KEY

YOUR NAME HERE

April 22, 2008

Chem 120B Midterm #2

Definitions and Useful Formulas:

Boltzmann distribution:

$$p(\nu) = \frac{e^{-\beta E(\nu)}}{Q}$$

Partition function:

$$Q = \sum_{\nu} e^{-\beta E(\nu)}$$

First and second laws of thermodynamics:

$$dE = đw + đq, \qquad dS \geq \frac{đq}{T}$$

Gibbs free energy:

$$G = E - TS + pV, \quad dG = -SdT + Vdp + \sum_j \mu_j dN_j$$

Gibbs-Duhem equation:

$$SdT - Vdp + Nd\mu = 0$$

Clausius-Clapeyron equation:

$$\frac{dp}{dT} = \frac{\Delta S}{\Delta V}$$

Chemical potential in ideal solution:

$$\mu_j = \mu_j^{(0)}(T,p) + k_{\mathrm{B}} T \ln x_j$$

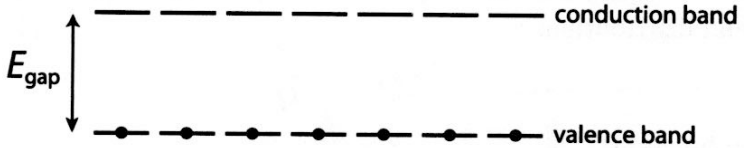
Debye screening length:

$$\lambda = \sqrt{\frac{\epsilon}{4\pi\beta I}},$$

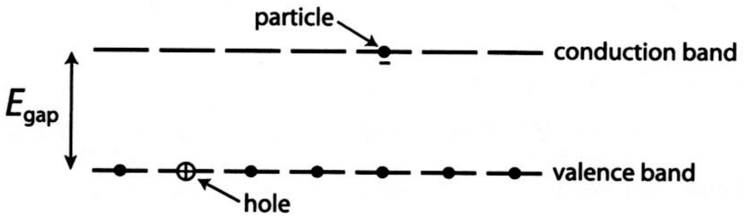
Ionic strength:

$$I = \sum_j q_j^2 \frac{N_j}{V}$$

1. Semiconducting materials are characterized by a gap in the spectrum of electronic states. At zero temperature, all states below the gap (the *valence band*) are filled, and all states above the gap (the *conduction band*) are empty, as sketched below:



At finite temperature, thermal fluctuations will excite some small fraction of electrons into the higher energy states. These excitations not only create negatively charged *particles* in the conducting band, but also positively charged *holes* in the valence band:



Both particles and holes can move throughout the material. We will treat them as distinct chemical species, and consider their motion through conduction and valence bands as simple translational motion. In other words we will think of them as if they were ions in solution.

10 pts (i) For a semiconductor with a given density ρ_- of electrons in the conduction band, spatial regions larger than a certain size ℓ_{neutral} will almost invariably contain equal numbers of particles and holes. Write this critical length scale in terms of temperature T, ρ_-, the crystal's dielectric constant ϵ, and the charge of an electron q_{elec}.

$$l_{neutral} = \sqrt{\frac{\epsilon}{4\pi\beta I}}$$

$$I = \sum_j q_j^2 \frac{N_j}{V} = q_{elec}^2 \rho_- + q_{hole}^2 \rho_{hole}$$

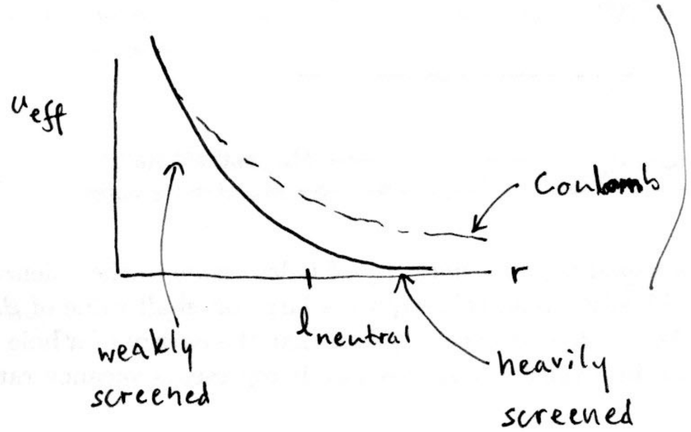
$$\underbrace{q_{hole} = -q_{elec}, \quad \rho_{hole} = \rho_-}$$

$$I = 2\rho_- q_{elec}^2$$

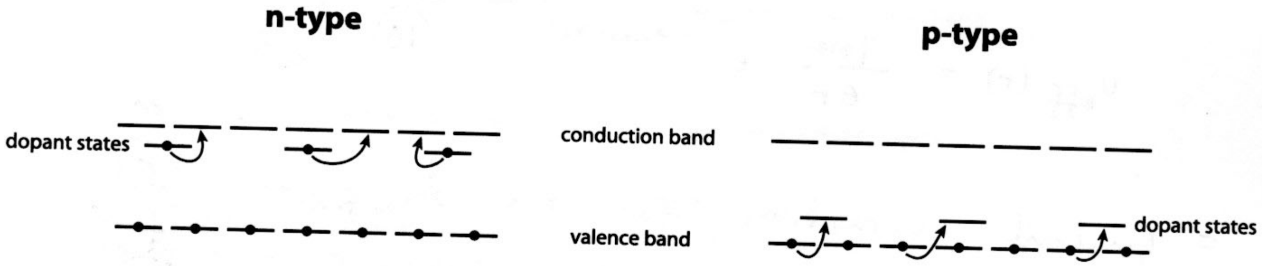
10 pts (ii) Describe the effective interaction between two conducting electrons, as mediated by the crystal and by other particles and holes. The length scale ℓ_{neutral} should figure into your answer. Write an equation for this interaction, or plot its dependence on distance, in support of your description.

$$u_{\text{eff}}(r) = \frac{q_{\text{elec}}^2}{\epsilon r} e^{-r/\ell_{\text{neutral}}}$$

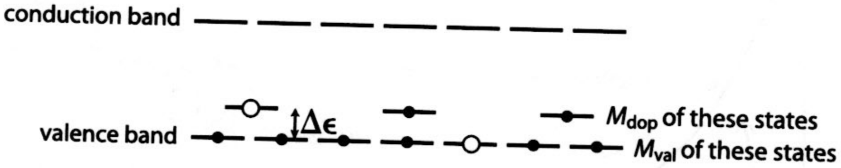
- $\approx$ Coulomb interaction for $r \ll \ell_{\text{neutral}}$
- ≈ 0 for $r \gg \ell_{\text{neutral}}$ due to screening



To enhance their conductivity, semiconductors are often doped with other materials that increase the concentration of charge carrying species. In an *n-type* semiconductor, dopants provide electrons to the conduction band. In a *p-type* semiconductor, dopants induce holes in the valence band.



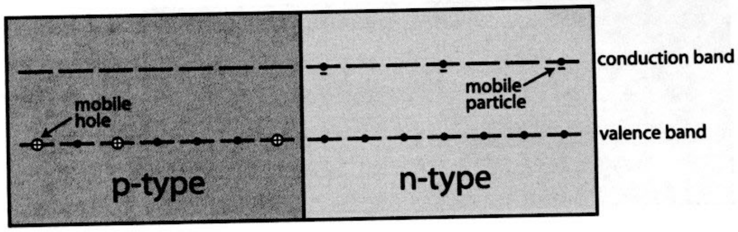
10 pts (iii) Consider a p-type semiconductor with M_{val} valence band states , and M_{dop} dopant states whose energy is higher by an amount $\Delta\epsilon$. A single hole can occupy any one of these valence or dopant states.



Under what circumstances would the vast majority of holes reside in the valence band at equilibrium? Specifically, would this require a large or small value of $\beta\Delta\epsilon$? A large or small value of $M_{\text{dop}}/M_{\text{val}}$? Explain. (Note that the energy of a hole in a dopant state is *lower* than in a valence state because it represents vacancy rather than occupation.)

- small $\beta\Delta\epsilon$, so thermal fluctuations can easily excite a hole into a valence state
- small $\frac{M_{\text{dop}}}{M_{\text{val}}}$, so entropy of hole in valence band much larger than in dopant band.

A common component of semiconductor technology is the *p-n junction*, in which a p-type semiconductor is juxtaposed with an n-type semiconductor:

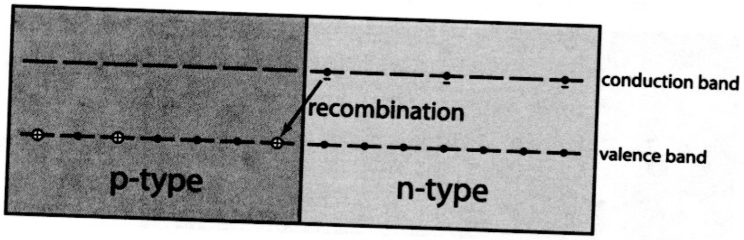


10 pts (iv) Using the analogy with dilute solutions, write the chemical potential μ_{part} of particles residing in the conduction band of the n-type region as a function of temperature (T), the fraction of filled states in the conduction band (x_{part}), and a standard state chemical potential ($\mu^{(0)}_{\text{part}}$) that does not depend on the fraction of filled states. Write a similar expression for the chemical potential μ_{hole} of holes in the valence band of the p-type region, involving the fraction x_{hole} of vacant states in the valence band and $\mu^{(0)}_{\text{hole}}$. Here you do *not* need to consider interactions among charge carriers.

$$\mu_{part} = \mu^{(0)}_{part} + k_B T \ln x_{part}$$

$$\mu_{hole} = \mu^{(0)}_{hole} + k_B T \ln x_{hole}$$

Near the p-n interface, particles from the n-type material can *recombine* with holes in the p-type material:



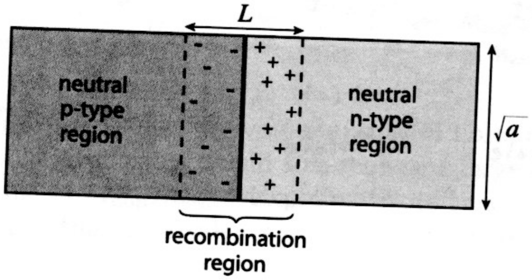
The recombination region is nearly saturated with particle-hole pairs, which as a result have no translational freedom. We can therefore write the chemical potential of these pairs as

$$\mu_{\text{pair}} = \mu_{\text{pair}}^{(0)} + \mu_{\text{pair}}^{\text{non-ideal}}$$

By itself, recombination of a particle and a hole is energetically favorable:

$$\mu_{\text{pair}}^{(0)} - (\mu_{\text{part}}^{(0)} + \mu_{\text{hole}}^{(0)}) = -E_{\text{gap}}$$

But recombination also removes negative charge from the originally neutral n-type material, and adds negative charge to the originally neutral p-type material. An electrostatic imbalance results, as sketched below.



The reversible work required to create such an electrostatic imbalance, including interactions among *all* charges, is approximately

$$w(L) = \frac{\pi a \rho_{\text{dop}}^2}{6\epsilon} L^3.$$

The width of the recombination region, $L = 2N_{\text{pair}}/(a\rho_{\text{dop}})$, is proportional to the number N_{pair} of recombined pairs. The cross-sectional area of the recombination region a is just a constant determined by the size of the device.

10 pts (v)Explain why the effect of $w(L)$ is considered non-ideal, and calculate its contribution to the Gibbs free energy, $G^{\text{non-ideal}}$.

(Physically, $w(L)$ is non-ideal b/c it involves influence of
or "solutes" upon other solutes. Mathematically, it is
(non-linear in N_{pair}.

$$G^{\text{non-ideal}} = w(L)$$

10 pts (vi) Calculate the chemical potential of recombined particle-hole pairs μ_{pair} as a function of L, ρ_{dop}, ϵ, and $\mu^{(0)}_{\text{pair}}$. When taking derivatives, don't forget that $L = 2N_{\text{pair}}/(a\rho_{\text{dop}})$ is a function of N_{pair}.

$$G = N\mu^{(0)}_{pair} + w(L)$$

$$\mu_{pair} = \left(\frac{\partial G}{\partial N_{pair}}\right) = \mu^{(0)}_{pair} + \frac{\pi a \rho_{dop}^2}{6\epsilon} 3L^2 \underbrace{\frac{dL}{dN_{pair}}}_{2/a\rho_{dop}}$$

$$= \mu^{(0)}_{pair} + \frac{\pi \rho_{dop}}{\epsilon} L^2$$

Particle-hole recombination can be thought of as a chemical equilibrium:

$$\text{particle} + \text{hole} \rightleftharpoons \text{recombined pair}$$

10 pts (vii) By imposing the thermodynamic condition of chemical equilibrium, determine the width of the recombination region L as a function of x_{part}, x_{hole}, E_{gap}, ρ_{dop}, and ϵ.

$$\mu_{\text{part}} + \mu_{\text{hole}} = \mu_{\text{pair}}$$

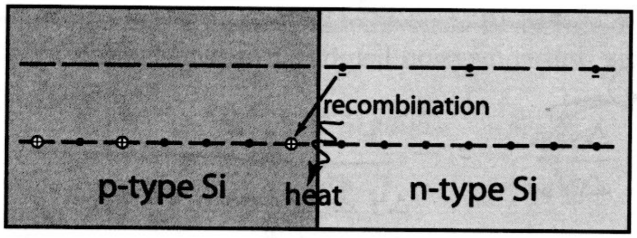
$$\mu^{(0)}_{\text{part}} + k_B T \ln x_{\text{part}} + \mu^{(0)}_{\text{hole}} + k_B T \ln x_{\text{hole}} = \mu^{(0)}_{\text{pair}} + \frac{\pi \rho_{\text{dop}}}{\epsilon} L^2$$

$$\frac{\pi \rho_{\text{dop}}}{\epsilon} L^2 = -\underbrace{\left(\mu^{(0)}_{\text{pair}} - \left(\mu^{(0)}_{\text{part}} + \mu^{(0)}_{\text{hole}}\right)\right)}_{-E_{\text{gap}}} + k_B T \ln x_{\text{part}} x_{\text{hole}}$$

$$L = \sqrt{\left(\frac{\epsilon}{\pi \rho_{\text{dop}}}\right)\left(E_{\text{gap}} + k_B T \ln x_{\text{part}} x_{\text{hole}}\right)}$$

for working out consequences of results from previous questions

2. When current flows across a p-n junction, each electronic charge transported across the recombination region delivers an energy E_{gap} to the crystalline lattice in the form of heat.



If this heat were not dissipated, the crystal would eventually melt.

The remaining problems concern this melting phenomenon and behavior of the molten state, in which Si serves as a solvent for dissolved dopants. They do not involve the occupancy of electronic states, i.e., you do not need to think about particles and holes to answer these questions.

Some relevant properties of silicon (the most commonly used semiconductor) are listed below for ambient pressure (1 atm).

Melting temperature:	$T_{\text{m}} = 1700$ K
Specific heat of solid Si:	$C_{\text{p}}^{(\text{solid})} = 0.8$ J/g·K
Specific heat of liquid Si:	$C_{\text{p}}^{(\text{liquid})} = 1.0$ J/g·K
Specific volume of solid Si:	$V^{(\text{solid})} = 0.43$ cm^3/g
Specific volume of liquid Si:	$V^{(\text{liquid})} = 0.40$ cm^3/g
Specific entropy of melting:	$\Delta S_{\text{m}} = 1$ J/g·K
Band gap in crystalline Si:	$E_{\text{gap}} = 1.6 \times 10^{-19}$ J

10 pts (i) How many transported electronic charges are needed to fully melt a device of mass 1 g, initially operating at temperature $T_0 = 298$ K? Assume here that thermodynamics of the device are the same as those of pure silicon, and that the properties of liquid and solid phases listed in the table above do not depend on temperature.

Latent heat $L = T_m \Delta S_m$

$$E_{gap} \times (\text{\# of charges}) = C_p^{(solid)} (T_m - T_o) + L$$

$$\text{\# of charges} = \frac{(0.8 \frac{J}{K})(1700\ K - 298\ K) + (1700\ K)(1 \frac{J}{K})}{1.6 \times 10^{-19}\ J}$$

$= 1.8 \times 10^{22}$

≈ 0.03 mol.

10 pts (ii) Professor Relssieg has filed a patent proposing to extend a device's lifetime by operating it under high pressure, which he presumes will raise the melting point. Calculate the change in melting temperature ΔT_{m} of pure silicon when pressure is increased from 1 atm to 10 atm? Should Relssieg's patent be approved? [You might find the following unit conversion helpful: 1 atm·cm^3 ≈ 0.1 J.]

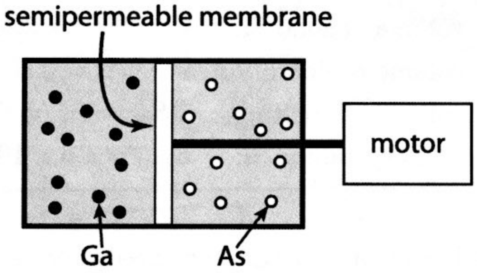
$$\frac{dp}{dT} = \frac{\Delta S_m}{\Delta V_m} = \frac{1 \ \mathrm{J/g \cdot K}}{0.4 \ \cancel{g}/\mathrm{cm^3/g} - 0.43 \ \cancel{g}/\mathrm{cm^3/g}} = -\frac{1}{0.03} \ \frac{\mathrm{J}}{\mathrm{K}} \ \mathrm{cm}^{-3}$$

$$\Delta T = \Delta p \ \frac{\Delta V_m}{\Delta S_m} = -9 \ \mathrm{atm} \cdot 0.03 \ \mathrm{cm^3 \cdot K / J}$$

$$= -0.27 \ \frac{\mathrm{atm \cdot cm^3}}{\mathrm{J}} \ \mathrm{K} = -0.027 \ \mathrm{K}$$

↳ Melting point <u>decreases</u> since $\Delta V_m < 0$. No patent for Relssieg!

10 pts (iii) Professor Relssieg has also submitted a patent to harness mechanical work from p-n junctions that have melted. His idea is to insert a semipermeable membrane between the p-type and n-type regions, which allows the molten silicon solvent to pass through but not dopant atoms. Relssieg expects to use the osmotic pressure on the membrane to drive a motor, as sketched below.



To demonstrate this new machine, Relssieg will use a junction whose p-type dopant (gallium) is present at the same concentration as the n-type dopant (arsenic) on the other side of the membrane. Assuming that the silicon/gallium and silicon/arsenic solutions behave ideally, explain why Relssieg's idea will not work.

Osmotic pressure depends only on solute concentration, and is therefore equal on either side of membrane.

No net force ⟹ no work