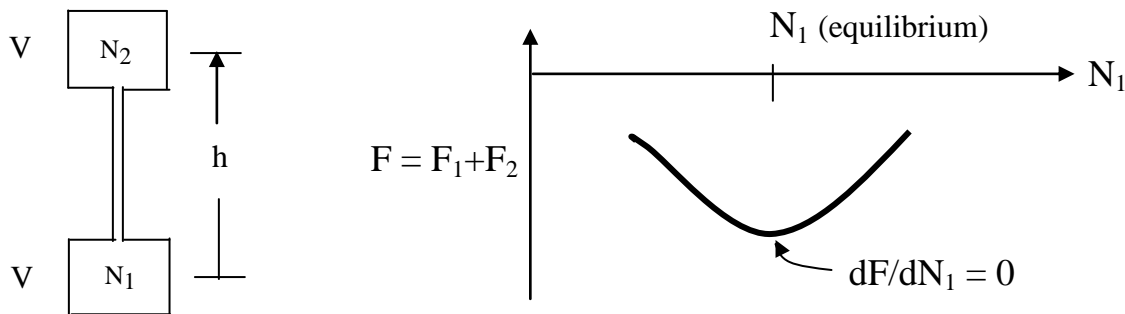


Recall that the free energy $F = U - TS$ of a system at *constant temperature and volume* is a minimum in equilibrium. We will now use this Minimum Free Energy Principle to compute how atmospheric pressure changes with altitude.

This general method will be used for a number of other problems in the course. We simplify the atmosphere problem by assuming that there are two gas containers, one at sea level and the other at some altitude h . A small tube through which gas can flow freely connects the containers. The containers have the same volume V and temperature T . There are N particles. In equilibrium there will be N_1 particles in the lower container and N_2 in the upper container ($N_1 + N_2 = N$). You will compute the ratio N_2/N_1 , which, by the ideal gas law, equals p_2/p_1 .



Because $N = N_1 + N_2$ is conserved, in equilibrium any change in F from gaining a molecule in one part must just cancel the change from losing one in the other: The chemical potential for an ideal gas here is just: $\mu_1 = mgh_1 + kT \ln \frac{n_1}{n_T}$, where n_T is some function of T giving the density of thermally available quantum states. We can determine the chemical potentials for the two containers and apply the equilibrium condition:

$$\left. \frac{dF}{dN_1} \right|_{T, N_2} + \left. \frac{\partial F_2}{\partial N_2} \right|_{T, N_1} \frac{\partial N_2}{\partial N_1} \bigg|_{T, N_{\text{tot}}} = \mu_1 - \mu_2 = 0, \text{ with } \mu_i \equiv \left. \frac{\partial F}{\partial N_i} \right|_T = \text{chemical potential}$$

a) Write the chemical potentials of the two gases in terms of N_1 , N_2 , kT , V , n_T , and mgh :

$\mu_1 = \mu_2$ are both given by $\mu_i = kT \ln(n_i/n_T) + mgh$ for $i = 1$ and 2 .

$\mu_2 =$

b) Use the Equilibrium Condition and solve for the ratio of pressures $p_2/p_1 = N_2/N_1$:

$$\mu_1 = \mu_2, \text{ so } \ln(n_2/n_1) = -mgh/kT$$

Note that n_T cancels out, because we are comparing two regions of the same gas at the same temperature. In later problems, where we are comparing different states (e.g., gas and solid), it will not cancel.

c) Compute the pressure (in atm) at the top of Mt. Everest, which has a height of 10,000 meters above sea level. Assume an average temperature of 250 K and a particle mass of 4.7×10^{-26} kg.

$$\begin{aligned} mgh/kT &= (4.7 \times 10^{-26} \text{ kg})(10^4 \text{ m}) / (1.38 \times 10^{-23})(250) = 1.36 \\ p &= (1 \text{ atm}) e^{-1.36} = 0.26 \text{ atm} \end{aligned}$$