Lecture 31 (2-14), Mar 30, 2023

Chemical (Diffusive) Equilibrium

- Consider once again 2 systems with U_1, N_1, V_1 and U_2, N_2, V_2 being brought together; what happens if we allow exchange of U and N?
- Initially if we keep the barrier, the energy will exchange such that thermal equilibrium is reached with systems having U_1' and U_2'
  - Note we have to allow exchange of energy because particles carry energy, so we can't exchange particles without exchanging energy
- We want to determine $U_1'', U_2'', N_1'', N_2''$ that maximizes entropy: $S = S_1(U_1'', N_1'') + S_2(U - U_1'', N - N_1'')$
  - We want $\dfrac{\partial S}{\partial U_1''} = 0 \implies \dfrac{\partial S_1}{\partial U_1''} = \dfrac{\partial S_2}{\partial (U - U_1'')}$
  - And also $\dfrac{\partial S}{\partial N_1''} = 0 \implies \dfrac{\partial S}{\partial N_1''} = \dfrac{\partial S}{\partial (N - N_1'')}$
  - Therefore we have that the system property $\dfrac{\partial S_i}{\partial N_i}$ for both systems must be equal
  - S has units of energy per temperature, so $\dfrac{\partial S}{\partial N}$ also has units of energy per temperature
- Define $-\dfrac{\mu}{T} = \dfrac{\partial S}{\partial N}$, where μ is the *chemical potential* (or *diffusive potential*)
  - μ has units of energy
  - Note we defined it with the minus sign, so that the particles end up flowing from regions with higher chemical potential to lower chemical potential
- Example: ideal gas
  - $$\frac{\mu}{T} = -\frac{\partial}{\partial N} kN \left(\ln \left(\frac{V}{N} \left(\frac{U}{3N} \right)^{\frac{3}{L}} \left(\frac{4\pi m}{h^2} \right)^{\frac{3}{2}} \right) + \frac{5}{2} \right)$$
    $$= -k \ln \left(\frac{V}{N} \left(\frac{1}{2} kT \right)^{\frac{3}{2}} \left(\frac{4\pi m}{h^2} \right)^{\frac{3}{2}} \right)$$
  - Where we have replaced $\dfrac{U}{3N} = \dfrac{1}{2} kT$
  - Therefore $\mu(T, V, N) = -kT \ln \left(\dfrac{\text{const}}{n \lambda_d^3} \right)$
  - As the number density n increases, the log goes down, so we need the minus sign to have μ higher in regions of higher number density
  - μ is a proxy for the density

Applications to Chemistry

- Suppose we have a gas of N_h hydrogen atoms occupying some space; as hydrogen atoms bump into each other, some of them may be ionized so we have some protons N_p and electrons N_e
- All 3 gases exist in thermal and chemical equilibrium
- The equilibrium condition is specified by two of the energies and a Δ (for every Δ in hydrogen gained, we lose Δ protons and Δ electrons)
- Note we need to consider each hydrogen has lower energy than a proton and an electron together; to do this we need to consider the rest energies of the particles to get the ionization energy
- Maximize entropy: $\dfrac{n_e n_p}{n_h} = \dfrac{1}{\left(\frac{4\pi}{h^2} m_e \frac{kT}{2} \right)^{\frac{3}{2}}} = e^{-\frac{I}{kT}}$ where $n_e = \dfrac{N_e}{V} = \dfrac{N_p}{V} = n_p, n_h = \dfrac{N_h}{V}$ and I is the ionization energy, 13.6 eV
  - This is known as the Saha equation
  - At low temperatures, $-\dfrac{I}{kT} \gg 1$ so $n_e n_p \approx 0$ – there is very little interaction because the particles move slowly
  - As the gas is heated, increased particle velocity leads to more interaction and more breakdown

- In general if we have stoichiometric coefficients, we can do the derivation to find each number density being taken to the power of their stoichiometric coefficient
- We can also express the law as $\frac{n_B^{\nu_B} n_C^{\nu_C}}{n_A^{\nu_A}} = K(T)$, which is known as the law of mass action
- $e^{-\frac{I}{kT}}$ is known as the *Boltzmann factor*