

## Problem 1

Kittel & Kroemer, Chapter 9, problem 1 [Thermal expansion near absolute zero.]

(a): 1 point

Prove the three Maxwell relations

$$\begin{aligned}(\partial V/\partial \tau)_p &= -(\partial \sigma/\partial p)_\tau, \\ (\partial V/\partial N)_p &= +(\partial \mu/\partial p)_N \\ (\partial \mu/\partial \tau)_N &= -(\partial \sigma/\partial N)_\tau.\end{aligned}$$

We showed in class from the form of  $dG$  that  $V = (\partial G/\partial p)_{\tau,N}$ ,  $\sigma = -(\partial G/\partial \tau)_{p,N}$ , and  $\mu = (\partial G/\partial N)_{\tau,p}$ . From these, we can show all three relations:

$$\begin{aligned}(\partial V/\partial \tau)_p &= (\partial^2 G/\partial \tau \partial p) = -(\partial \sigma/\partial p)_\tau \\ (\partial V/\partial N)_p &= (\partial^2 G/\partial N \partial p) = +(\partial \mu/\partial p)_N \\ (\partial \mu/\partial \tau)_N &= (\partial^2 G/\partial \tau \partial N) = -(\partial \sigma/\partial N)_\tau.\end{aligned}$$

(a): 1 point

Here we use the result that we can take partial derivatives in any order (partial derivatives commute).

(b): 1 point

Show with the help of the first Maxwell relation above and the third law of thermodynamics that the volume coefficient of thermal expansion

$$\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial \tau} \right)_p$$

approaches zero as  $\tau \rightarrow 0$ .

From the first Maxwell relation,

$$\alpha = -\frac{1}{V} (\partial \sigma/\partial p)_\tau$$

This book's statement of the third law of thermodynamics is that the entropy approaches a constant as  $\tau \rightarrow 0$ , independent of any parameters, including pressure. Thus  $(\partial \sigma/\partial p)_\tau$  goes to zero as  $\tau \rightarrow 0$ , and thus so must  $\alpha$ .

(b): 1 point

## Problem 2

Kittel & Kroemer, Chapter 9, problem 2 [Thermal ionization of hydrogen.]

Consider the formation of atomic hydrogen in the reaction  $e + H^+ \leftrightarrow H$ , where  $e$  is an electron, as the adsorption of an electron on a proton  $H^+$ .

**(a): 1 point**

Show that the equilibrium concentrations of the reactants satisfy the relation

$$[e][H^+]/[H] \simeq n_Q e^{-I/\tau},$$

where  $I$  is the energy required to ionize atomic hydrogen, and  $n_Q \equiv (m\tau/2\pi\hbar^2)^{3/2}$  refers to the electron. Neglect the spins of the particles; this assumption does not affect the final result. The result is known as the Saha equation. If all the electrons and protons arise from the ionization of hydrogen atoms, then the concentration of protons is equal to that of the electrons, and the electron concentration is given by

$$[e] = [H]^{1/2} n_Q^{1/2} e^{-I/2\tau}.$$

A similar problem arises in semiconductor physics in connection with the thermal ionization of impurity atoms that are donors of electrons.

The “equation” for this chemical reaction is  $e + H^+ - H = 0$ , from which we see that the coefficients are  $\nu_e = 1$ ,  $\nu_{H^+} = 1$ , and  $\nu_H = -1$ . The law of mass action then gives us that

$$[e][H^+][H]^{-1} = K(\tau),$$

where  $K(\tau)$  is the equilibrium constant, and we are denoting concentrations with square brackets. The equilibrium constant is given by (using Eq. 34)

$$K(\tau) = (n_{Q,e} n_{Q,H^+} n_{Q,H}^{-1}) e^{-(F_{e,int} + F_{H^+,int} - F_{H,int})/\tau}.$$

The masses of  $H$  and  $H^+$  only differ by an electron mass; they are very similar. This means that  $n_{Q,H^+} n_{Q,H}^{-1} \approx 1$ , and so our result simplifies:

$$K(\tau) \simeq n_{Q,e} e^{-(F_{e,int} + F_{H^+,int} - F_{H,int})/\tau}.$$

The internal free energy of the electron/ $H^+$  should exceed the internal free energy of the bound hydrogen atom by  $I$ , the ionization energy. Thus

$$K(\tau) \simeq n_{Q,e} e^{-I/\tau},$$

which gives the result.

(a): 1 point

**(b): 1 point**

Let  $[\text{H}(\text{exc})]$  denote the equilibrium concentration of H atoms in the first excited electronic state, which is  $\frac{3}{4}I$  above the ground state. Compare  $[\text{H}(\text{exc})]$  with  $[e]$  for conditions at the surface of the Sun, with  $[\text{H}] \sim 10^{23} \text{cm}^{-3}$  and  $T \sim 5000 \text{ K}$ .

For this we can use the Boltzmann factor; the proportion of excited atoms compared to the ground state is given by  $[\text{H}(\text{exc})]/[H] = 4e^{-(3I/4)/k_B T}$ , where the factor of 4 comes from the 4-fold degeneracy of the first hydrogen excited state compared to the ground state (one 2s orbital, three 2p orbitals). We can relate this to the electron concentration using the equation above, so that

$$\begin{aligned} [\text{H}(\text{exc})]/[e] &= \frac{[\text{H}(\text{exc})]}{[H]^{1/2} n_Q^{1/2} e^{-I/2\tau}} \\ &= \frac{[\text{H}(\text{exc})]/[H]}{n_Q^{1/2} e^{-I/2\tau}} [H]^{1/2} \\ &= 4 \frac{e^{-(3I/4)/k_B T}}{n_Q^{1/2} e^{-I/2\tau}} [H]^{1/2} \\ &= 4([H]/n_Q)^{1/2} e^{-(I/4)/k_B T} \end{aligned}$$

**(b): 1 point**

The ionization energy of hydrogen is  $I = 13.6 \text{ eV}$ . Using the mass of the electron and the temperature, we can find that  $n_Q = 8.54 \times 10^{20} \text{ cm}^{-3}$ , so that  $[H]/n_Q = 117$ . We can plug all of this in to find

$$[\text{H}(\text{exc})]/[e] = 4 \times 10.8 e^{-(13.6/4)/0.431} = 1.6 \times 10^{-2},$$

or equivalently

$$[e]/[\text{H}(\text{exc})] = 62.$$

The free electrons are more populous than the excited hydrogen. This is not what you would expect with a naive application of the Boltzmann factor, treating ionized hydrogen as having an energy of  $I$  above the ground state!

## Problem 3

**Kittel & Kroemer, Chapter 9, problem 3 [Ionization of donor impurities in semiconductors.]: 2 points**

A pentavalent impurity (called a donor) introduced in place of a tetravalent silicon atom in crystalline silicon acts like a hydrogen atom in free space, but with  $e^2/\epsilon$  playing the role of  $e^2$  and an effective mass  $m^*$  playing the role of the electron mass  $m$  in the description of the ionization energy and radius of the ground state of the impurity atom, and also for the free electron. For silicon the dielectric constant  $\epsilon = 11.7$  and, approximately,  $m^* = 0.3m$ . If there are  $10^{17}$  donors per  $\text{cm}^3$ , estimate the concentration of conduction electrons at 100 K.

Recall that the hydrogen energy levels are proportional to  $m_e e^4$ . This means that in this effective model, the ionization energy  $I$  should be related to the free hydrogen ionization energy  $I_0$  as  $I = I_0(m^*/m)/\epsilon^2 = 2.2 \times 10^{-3} I_0$ . With  $I_0 = 13.6$  eV, this makes  $I = 0.0298$  eV. At 100 K,  $k_B T = 0.00862$  eV. The quantum concentration for the electrons, using  $m^*$  and 100 K, is  $n_Q \approx 4 \times 10^{17} \text{ cm}^{-3}$ . The concentration of conduction electrons should be equal to the concentration of *ionized* donors ( $[e] = [\text{Si}^+]$ ; the total donor concentration is equal to the concentration of the ionized donors + the concentration of the unionized donors:  $[\text{donors}] = [\text{Si}^+] + [\text{Si}] = 10^{17} \text{ cm}^{-3}$ . We can now use the law of mass action to relate the electron and donor concentrations:

$$[e][\text{Si}^+][\text{Si}]^{-1} = n_Q e^{-I/\tau},$$

or

$$[e]^2 = ([\text{donors}] - [e])n_Q e^{-I/\tau},$$

or

$$e^{I/\tau}[e]^2 + n_Q[e] - n_Q[\text{donors}] = 0.$$

This is a quadratic equation for  $[e]$ , which we can solve:

$$\begin{aligned} [e] &= \frac{e^{-I/\tau}}{2} \left( -n_Q + \sqrt{n_Q^2 + 4n_Q[\text{donors}]e^{I/\tau}} \right) \\ &= \frac{e^{-I/\tau}}{2} \left( -4 + \sqrt{(4)^2 + 4(4)(1)e^{I/\tau}} \right) \times 10^{17} \text{ cm}^{-3} \\ &= 2e^{-I/\tau} \left( -1 + \sqrt{1 + e^{I/\tau}} \right) \times 10^{17} \text{ cm}^{-3} \\ &= 0.298 \times 10^{17} \text{ cm}^{-3}. \end{aligned}$$

A substantial fraction ( $\sim 1/3$ ) of the donors give their conduction electrons.

## Problem 4

Kittel & Kroemer, Chapter 9, problem 4 [Biopolymer growth.]

Consider the chemical equilibrium of a solution of linear polymers made up of identical units. The basic reaction step is  $\text{monomer} + N\text{mer} = (N + 1)\text{mer}$ . Let  $K_N$  denote the equilibrium constant for this reaction.

**(a): 1 point**

Show from the law of mass action that the concentrations  $[\dots]$  satisfy

$$[N + 1] = [1]^{N+1}/K_1 K_2 K_3 \cdots K_N$$

For  $1 \rightarrow 2$ , the reaction equation is  $\text{monomer} + \text{monomer} - (2)\text{mer} = 0$ , so the law of mass action gives

$$[1][1][2]^{-1} = K_1,$$

or

$$[2] = [1]^2/K_1.$$

For  $2 \rightarrow 3$ , the reaction equation is  $\text{monomer} + (2)\text{mer} - (3)\text{mer} = 0$ , so the law of mass action gives

$$[1][2][3]^{-1} = K_2,$$

or

$$[3] = [1][2]/K_2.$$

Plugging in the result for  $1+1$ , this becomes

$$[3] = [1]^3/K_1 K_2.$$

We can immediately see how this generalizes to the result we want,

$$[N + 1] = [1]^{N+1}/K_1 K_2 K_3 \cdots K_N.$$

(This could be proven more rigorously using induction, but this is fine for us.)

(a): 1 point

**(b): 1 point**

Show from the theory of reactions that for ideal gas conditions (an ideal solution):

$$K_N = \frac{n_Q(N)n_Q(1)}{n_Q(N+1)} e^{(F_{N+1}-F_N-F_1)/\tau}.$$

Here

$$n_Q(N) = (2\pi\hbar^2/M_N\tau)^{-3/2},$$

where  $M_N$  is the mass of the  $N$ mer molecule, and  $F_N$  is the free energy of one  $N$ mer molecule.

From the result for the equilibrium constant for ideal gases (Eq. 34), and from the reaction equation monomer +  $N$ mer  $\rightarrow$   $(N+1)$ mer = 0, we immediately have

$$K_N = \frac{n_Q(N)n_Q(1)}{n_Q(N+1)} e^{(F_{N+1}-F_N-F_1)/\tau}.$$

(b): 1 point

**(c): 1 point**

Assume  $N \gg 1$ , so that  $n_Q(N) \simeq n_Q(N+1)$ . Find the concentration ratio  $[N+1]/[N]$  at room temperature if there is zero free energy change in the basic reaction step: that is, if  $\Delta F = F_{N+1} - F_N - F_1 = 0$ . Assume  $[1] = 10^{20} \text{ cm}^{-3}$ , as for amino acid molecules in a bacterial cell. The molecular weight of the monomer is 200.

From the result from part (a) we can see that

$$[N+1]/[N] = [1]/K_N.$$

From part (b), we can plug in  $K_N$  (using  $\Delta F = 0$ ):

$$[N+1]/[N] = [1] \frac{n_Q(N+1)}{n_Q(N)n_Q(1)}.$$

If  $n_Q(N) \simeq n_Q(N+1)$ , this becomes

$$[N+1]/[N] \simeq \frac{[1]}{n_Q(1)}.$$

Now we need the quantum concentration at room temperature 293 K with molecular weight 200 (mass 200 times the mass of a proton), which gives  $n_Q(1) = 2.7 \times 10^{27} \text{ cm}^{-3}$ . Thus

$$[N+1]/[N] \simeq 3.7 \times 10^{-8}.$$

This means it is very unlikely for the reaction to go in the direction of large molecules.

(c): 1 point

**(d): 1 point**

Show that for the reaction to go in the direction of long molecules we need  $\Delta F < -0.4$  eV, approximately. This condition is not satisfied in Nature, but an ingenious pathway is followed that simulates the condition.

The condition for the reaction to go in the direction of large molecules is roughly that  $[N + 1]/[N] \approx 1$ . For this to happen, returning to our expression for  $[N + 1]/[N]$  in the previous section, we need

$$1 = \frac{[1]}{n_Q(1)} e^{-\Delta F/\tau}.$$

Solving this for  $\Delta F$ , we have

$$\Delta F = -\tau \ln(n_Q(1)/[1]).$$

At room temperature  $\tau = 0.0256$  eV, and we can calculate:

$$\Delta F = -0.44 \text{ eV}.$$

Any  $\Delta F$  lower than this will increase  $[N + 1]/[N]$  above 1 and the reaction will go in the direction of large molecules.

**(d): 1 point**

## Problem 5

Kittel & Kroemer, Chapter 9, problem 5 [Particle-antiparticle equilibrium.]

### (a): 1 point

Find a quantitative expression for the thermal equilibrium concentration  $n = n^+ = n^-$  in the particle-antiparticle reaction  $A^+ + A^- = 0$ . The reactants may be electrons and positrons; protons and antiprotons; or electrons and holes in a semiconductor. Let the mass of either particle be  $M$ ; neglect the spins of the particles. The minimum energy release when  $A^+$  combines with  $A^-$  is  $\Delta$ . Take the zero of the energy scale as the energy with no particles present.

From the law of mass action, we have (treating the particles as being in the classical regime)

$$n^+ n^- = n_{Q+} n_{Q-} e^{-\Delta/\tau}.$$

The masses of the particles are equal, so that  $n_{Q+} = n_{Q-} \equiv n_Q$ . If the particles have equal concentration,  $n^+ = n^- \equiv n$ , so that we have

$$\begin{aligned} n &= n_Q e^{-\Delta/2\tau} \\ &= (M\tau/2\pi\hbar^2)^{3/2} e^{-\Delta/2\tau} \end{aligned}$$

(a): 1 point

### (b): 1 point

Estimate  $n$  in  $\text{cm}^{-3}$  for an electron (or a hole) in a semiconductor  $T = 300$  K with a  $\Delta$  such that  $\Delta/\tau = 20$ . The hole is viewed as the antiparticle to the electron. Assume that the electron concentration is equal to the hole concentration; assume also that the particles are in the classical regime.

Still working in the classical regime, and taking  $M$  to be the electron mass, we can plug in values to obtain

$$n = (1.25 \times 10^{19} \text{ cm}^{-3}) e^{-10} = 5.7 \times 10^{14} \text{ cm}^{-3}.$$

(b): 1 point

### (c): 1 point

Correct the result of (a) to let each particle have a spin  $1/2$ . Particles that have antiparticles are usually fermions with spins of  $1/2$ .

The effect of having spin  $1/2$  is to shift the chemical potential to  $\mu = \tau \ln(n/n_Q) - \tau \ln 2 = \tau \ln(n/(2n_Q))$ . So, the effect is equivalent to doubling  $n_Q$  for each species:

$$n = 2(M\tau/2\pi\hbar^2)^{3/2} e^{-\Delta/2\tau}$$

(c): 1 point