PHYSICS 112
Homework 8 Solutions

1. (a) In the reaction
$$e + H^+ \longleftrightarrow H$$
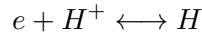
we have $\nu_e = 1, \nu_{H^+} = 1, \nu_H = -1$ and so the law of mass action gives us

$$\frac{n_e \, n_{H^+}}{n_H} = \frac{n_{Qe} \, n_{QH^+}}{n_{QH}} \frac{1}{Z_H(\text{int})} \qquad (1)$$

where $Z_H(\text{int}) = e^{\beta \Delta E}$ is the internal partition function of the hydrogen atom (we just include the lowest state with energy $-\Delta E$). There are no internal degrees of freedom of the electron, and those of the proton are of much too high energy to be important, so we have set $Z_e(\text{int}) = Z_{H^+}(\text{int}) = 1$. Now

$$n_{Qe} = \left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3/2}, \qquad (2)$$

with similar expressions for n_{QH^+} and n_{QH}. Since the mass of the hydrogen atom is almost the same as that of the proton, the factors of n_{QH^+} and n_{QH} cancel in Eq. (1) to a good approximation. Furthermore, there are an equal number of protons and electrons, so $n_e = n_{H^+}$, and hence, taking the square root of Eq. (1), we get

$$\boxed{n_e = (n_H \, n_{Qe})^{1/2} \exp(-\beta \Delta E/2),} \qquad (3)$$

which is known as the Saha equation.

(b) When half the hydrogen atoms are ionized, we have $n_e = n_H$, for which Eq. (3) gives (when squared)

$$\boxed{\frac{n_H}{n_{Qe}} = \exp\left(-\frac{\Delta E}{k_B T_i}\right),}$$

where T_i is the temperature,

2. (a) Referring to the handout on equilibrium in chemical reactions, we have $\nu_{A^+} = \nu_{A^-} = 1$, and $Z_{A^+}(\text{int}) = Z_{A^-}(\text{int}) = \exp(-\beta \Delta E/2)$. Hence Eq. (16) of that handout gives

$$\frac{n_{A^+}}{n_Q} \frac{n_{A^-}}{n_Q} \frac{1}{e^{-\beta \Delta E}} = 1, \qquad (4)$$

where

$$n_{Q+} = n_{Q-} = n_Q = \left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3/2}.$$

Equation (4) gives

$$\boxed{n_{A^+} = n_{A^-} = n_Q \, e^{-\beta \Delta E/2}.} \qquad (5)$$

(b) Putting in the mass of the electron, and the given temperature of the sun we get

$$\frac{\Delta E}{2k_B T} = \frac{mc^2}{k_B T} = \frac{0.51 \times 10^6 \times 11,600}{1.5 \times 10^7} = 394.$$

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$$n_Q = \left(\frac{9.1 \times 10^{-28} \times 1.38 \times 10^{-16} \times 1.5 \times 10^7}{2 \times 3.142 \times (1.05 \times 10^{-24})^2} \right)^{3/2} = 1.4 \times 10^{26} \text{cm}^{-3} .$$

Hence the density of thermally produced electrons at the center of the sum, given by Eq. (5), is

$$1.4 \times 10^{26} \times \exp(-394) \simeq \boxed{10^{-145} \text{ cm}^{-3} .}$$

This is a *really tiny* number. In the volume of the sun, not one pair would be produced. However, if the sun were only 10 times hotter, pairs *would* be produced; the density would then be $4.4 \times 10^{27} \times \exp(-39) \simeq 5 \times 10^{10} \text{ cm}^{-3}$.

3. (a) Maxwell equations arise because the order of a mixed second derivative is unimportant, i.e.

$$\left(\frac{\partial}{\partial y} \left(\frac{\partial f}{\partial x} \right)_y \right)_x = \left(\frac{\partial}{\partial y} \left(\frac{\partial f}{\partial x} \right)_x \right)_y . \tag{6}$$

We apply this first with f the Gibbs free energy G, $x = T$ and $y = P$. Now

$$\left(\frac{\partial G}{\partial T} \right)_P = -S, \qquad \left(\frac{\partial G}{\partial P} \right)_T = V ,$$

and applying Eq. (6) gives

$$\boxed{\left(\frac{\partial V}{\partial T} \right)_P = - \left(\frac{\partial S}{\partial P} \right)_T .} \tag{7}$$

Next apply Eq. (6) with f the Gibbs free energy G, $x = N$ and $y = P$. We have

$$\left(\frac{\partial G}{\partial N} \right)_P = \mu, \qquad \left(\frac{\partial G}{\partial P} \right)_N = V ,$$

and applying Eq. (6) gives

$$\boxed{\left(\frac{\partial V}{\partial N} \right)_P = \left(\frac{\partial \mu}{\partial P} \right)_N .}$$

Next apply Eq. (6) with f the Gibbs free energy G, $x = N$ and $y = T$. We have

$$\left(\frac{\partial G}{\partial N} \right)_T = \mu, \qquad \left(\frac{\partial G}{\partial T} \right)_N = -S ,$$

and applying Eq. (6) gives

$$\boxed{\left(\frac{\partial \mu}{\partial T} \right)_N = - \left(\frac{\partial S}{\partial N} \right)_T .}$$

Note: We have omitted subscripts of those variables which are constant of *both* sides of the equation.

(b) From Eq. (7) the volume coefficient of thermal expansion α is given by

$$\alpha \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = -\frac{1}{V} \left(\frac{\partial S}{\partial P} \right)_T .$$

According to the third law of thermodynamics, $S = 0$ at $T = 0$ and hence $(\partial S / \partial P)_T = 0$ at $T = 0$. We conclude that $\boxed{\alpha \to 0 \text{ for } T \to 0.}$

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4. To a good approximation, the Clausius-Clapeyron equation can be written

$$\frac{dP}{dT} = \frac{L}{k_B T^2}\, P\,,$$

see Eq. (18) of Ch. 10 of the book, where L is the latent heat per molecule. We have $L = 2260/(N_A/18)\,\mathrm{J}$ where $N_A = 6 \times 10^{23}$ is Avogadro's number and 18 is the molecular weight of water in grams. Also $T = 373\,\mathrm{K}$ and $P = 1\,\mathrm{atm}$. Hence we have

$$\frac{1}{P}\frac{dP}{dT} = \frac{2260 \times 18}{1.38 \times 10^{-19} \times 373^2 \times 6 \times 10^{23}} = 0.035\,\mathrm{K}^{-1}.$$

Taking the inverse and setting $P = 1\,\mathrm{atm}$. gives

$$\boxed{\frac{dT}{dP} = 28\,\mathrm{K/atm}.}$$

5. The Clausius-Clapeyron equation can be written in the form

$$\frac{dP}{dT} = \frac{s_s - s_l}{v_s - v_l}\,,$$

where subscripts 's' and 'l' refer to 'solid' and 'liquid'.

(a) The result that $dP/dT \to 0$ for $T \to 0$ implies that $s_s = s_l$ at $T = 0$. This is required by the third law of thermodynamics.

(b) The result that $dp/dT < 0$ at low but non-zero T implies that the entropy of the liquid is *less* than that of the solid, since the volume of the liquid is greater (^{3}He, like most liquids with the notable exception of water, contracts when it solidifies).

This is surprising since usually liquids have a lot more disorder than solids and so have a higher entropy. However, ^{3}He at low-T is a *degenerate Fermi liquid* in which the occupancy of most (single-particle) quantum states is either 0 or 1, and so the entropy is low. (If the occupancy is exactly 0 or 1 the entropy from that state is zero. Why?)

In fact the entropy is proportional to T since $C_V = T\,dS/dT$ and we showed that the specific heat C_V is proportional to T.