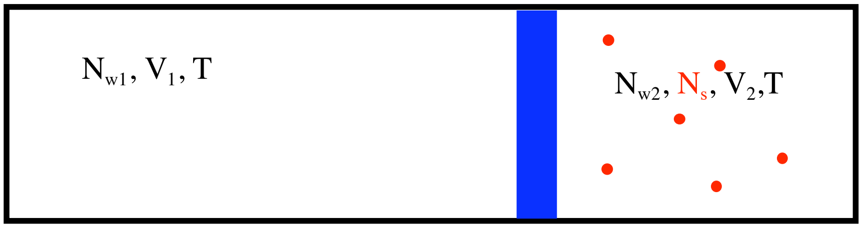
Lecture 20: Aqueous solutions: Solutes and chemical reactions in solution

Midterm coming up Friday, Oct 29. Formula sheet; fact sheet.
Problem Set 3 due today, I will post solutions immediately.
Comments on exam:
Closed book, no notes, etc. Problems (no bio, no chem). Empty calculator allowed. Formula sheet will be provided.
Advice:
I will give you today (or get on line from website) a sheet with (i) a small amount of data to memorize and (ii) the formula sheet that you will get with your exam.
The formula sheet should be a useful study guide. Know what the variables mean and when the formulas apply.
Study the course notes carefully. Go over problem sets.
I am not going to quiz you on biology or biochemistry. I hope you have learned a lot from the reading; but, don't feel that you need to memorize facts. That is not what I will ask you.
I am not going to ask you to do "proofs," so—in your studying, work to understand the meaning and the logic.
I cannot realistically expect you to solve long complicated problems on a 50 minute exam.

Osmotic pressure and osmotic forces in fluids: Why do solutions—even rather concentrated ones—behave like ideal gases?

(thermal bath at temperature T)
In the cylinder at the right, both sides contain water; however, the right side has an additional solute while the left side does not.
The partition is semipermeable, i.e., it passes water but not solute.



If the partition is fixed, then a few water molecules (very few, since water is virtually incompressible) will pass from left to right, until an equilibrium pressure difference ΔP is set up:

$\Delta P = c_s k_B T$ or, more generally, when there is some solute on both sides, $\boxed{\Delta P = \Delta c_s k_B T\,.}$

(this is called the van't Hoff relation, it is valid when $c_s \equiv \dfrac{N_s}{V}$ is sufficiently low)

This pressure is independent of the solute type (at low solute density, just as for an ideal gas).
If the partition is moveable, then the additional pressure will force the piston to the left until it hits the end of the container.

This pressure difference is entropic in origin (like the pressure of the ideal gas). However, in this situation, where there are many water molecules around interacting with one another and with the solute molecules, it seems surprising that the "ideal gas" result still holds (to a good approximation).
Why is this? And, more generally, how can we derive van't Hoff?

Let's look back at the ideal-gas result in the Canonical description (for example):
Recall that we found $F(V) = -kT\ln Z(V)$ with $Z(V) = C(N,T)\int_V (dr_1)..(dr_N) \propto V^N$, so

$$F(V) = -Nk_BT\ln V + \ldots \text{ and } P = -\left.\frac{\partial F}{\partial V}\right|_{N,T} = \frac{Nk_BT}{V}.$$

Q: What goes wrong with this when the gas molecules start to interact with one another? (i.e., real, non-ideal gases and liquids, including water "w")

A: The total energy is now $E(\vec{r}_1,\vec{p}_1,\ldots)=\sum_{i=1}^{N_w}\frac{\vec{p}_i^{\,2}}{2m}+\sum_{i>j=1}^{N_w}v_{ww}\left(\vec{r}_i-\vec{r}_j\right)$ **20.2**

This is written for spherical (i.e., rotationally invariant) atoms/molecules. You need additional internal, orientational variables, if the molecules have shape.

Now calculate the water partition function,

$$Z_w(T,V,N_w)=\frac{1}{N_w!(2\pi\hbar)^{3N_w}}\int_V\left(d^3r_1\right)..\left(d^3r_{N_w}\right)\left(d^3p_1\right)..\left(d^3p_{N_w}\right)e^{-\frac{E(\ )}{k_BT}}.$$

You can still do the momentum integrals, just as before; however, the r-dependence of the interaction energy makes it impossible to do the displacement integrals, so this is a *VERY* hard problem. There are various ways of approaching it perturbatively and numerically; however, the simple V dependence is lost. That's why water, other fluids, and dense gases no longer satisfy the ideal gas law.

Q: So, now, with the solute particles AND the water particles, how can you possibly expect to get back to the ideal-gas law?

A: The water is NOT described by the ideal gas law. The fact that the solute is effectively an ideal gas is due to the incompressibility of the water.

$$E_{w+s}(\vec{r}_1,\vec{p}_1,\ldots)=\sum_{i=1}^{N_w}\frac{\vec{p}_i^{\,2}}{2m}+\sum_{i>j=1}^{N_w}v_{ww}\left(\vec{r}_i-\vec{r}_j\right)+\sum_{i=1}^{N_s}\frac{\vec{P}_i^{\,2}}{2M}+\sum_{i>j=1}^{N_s}v_{ss}\left(\vec{R}_i-\vec{R}_j\right)+\sum_{i,j=1}^{N_w,N_s}v_{ws}\left(\vec{r}_i-\vec{R}_j\right).$$

As long as the solvent molecules are sufficiently dilute so that they spend very little time near one another, we can ignore the solute-solute interactions v_{ss}. (This much is like the ideal gas!)

But, the water-solute interactions CANNOT be ignored. However, simplification comes about because of the high and constant density of the water: This means that, in all likely configurations each solute molecule is surrounded by (roughly) the same configuration of waters, so the value of the sum $\sum_{i=1}^{N_w}v_{ws}\left(\vec{r}_i-\vec{R}_j\right)=\varepsilon_s$ for each solute molecule j is (almost) the same in all microstates (at least, all that have any significant weight in the ensemble).

ε_s is called the solvation energy (c.f., Lect. 11.2) and depends on the type of solute molecule. Solvation energies are generally negative and represent the energy lowering per solute molecule due to the water molecules surrounding the solute. Molecules (e.g., fats, hydrocarbon chains) for which this term is significantly positive don't dissolve well in water.

This decouples the water-molecule integrals from the solute-molecule integrals. Thus, z(T) for gases

$$Z_{w+s}(T,V,N_w,N_s)=Z_w(T,V,N_w)\frac{e^{-\frac{N_s\varepsilon_s}{k_BT}}}{N_s!}\int_V\left(dR_1\right)..\left(dR_{N_s}\right)\left(dP_1\right)..\left(dP_{N_s}\right)e^{-\frac{KE_s}{k_BT}}$$

$$=Z_w(T,V,N_w)\cdot\frac{1}{N_s!}\left(\frac{e^{-\frac{\varepsilon_s}{k_BT}}V}{\lambda_{th,s}^3}\right)^{N_s}.$$

And, taking logs, $F_{w+s}(T,V,N_w,N_s)=F_w(T,V,N_w)+F_s(T,V,N_s)$.

The water free energy, we don't know and can't calculate; but, the solute term has the ideal-gas form.

Notes:

1. If there is more than one kind of solute, then there are additional ideal-gas-like factors.
2. When the solute molecules have internal states i, you can add in the internal states via the internal partition function, just as we did for the gas in Lect. 19. However, if those states produce significantly different solvation energies, then you have to include an i-dependence in the solvation energies.

Now, lets look at the pressure via $P = -\frac{\partial F_{w+s}}{\partial V} = -\frac{\partial F_w}{\partial V} - \frac{\partial F_s}{\partial V} = P_w + P_s$.

The volume-dependence of the solute free energy is in the usual form

$F_s = -N_s k_B T \ln V + (\text{independent of volume})$, so $P_s = -\frac{\partial F_s}{\partial V} = \frac{N_s k_B T}{V} = c_s k_B T$. QED

Note: Osmotic pressures are LARGE when solute concentrations are in the 1 M range:
1 mole of ideal gas comprises 22.4 L under “standard” conditions (1 atmosphere pressure and O C).
It follows that a 1 M solute exerts ~22.4 atm or 2.2x10^6 N/m^2 osmotic pressure!

Chemical reactions in solution

Aqueous solutions to which these considerations approximations apply are called “ideal solutions.” Describing reactions in ideal aqueous solutions is easy because the expression for the chemical potentials of the various dissolved species are of the ideal-gas form:

Note that the solvation factor $e^{-\frac{\varepsilon_s}{k_s T}}$ enters multiplying the internal partition function, so we can read off results from Lect. 19, $\mu_\alpha = k_B T \ln\left(\frac{n_\alpha \lambda_{th,\alpha}^3}{e^{-\frac{\varepsilon_\alpha}{k_B T}} z_\alpha(T)}\right) \Leftrightarrow n_\alpha = \frac{z_\alpha(T) e^{-\frac{\varepsilon_\alpha}{k_B T}} \cdot e^{\frac{\mu_\alpha}{k_B T}}}{\lambda_{th,\alpha}^3}$.

Comment: When you look at the formula for μ_α, you can see that the only variable other than T which appears at the right is the density/concentration $n_\alpha = N_\alpha / V$. Thus, chemists often write this as,

$\mu_\alpha = k_B T \ln\left(\frac{n_\alpha}{n_\alpha^0}\right) + \mu_\alpha^0(T)$, where $\mu_\alpha^0(T)$ is called the “standard chemical potential” for species α in aqueous solution at temperature T and reference density/concentration defined conventionally as 1 M.
Standard chemical potentials--which include information about both the solvation energy and the internal states--can be looked up in tables.
The fact that the chemical potential μ_α depends only on n_α and NOT on the density of other solute species, is a simplification of the low-density/ideal solution regime.

Thus, for $A + B \Leftrightarrow C$, we find $\mu_A + \mu_B = \mu_C$ implies,

$$\frac{n_C}{n_A n_B} = K_{eq}(T) = \frac{e^{-\frac{\varepsilon_C}{k_B T}}}{e^{-\frac{\varepsilon_A}{k_B T}} e^{-\frac{\varepsilon_B}{k_B T}}} \cdot \frac{z_C(T)}{z_A(T) z_B(T)} \cdot \left(\frac{\lambda_{th,A} \lambda_{th,B}}{\lambda_{th,C}}\right)^3$$

$$\boxed{\frac{n_C}{n_A n_B} = \frac{1}{T^{3/2}} \left(\frac{2\pi\hbar^2 m_C}{m_A m_B}\right)^{3/2} \cdot \frac{z_C(T)}{z_A(T) z_B(T)} \cdot e^{\frac{(\varepsilon_A + \varepsilon_B - \varepsilon_C)}{k_B T}}.} \quad \text{Mass action aqueous solution}$$

Easy to generalize to more complicated reactions.
In this form, the concentrations/densities are in “natural” units of n_X =particles/m^3.
It is conventional in solution chemistry to rewrite this in terms of molar concentrations [X]:
The conversion is given by

$$[X]\,\frac{\text{mol}}{\text{litre}} = N_A[X]\,\frac{\text{particles}}{\text{litre}} = 10^3 N_A[X]\,\frac{\text{particles}}{\text{m}^3}^{3} = n_X\,, \qquad \textbf{20.4}$$

so $n_X = c_0[X]$ with $c_0 = 6.02\times 10^{26}\,\dfrac{\text{m}^3}{\text{mol}\cdot\text{litre}}$.

Thus,

$$\frac{[AB]}{[A][B]} = c_0 K_{eq}(T) \equiv K_{eq}^{(M)}(T).$$

- These equilibrium constants are tabulated.
- Note dependence on T, especially exponential dependence (strongest).
- The AB “binding” terms push reaction to the right (since $\varepsilon_{AB} < 0$); this effect is weaker at higher temperature.
- Simple formulas fail for higher concentrations, where interactions become important.