

7.8: Examples

7.8.1: Osmotic Pressure

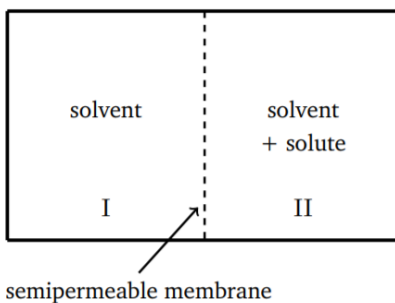


Figure 7.8.1: Illustrating the set-up for calculating osmotic pressure

An example of the use of the idea of the partition function in a very simple way is provided by the osmotic pressure. Here one considers a vessel partitioned into two regions, say, I and II, with a solvent (labeled A) on one side and a solution of the solvent plus a solute (labeled B) on the other side. The separation is via a semipermeable membrane which allows the solvent molecules to pass through either way, but does not allow the solute molecules to pass through. Thus the solute molecules stay in region II, as the Fig. 7.8.1. When such a situation is set up, the solvent molecules pass back and forth and eventually achieve equilibrium with the average number of solvent molecules on each side not changing any further. What is observed is that the pressure in the solution p_{II} is higher than the pressure p_I in the solvent in region I. Once equilibrium is achieved, there is no further change of volume or temperature either, so we can write the equilibrium condition for the solvent as

$$\mu_A^{(I)} = \mu_A^{(II)} \quad (7.8.1)$$

Correspondingly, we have $z_A^{(I)} = z_A^{(II)}$, for the fugacities. The partition function has the form

$$\begin{aligned} Z &= \sum_{N_A, N_B} z_A^{N_A} z_B^{N_B} Q_{N_A, N_B} \\ &= \sum_{N_A} z_A^{N_A} Q_{N_A, 0} + \sum_{N_A} z_A^{N_A} z_B Q_{N_A, 1} + \cdots \\ &= Z_A \left(1 + \frac{1}{z_A} \sum_{N_A} z_A^{N_A} z_B Q_{N_A, 1} + \cdots \right) \end{aligned} \quad (7.8.2)$$

Here Z_A is the partition function for just the solvent. For simplicity, let us take the volumes of the two regions to be the same. Then we may write

$$\log Z_A = \frac{p_I V}{kT} \quad (7.8.3)$$

even though this occurs in the formula for the full partition function in region II, since z_A is the same for regions I and II. Going back to Z , we expand log in powers of z_B , keeping only the lowest order term, which is adequate for dilute solutions. Thus

$$\log Z \approx \log Z_A + z_B \left(\frac{1}{Z_A} \sum_{N_A} z_A^{N_A} Q_{N_A, 1} \right) \quad (7.8.4)$$

The derivative of the partition function with respect to μ_B is related to N_B , as in Equation 7.4.16, so that

$$\left(\frac{1}{Z_A} \sum_{N_A} z_A^{N_A} Q_{N_A, 1} \right) = N_B \quad (7.8.5)$$

Further, log Z is given by $\frac{p_{II} V}{kT}$. Using these results, Equation 7.8.4 gives

$$p_{II} = p_I + \frac{N_B}{V} kT = p_I + n_B kT \quad (7.8.6)$$

where n_B is the number density of the solute. The pressure difference $p_{II} - p_I$ is called the osmotic pressure.

7.8.2: Equilibrium of a Chemical Reaction

Here we consider a general chemical reaction of the form



If the substances A, B, C, D can be approximated as ideal gases, the partition function is given by

$$\log Z = z_A Q_{1A} + z_B Q_{1B} + z_C Q_{1C} + z_D Q_{1D} \quad (7.8.8)$$

For the individual chemical potentials, we can use the general formula in 7.5.10 but with the correction due to the βmc^2 factor as in Equation 7.7.5, since we have different species of particles here. Thus

$$\beta\mu = \log n + \beta mc^2 - \log \left(\frac{mkT}{2\pi\hbar^2} \right)^{\frac{3}{2}} \quad (7.8.9)$$

The condition of equilibrium of the reaction is given as $\nu_A\mu_A + \nu_B\mu_B - \nu_C\mu_C - \nu_D\mu_D = 0$. Using Equation 7.8.9, this becomes

$$\log \left(\frac{n_A^{\nu_A} n_B^{\nu_B}}{n_C^{\nu_C} n_D^{\nu_D}} \right) = -\beta c^2 (\nu_A\mu_A + \nu_B\mu_B - \nu_C\mu_C - \nu_D\mu_D) + \nu_A f_A + \nu_B f_B - \nu_C f_C - \nu_D f_D \quad (7.8.10)$$

$$f = \log \left(\frac{mkT}{2\pi\hbar^2} \right)^{\frac{3}{2}}$$

The total pressure of the mixture of the substances is given from $pV = kT \log Z$ as

$$p = (n_A + n_B + n_C + n_D)kT \quad (7.8.11)$$

So if we define the concentrations,

$$x_i = \frac{n_i}{\sum_j n_j}, \quad i = A, B, C, D \quad (7.8.12)$$

then we can rewrite Equation 7.8.10 as

$$\frac{x_A^{\nu_A} x_B^{\nu_B}}{x_C^{\nu_C} x_D^{\nu_D}} p^{\nu_A + \nu_B - \nu_C - \nu_D} = \exp(-\beta \epsilon + \nu_A \phi_A + \nu_B \phi_B - \nu_C \phi_C - \nu_D \phi_D) \equiv K \quad (7.8.13)$$

$$\epsilon = (\nu_A m_A + \nu_B m_B - \nu_C m_C - \nu_D m_D) c^2$$

$$\phi = f + \log kT$$

With our interpretation of the masses as rest energy, we see that ϵ is the heat of reaction, i.e., the total energy released by the reaction. ϵ is positive for an exothermic reaction and negative for an endothermic reaction. K , in Equation 7.8.13 is known as the reaction constant and is a function only of the temperature (and the masses of the molecules involved, but these are fixed once a reaction is chosen). The condition in Equation 7.8.13 on the concentrations of the reactants is called the law of mass action.

7.8.3 Ionization Equilibrium

Another interesting example is provided by ionization equilibrium, which is of interest in plasmas and in astrophysical contexts. Consider the ionization reaction of an atom X



There is a certain amount of energy ϵ_I needed to ionize the atom X . Treating the particles involved as different species with possible internal states, we can use Equation 7.7.7 to write

$$\log Z = z_X g_X Q_{1X} + z_e g_e Q_{1e} + z_{X^+} g_{X^+} Q_{1X^+} \quad (7.8.15)$$

By differentiation with respect to μ , we find, for each species,

$$z = \frac{n}{g} e^{\beta m c^2} \left(\frac{2\pi \hbar^2}{m k T} \right)^{\frac{3}{2}} \quad (7.8.16)$$

The condition for equilibrium $\mu_X - \mu_{X^+} - \mu_e = 0$ is the same as $\left(\frac{z_X}{z_{X^+} z_e} \right) = 1$. Using Equation 7.8.16, this becomes

$$1 = \frac{n_X}{g_X} \frac{g_{X^+}}{n_{X^+}} \frac{g_e}{n_e} e^{\beta(m_X - m_{X^+} - m_e)c^2} \left(\frac{m_X + m_e}{m_X} \right)^{\frac{3}{2}} \left(\frac{kT}{2\pi \hbar^2} \right)^{\frac{3}{2}} \quad (7.8.17)$$

The mass of the atom X is almost equal to the mass of X^+ and the electron; the difference is the binding energy of the electron in X . This is the ionization energy ϵ_I , $(m_X - m_{X^+} - m_e)c^2 = -\epsilon_I$. Using this, Equation 7.8.17 can be rewritten as

$$\left(\frac{n_X + n_e}{n_X} \right) = \left(\frac{g_X + g_e}{g_X} \right) e^{\beta \epsilon_I} \left(\frac{m_X + m_e}{m_X} \right)^{\frac{3}{2}} \left(\frac{kT}{2\pi \hbar^2} \right)^{\frac{3}{2}} \quad (7.8.18)$$

This is known as Saha's equation for ionization equilibrium. It relates the number density of the ionized atom to that of the neutral atom. (While the mass difference is important for the exponent, it is generally a good approximation to take $m_X \approx m_{X^+}$ in the factor $\left(\frac{m_{X^+}}{m_X} \right)^{\frac{3}{2}}$. So it is often omitted.) The degeneracy for the electron states, namely g_e , is due to the spin degrees of freedom, so $g_e = 2$. The degeneracies g_X and g_{X^+} will depend on the atom and the energy levels involved.

The number densities can be related to the pressure by the equation of state; they are also important in determining the intensities of spectral lines. Thus by observation of spectral lines from the photospheres of stars, one can estimate the pressures involved.

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