN)) and can be omitted.

The integrand has the form $e^{\frac{Q(V)}{k_BT}}$ with $Q(V) = -PV - F(V)$. This has a maximum at $V=V^*(P)$,

where $0 = \frac{\partial Q}{\partial V}\left(V^*\right) = -P - \left.\frac{\partial F}{\partial V}\right|_{V=V^*}$, i.e., at the volume for which the pressure defined by

$\left.\frac{\partial F}{\partial V}\right|_{T,N} = -P$ agrees with the pressure enforced by the piston weight.

We now expand around $V=V^*$ and show that Q is maximum there and that the maximum is very narrow:

$$\frac{\partial^2 Q}{\partial V^2} = -\frac{\partial^2 F}{\partial V^2} = \frac{\partial P}{\partial V} = \frac{-1}{V\left(-\frac{1}{V}\frac{\partial V}{\partial P}\right)} = -\frac{1}{V\kappa_T},$$

where κ_T is the "isothermal compressibility" which is intrinsically positive. It follows that,

$$e^{\frac{Q(V)}{k_BT}} = e^{\frac{Q\left(V^*\right)}{k_BT}} e^{-\frac{1}{2V^* k_BT\kappa_T}\left(V-V^*\right)^2} \ldots,$$

where the V* means that the denominator is extensive, so that the exponent is only appreciable for $\left|V - V^*\right| \sim \sqrt{V}$ and the remaining terms in the Taylor expansion are small. You can then do the Gaussian integral and take ln to get $G = -kT \ln \mathcal{Z}$ as $G(T,P,N) = F\left(T,V^*(P,T),N\right) + PV^*(P,T) + \text{small}$, which is, indeed, the Gibbs free energy.

Conditions for chemical equlibrium:
Suppose the chemical reaction $A + B \Leftrightarrow C$ is possible
(i.e., C=AB, bound together, typically with some binding energy B).
In the absence of this reaction, we can consider a closed container V in a thermal bath T with initially N_A^0, N_B^0, N_C^0 and a Helmholtz free energy $F\left(T,V,N_A^0,N_B^0,N_C^0\right)$.

Suppose now the reaction is allowed to proceed. Possible states include all N_A,N_B,N_C of the form, $N_A = N_A^0 - M, N_B = N_B^0 - M, N_C = N_C^0 + M$ for any integer M positive or negative (except that $N_\alpha \geq 0, \alpha = A,B,C$. M is sometimes called the "degree of reaction."
Positive M means the reaction is going to the right; negative M, to the left.
Chemical equilibrium is a bit like the removal of an internal constraint:
The reaction stops when the system comes to a new equilibrium, at which point the new Helmholtz free energy is a minimum, i.e., $F(T,V,N_A^0 - M, N_B^0 - M, N_C^0 + M)$ with M=M* such that $\left.\frac{\partial F}{\partial M}\right|_{M=M^*} = 0$, i.e., $\frac{\partial F}{\partial N_A}(-1) + \frac{\partial F}{\partial N_A}(-1) + \frac{\partial F}{\partial N_A}(+1) = 0$, which gives the condition for equilibrium: $\boxed{\mu_A + \mu_B = \mu_C}$.
More generally, consider $\nu_A A + \nu_B B + \ldots \Leftrightarrow \nu_C C + \nu_D D + \ldots$, then a M "units" of reaction, lead us to minimize $F(T,V,N_A^0 - \nu_A M, N_B^0 - \nu_B M, \ldots, N_C^0 + \nu_C M, N_D^0 + \nu_D M + \ldots)$, and setting $\frac{\partial F}{\partial M} = 0$ (minimum!), we find $\boxed{\nu_A \mu_A + \nu_B \mu_B + \ldots = \nu_C \mu_C + \nu_D \mu_D + \ldots}$ as the general condition for chemical equilibrium.
As you can see, this is entirely general: there is no restriction to ideal gases, ideal solutions, low densities, etc.
Comments:
(a) I have derived this result in the constant-volume ensemble. The same result can be derived in any of the other ensembles. (ensemble equivalence!) I'll give you a problem on the next homework.
(b) If there is more than one reaction possible among the species present, then there will one condition of this type for each kind of reaction possible.

To turn this into a condition on the particle densities $\{n_\alpha\}$ requires writing $\mu_\alpha\left(T,\{n_\beta\}\right)$, which is complicated in general but simplifies in special limits (low densities).
I am going to start by looking at gas-phase reactions (then we will go on to reactions in aqueous solution):

The Law of Mass Action for ideal-gas reactions:
We treat generally gas mixtures which are at a density sufficiently low so that the gas molecules contribute independently to the total energy.
Of course, gas molecules always interact with one another. That is what produces the collisions that allow the gas to equilibrate. Without ANY interactions equlibration could not take place. Thus, the assumption here is that the molecular encounters are sufficiently infrequent so that their energies do not contribute appreciable to the total energy.

When this is the case, we can write for any microstate n of the system,

$$E_n = \sum_{k=1}^{N_A}\left(\frac{\vec{p}_k^{\,2}}{2m_A}+\varepsilon^A_{i_k}\right)+\sum_{k=1}^{N_B}\left(\frac{\vec{p}_k^{\,2}}{2m_B}+\varepsilon^B_{i_k}\right)+\ldots$$

, where in addition to the kinetic energy of each particle (note the different masses for different species) there are a set of internal states with energies $\varepsilon_i^\alpha, i = 0,1,2,3,\ldots$ (this will be important). Note that $\varepsilon_i^\alpha < 0$, since these are bound systems. These states describe the binding energies of the atoms making up the molecule α and the energies of the various internal motions (rotations, vibrations,…) of the atoms relative to the center of mass. Because these states are independent of the centre-of-mass motion, when we sum over states for each molecule k, we will need to integrate (s we did for the ICMG) over the coordinates $\vec{r}_k, \vec{p}_k$ of the C of M and, in addition, sum over the possible internal states labeled by i.

Now, imagine a canonical ensemble at fixed temperature T. We want to construct the partition function,

$$Z(T,V,N_A,N_B,\ldots)=\sum_n e^{-\frac{E_n}{k_BT}}$$

$$=\left(\frac{1}{N_A!}\sum_{\{i_k\}}\int\prod_{k=1}^{N_A}\left(\left(d^3r_k\right)\left(d^3p_k\right)e^{-\frac{1}{k_BT}\left(\frac{\vec{p}_k^{\,2}}{2m_A}+\varepsilon^A_{i_k}\right)}\right)\right)\cdot\left(\frac{1}{N_B!}\sum_{\{i_k\}}\int\prod_{k=1}^{N_B}(\text{same thing for B})\right)\cdot\ldots$$

$$=Z_A(T,V,N_A)\cdot Z_B(T,V,N_B)\cdot\ldots,$$

where $Z_\alpha(T,V,N_\alpha)=\frac{1}{N_\alpha!}\left(\frac{V}{\lambda^3_{\alpha,th}}z_\alpha(T)\right)^{N_\alpha}$ and $z_\alpha(T)=\sum_i e^{-\frac{\varepsilon_i^\alpha}{k_BT}}$ is called the "internal partition function" of the species α.

Notes:

(a) A monatomic molecule like He has no internal state, so z(T)=1 and we are back to the ICMG (unless, of course, we are looking at high-enough temperatures so that there is significant excitation of atomic electronic states above the ground state).

(b) Diatomic or polyatomic molecules have in general a complicated spectrum of internal states. These are no the subject of this course, so we will replace the real molecules by simplified models. One useful model for a composite molecule C=AB is just to represent the internal state by a single energy level $\varepsilon_{AB}<0$, which will be negative—representing binding. Or, we could be a little more sophisticated and say that there were several "bound states" of AB but all with energies close to ε_{AB}.

In order to derive expressions for the chemical potentials μ_α of the various species, we are going to calculate the free energy, $F(T,V,N_A,N_B,\ldots)\equiv -k_BT\ln Z(T,V,N_A,N_B,\ldots)$. But Z is a product, so F becomes a sum of separate terms for each species,

$$F(T,V,N_A,N_B,\ldots)=F_A(T,V,N_A)+F_B(T,V,N_B)+\ldots,$$ where

$$F_\alpha(T,V,N_\alpha)=-k_BT\left[\left(N_\alpha\ln\frac{V}{\lambda^3_{\alpha,th}}-N\alpha\ln N_\alpha+N_\alpha\right)+N_\alpha\ln z_\alpha(T)\right]$$

$$=F_\alpha^{ideal\ gas}(T,V,N_\alpha)-N_\alpha k_BT\ln z_\alpha(T).$$

To calculate the chemical potential μ_α, we are instructed by thermodynamics to take the derivative,

$$\mu_\alpha = \frac{\partial F}{\partial N_\alpha} = \frac{\partial F_\alpha}{\partial N_\alpha} = \mu_\alpha^{ideal\ gas} - k_B T \ln z_\alpha(T).$$

But, we already know the ideal gas result (Lect. 18.4),

$$n_\alpha \equiv \frac{N_\alpha}{V} = \frac{e^{\frac{\mu_\alpha}{k_B T}}}{\lambda_{th,\alpha}^3} \Leftrightarrow \mu_\alpha = k_B T \ln\left(n_\alpha \lambda_{th,\alpha}^3\right)$$ (as can also be read off from the top of the page),

so $$\boxed{\mu_\alpha = k_B T \ln\left(\frac{n_\alpha \lambda_{th,\alpha}^3}{z_\alpha(T)}\right) \Leftrightarrow n_\alpha = \frac{z_\alpha(T) e^{\frac{\mu_\alpha}{k_B T}}}{\lambda_{th,\alpha}^3}}.$$ (ideal gases with internal states)

With this result in hand, we can go back to our original reaction $A + B \leftrightarrow C$, for which we found the equilibrium condition, $\mu_A + \mu_B = \mu_C$, so now,

$$k_B T \ln\left(\frac{n_A \lambda_{th,A}^3}{z_A(T)}\right) + k_B T \ln\left(\frac{n_B \lambda_{th,B}^3}{z_B(T)}\right) = k_B T \ln\left(\frac{n_C \lambda_{th,C}^3}{z_C(T)}\right)$$, i.e.,

$$\left(\frac{n_A \lambda_{th,A}^3}{z_A(T)}\right) \cdot \left(\frac{n_B \lambda_{th,B}^3}{z_B(T)}\right) = \left(\frac{n_C \lambda_{th,C}^3}{z_C(T)}\right)$$, or, as it is usually written,

$$\frac{n_C}{n_A n_B} = K(T) = \frac{z_C(T)}{z_A(T) z_B(T)} \cdot \left(\frac{\lambda_{th,A} \lambda_{th,B}}{\lambda_{th,C}}\right)^3$$, where K(T) is called the equilibrium constant and is a function of temperature only. (This would not be true at high density!)

Note:

Simple "model" in which A and B have no internal states and C=AB is bound with $\varepsilon_C = -\Delta$ (Δ=binding energy>0), then $z_A = z_A = 1$ and $z_C(T) = e^{\frac{\Delta}{k_B T}}$, so $K(T) = \frac{1}{T^{3/2}} \left(\frac{2\pi\hbar^2 m_C}{m_A m_B}\right)^{3/2} e^{\frac{\Delta}{k_B T}}$.

Reality check: When D is large, so C is strongly bound, the exponential factor is large, which means that n_C is large relative to $n_A n_B$, as expected.

It is left as an exercise for the reader to show in the general case,

$$\nu_A A + \nu_B B + \ldots \leftrightarrow \nu_C C + \nu_D D + \ldots,$$ that $$\boxed{\frac{n_C^{\nu_C} n_D^{\nu_D} \cdots}{n_A^{\nu_A} n_B^{\nu_B} \cdots} = K(T) = \frac{z_C^{\nu_C} z_D^{\nu_D} \cdots}{z_A^{\nu_A} z_B^{\nu_B} \cdots} \cdot \left(\frac{\lambda_A^{\nu_A} \lambda_B^{\nu_B} \cdots}{\lambda_C^{\nu_C} \lambda_D^{\nu_D} \cdots}\right)^3}.$$

Note: At high densities, this kind of simple relation with K(T) (only) fails. Nothing prevents you from writing down the ratio $\frac{n_C^{\nu_C} n_D^{\nu_D} \cdots}{n_A^{\nu_A} n_B^{\nu_B} \cdots} = K$; however, in general $K(T, \{n_\alpha\})$.