Problem 1. Gibbs Free Energy for Several Components

Consider a gas consisting of three types of particles, A, B, C. A chemical reaction amongst particles converts an atom of A plus an atom of B to a molecule of C

$$A + B \leftrightarrow C \tag{1}$$

The energy is a function of S, V, N_A, N_B and N_C, i.e. $U(S, V, N_A, N_B, N_C)$. The change in energy is

$$dU = TdS - pdV + \mu_A dN_A + \mu_B dN_B + \mu_C dN_C \tag{2}$$

This problem will lead you to conclude that equilibirum between A, B and C is reached when

$$\mu_C = \mu_A + \mu_B \tag{3}$$

(a) Define the Gibbs Free energy $G = U - TS + PV$ and compute its differential dG.

(b) Generalize the scaling argumenents given in the book which led to to Eq. 22.5, to show that

$$G = \mu_A N_A + \mu_B N_B + \mu_C N_C \tag{4}$$

In particular consider how the energy of the system U changes if all extensive quantities are S, N_A, N_B, N_C are scaled by a factor λ.

(c) If a system is held at constant temperature and pressure, it will evolve it will evolve to minimize its Gibbs Free Energy. Equilibrium is reached when $dG = 0$. How does the Gibbs Free energy change if the reaction procedes by one step (i.e. we take one atoms of A one atom of B and make a C) at constant temperature and pressure. Argue that the system reaches equilibrium when

$$\mu_C - \mu_A - \mu_B = 0 \tag{5}$$

Hint: in one step of the forward reaction $A + B \to C$ the change in the number of A is $dN_A = -1$. What are dN_B and dN_C for one step? What is dG then? And what does it need to be in equilibrium?

Problem 2. Yields of three species

Consider three ideal gasses in equilibrium. They participate in the following chemical reaction

$$A + B \leftrightarrow C\,. \tag{6}$$

It is energetically favorable to form atom C, so that the energy of one molecule of C is

$$\epsilon_C = \frac{p^2}{2m_C} - \Delta\,, \tag{7}$$

where $\Delta > 0$ is the binding energy of C. The molecule C has only one internal state. The other two atoms have energies $\epsilon_A = p^2/2m_A$ and $\epsilon_B = p^2/2m_B$ and form simple ideal gasses

(a) If the partition function Z_{tot} of a gas of N indistinguishable particles is given by $Z_{\text{tot}} = Z_1^N/N!$, where Z_1 is the single–particle partition function, show that the chemical potential is given by

$$\mu = -k_B T \log\left(\frac{Z_1}{N}\right) \tag{8}$$

(b) Assume that at one moment there are N_A, N_B, and N_C particles of type A, B, and C, respectively. Determine the partition function of each species, and find the corresponding chemical potentials. You can check your results by doing the next part.

(c) Show that

$$n_A = \frac{e^{\mu_A/k_B T}}{\lambda_A^3} \tag{9}$$

$$n_B = \frac{e^{\mu_B/k_B T}}{\lambda_B^3} \tag{10}$$

$$n_C = \frac{e^{\mu_C/k_B T} e^{\beta\Delta}}{\lambda_C^3} \tag{11}$$

Here $n_A = N_A/V$ is the density of species A, and λ_A is the thermal wavelength of A, with an analogous notation for B and C.

(d) Show that in equilibrium the densities of A, B and C satisfy

$$\frac{n_A n_B}{n_C} = \frac{(2\pi m_{\text{red}} k_B T)^{3/2}}{h^3} e^{-\beta\Delta} \tag{12}$$

where $m_{\text{red}} = m_A m_B/(m_A + m_B)$ is the reduced mass. Note $m_C = m_A + m_B$.

Problem 3. The Saha Equation

The Saha equation describes the relative abundance of neutral hydrogen to ionized hydrogen at a given temperature. The reaction here is

$$p + e \leftrightarrow H \tag{13}$$

Read the setup of problem Blundell 22.5, and recognize that the results of the previous problem apply. The only difference is that in Blundell's part (a), they have approximated $m_{\text{red}} = m_e m_p/(m_e + m_p) \simeq m_e$. They (following Saha) also have approximated the internal partition function of the hydrogen atom as a single bound state with binding energy $\Delta = R = 13.6\,\text{eV}$. We evaluate the partition function of hydrogen with the same approximation in a previous problem.

(a) Do problem 22.6 parts (b) and (c).

Problem 4. Neutrality (Adapted from Kittel and Kroemer)

Consider a lattice of protons consisting of a total of N sites. The protons (located at the sites) share the available electrons which can hop from site to site. The total system is neutral so that the number of electrons is equal to the number of protons (or lattice sites). Electrons can hop from site to site, so each site does not need to be neutral. Suppose that each atom can exist in four states.

state	$N_{\text{electrons}}$	Energy
ground state	1	$-\frac{1}{2}\Delta$
positive ion	0	$-\frac{1}{2}\delta$
negative ion	2	$\frac{1}{2}\delta$
excited hydrogen	1	$\frac{1}{2}\Delta$

(a) Compute the grand potential $\Phi_G = -k_BT \log \mathcal{Q}$ of a site by evaluating the grand partition function, $\mathcal{Q}$.

(b) Determine the mean number of electrons per site as a function of the electron chemical potential and temperature.

(c) Determine the entropy and mean energy of a site as a function of the electron chemical potential and temperature.

This question had a bit too much algebra. A better question would be the one given below, which is how it will be written next year.

(d) By requiring that the mean number of electrons per site is one, find an equation which determines the chemical potential as a function of temperature. Your formula should in involve δ and T.

(e) Show that at the charge neutrality point

$$\mathcal{Q} = 4e^{\beta\delta/2} \cosh^2(\beta\Delta/4) \tag{14}$$

We used the indentity $(\cosh(x) + 1)/2 = \cosh^2(x/2)$, which is the hyperbolic analog of the cosine identity $(\cos(\theta) + 1)/2 = \cos^2\theta$.. Using this expression determine the the entropy per site. You should find

$$\frac{S}{k_B} = \log\left[4\cosh^2(\tfrac{\beta\Delta}{4})\right] - \frac{\beta\Delta}{2}\tanh(\tfrac{\beta\Delta}{4}) \tag{15}$$

Make a sketch of this function as function of $\beta\Delta$. What is the limit of this function as $\beta\Delta \to 0$? Give a physical interpretation of this limit.