3.012 Quiz 3
11.04.04
100 points total

YOUR NAME: ΛΛωΛΕ4 & NICOLA

3.012
Fall 2004

Time yourself carefully – do not spend most of your time on a single question. Also, give as much written explanation as possible of your reasoning. This quiz has 8 pages on 4 sheets, with questions on all the 8 pages (i.e., do not forget the last page of the last sheet).

1. **Bonding.** (50 points)

Life as a vegetable

A valence electron in a carotene molecule can be modeled as being confined in a 1-dimensional potential V(x) that is 0 for 0 $\leq$ x $\leq$ a, and infinite everywhere else.

a. (8 points) Write explicitly both the time-dependent *and* the stationary Schrödinger equations that describe the electron in the region inside this confining potential.

$$\text{TIME DEP.}: \quad -\frac{\hbar^2}{2m}\nabla^2\psi = i\hbar\frac{\partial\psi}{\partial t}$$

$$\text{STATIONARY}: \quad -\frac{\hbar^2}{2m}\nabla^2\varphi = E\varphi$$

b. (8 points) Show that the boundary conditions force a quantization in the energy levels of the electron, and write explicitly the wavefunctions (a.k.a. eigenfunctions) that satisfy those boundary conditions. Derive explicitly the quantized energy levels.

$$\text{GENERAL SOLUTION}: \quad \varphi(a) = A\sin kx + B\cos kx$$

$$\text{BOUNDARY CONDITIONS}: \quad \varphi(0) = 0, \quad \varphi(a) = 0$$

$$\varphi(0) = 0 \Rightarrow B = 0$$

$$\varphi(a) = 0 \Rightarrow A\sin ka = 0 \Rightarrow ka = n\pi$$

$$-\frac{\hbar^2}{2m}\nabla^2\left(A\sin\frac{n\pi}{a}x\right) = \frac{\hbar^2}{2m}\frac{n^2\pi^2}{a^2}A\sin\frac{n\pi}{a}x$$

$$n = 1,2,3...$$

$$\Rightarrow E = \frac{\hbar^2}{2m}\frac{n^2\pi^2}{a^2} = \frac{h^2}{8m}\frac{n^2}{a^2}$$

c. (8 points) Determine the wavelength of a photon that is able to excite an electron from the ground state to the first excited state (you can use the usual International System for your units of measure, given below, or atomic units, remembering that in those units h=2π, c=137.036, and the mass of the electron is 1).

Planck's constant	h	6.62618×10^{-34} J s
	$\hbar = \dfrac{h}{2\pi}$	1.05459×10^{-34} J s
Velocity of light in vacuum	c	2.99792×10^{8} m s^{-1}
Elementary charge (absolute value of electron charge)	e	1.60219×10^{-19} C
Atomic mass unit	a.m.u. $= \dfrac{1}{12} M_{12c}$	1.66057×10^{-27} kg
Electron mass	m or m_e	9.10953×10^{-31} kg $= 5.48580 \times 10^{-4}$ a.m.u.
Proton mass	M_p	1.67265×10^{-27} kg $= 1.007276$ a.m.u.

$$\varepsilon_{PHOTON} = \frac{hc}{\lambda} \qquad \varepsilon_{1\to2} = \frac{h^2}{8m}\frac{4}{a^2} - \frac{h^2}{8m}\frac{1}{a^2} = \frac{3h^2}{8m}\frac{1}{a^2}$$

$$\frac{hc}{\lambda} = \frac{3h^2}{8ma^2} \Rightarrow \lambda = \frac{8mca^2}{3h} = \begin{cases} \gg 58.16\,a^2 \ (\text{ATOMIC}) \\ \gg 1.1 \ 10^{12}\,a^2 \ (\text{INTERNAT.}) \end{cases}$$

d. (8 points) Determine the probability of finding the electron exactly in the middle of the molecule, after it has been excited by the photon in c).

PROBABILITY IS PROPORTIONAL TO $\left\| \varphi\left(\dfrac{a}{2}\right) \right\|^2 =$

$$= A^2 \, \text{sen}^2 \frac{\pi}{2} = 0 .$$

e. (8 points) What would be the solution to the time-dependent equation that you have written in a) ?

$$\Psi(x,t) = \varphi(x) e^{-i\frac{E t}{\hbar}} = A\,\text{sen}\,\frac{n\pi}{a}x\, e^{-i\frac{h}{8m}\frac{n^2}{a^2}t}$$

f. (10 points) On a hot day, the molecule tosses and turns, and at the end the confining potential V(x) turns out to be 0 in the region $-a/2 \leq x \leq a/2$, instead of $0 \leq x \leq a$. What would be the new boundary conditions ? How would the allowed eigenvalues for the stationary Schrödinger equation change ? What about the eigenfunctions ?

BOUNDARY CONDITIONS: $\varphi\left(-\frac{a}{2}\right) = 0$ $\varphi\left(\frac{a}{2}\right) = 0$.

THE PHYSICAL PROBLEM IS THE SAME, HENCE

SAME EIGENVALUES, SAME SHAPE FOR THE

EIGENFUNCTIONS

GROUND STATE

(I DIDN'T ASK AN EXPLICIT SOLUTION; JUST IN CASE, HERE IT IS:
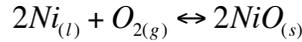
IF THE SOLUTIONS (POINT b))

WERE
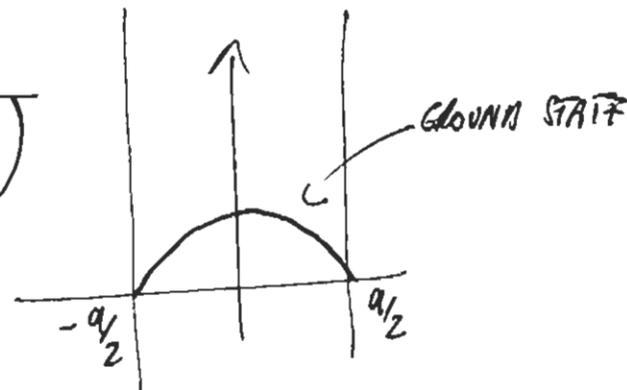
$$\left\{ A \sin \frac{n\pi}{a} x \right\}, \quad n = 1, 2 \dots$$

NOW THEY WILL BE

$$\left\{ A \sin\left[\frac{n\pi}{a}\left(x - \frac{a}{2}\right)\right] \right\} = $$

$$ \nearrow A \sin \frac{n\pi x}{a} \cos\left(-\frac{n\pi}{2}\right) + $$

$$+ A \cos \frac{n\pi x}{a} \sin\left(-\frac{n\pi}{2}\right) = $$

$$\searrow A \cos \frac{n\pi x}{a} \quad n = 1, 3, 5 \dots$$

$$= \nearrow $$

$$\searrow A \sin \frac{n\pi x}{a} \quad n = 2, 4, 6 \dots$$

1/4/04

THERMODYNAMICS SOLUTIONS

1. Consider the following reaction for the formation of solid nickel oxide:

$$2Ni_{(l)} + O_{2(g)} \leftrightarrow 2NiO_{(s)}$$

    a. (7 points) (i) Write an expression for the free energy change of this reaction in terms of the chemical potentials of each species, and then (ii) expand this expression in terms of appropriate models of the chemical potentials.

First we write out the free energy change, which is governed by the difference in chemical potentials:

$$\Delta \overline{G}_{rxn} = \sum_{i}^{products} v_i \mu_i - \sum_{j}^{reactants} v_i \mu_i = 2\mu_{NiO} - 2\mu_{Ni} - \mu_{O_2}$$

Note that this is the free energy change **per mole of O₂ consumed in the reaction**. Next, expanding the chemical potentials, we apply the general solution model as well as the ideal gas model:

$$\Delta \overline{G}_{rxn} = 2[\mu_{NiO,o} + RTl\ln a_{NiO}] - 2[\mu_{Ni,o} + RT\ln a_{Ni}] - [\mu_{O_2,o} + RT\ln P_{O_2}]$$

You could apply the standard approximation and set the activities of the pure Ni and NiO to 1, but this was not required for full credit.

    b. (7 points) What single measurement could you make to determine the equilibrium constant of this reaction? State any assumptions you need to make.

The equilibrium constant is given by the quotient of activities/partial pressures in the system:

$$K_{eq} = \frac{(a_{NiO})^2}{(a_{Ni})^2 P_{O_2}} = \frac{1}{P_{O_2}}$$

The second equality results from applying the standard approximation (activities of pure components = 1). Thus, by measuring the partial pressure of oxygen, we directly obtain the equilibrium constant.

c. (7 points) Liquid nickel is exposed to oxygen gas at 1900 K, and the system equilibrates at an oxygen partial pressure of 8.75×10^{-4} atm.

    i. Calculate the molar standard state free energy change $\Delta \overline{G}_{rxn,o}$ at 1900 K.

    ii. If the oxygen pressure in the equilibrated system is suddenly lowered, will the amount of solid NiO present increase or decrease? Show why.

The molar standard free energy change is determined from the equilibrium condition:

$$\Delta \overline{G}_{rxn} = 0$$

$$\Delta \overline{G}_{rxn,o} = -RT \ln K_{eq}$$

$$\Delta \overline{G}_{rxn,o} = -RT \ln \frac{1}{P_{O_2}} = -(8.3144)(1900) \ln \frac{1}{\left(8.75 \times 10^{-4}\right)} = -111,233 \frac{J}{mole}$$

If the oxygen pressure is suddenly decreased, the free energy change per mole of oxygen consumed becomes:

$$\Delta \overline{G}_{rxn} = \Delta \overline{G}_{rxn,o} + RT \ln \frac{1}{P_{O_2}} = -111,233 + RT \ln \frac{1}{P_{O_2}}$$

If P_{O2} is reduced, the (positive) **RT ln** term becomes greater in magnitude than $\Delta \overline{G}_{rxn,o}$, and the overall reaction free energy change in the *forward* direction will be **positive**. This implies that the reaction will spontaneously move in the *reverse* direction- some of the NiO will transform back into Ni and O_2.
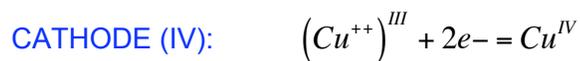
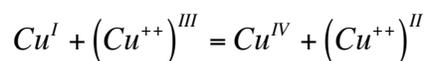2. Let's examine an electrochemical Daniell cell as shown below:
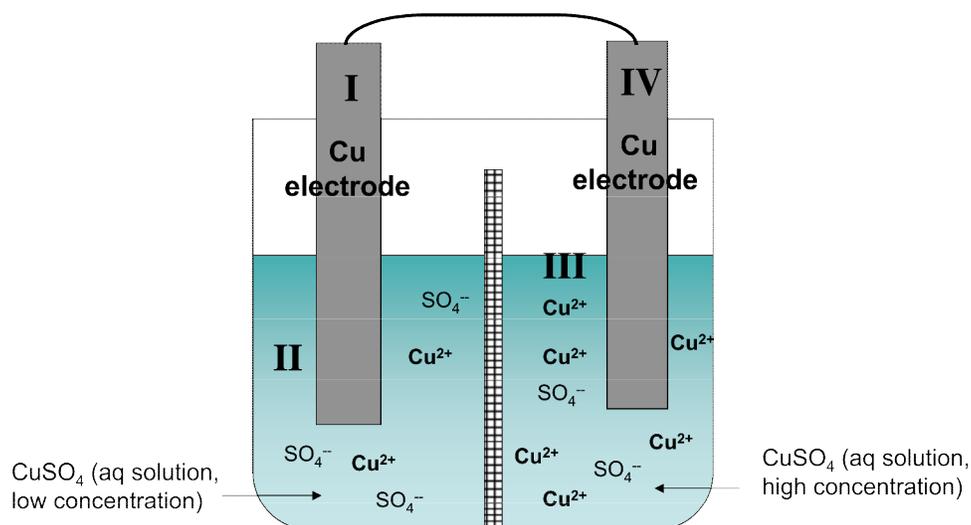
As in a standard Daniell cell, the membrane between the two aqueous solutions II and III allows only sulfate ions to pass.

  a. (7 points) Write the half-cell and overall reactions for the operation of this concentration cell.

The half-cell reactions are:

ANODE (I): $Cu^I = \left(Cu^{++}\right)^{II} + 2e-$

CATHODE (IV): $\left(Cu^{++}\right)^{III} + 2e- = Cu^{IV}$

The overall cell reaction is:

$$Cu^I + \left(Cu^{++}\right)^{III} = Cu^{IV} + \left(Cu^{++}\right)^{II}$$

  b. (14 points) Write an expression for the EMF ($\Delta\phi$) of this battery, and show that if the activity coefficient of Cu^{++} ions is independent of Cu^{++} concentration, then this battery generates a non-zero EMF that depends only on the temperature and the concentrations of Cu^{++} in each aqueous phase.

We apply the Nernst equation to this concentration cell:

$$\Delta\phi = -\frac{1}{2F}\Delta\overline{G}_{rxn} = -\frac{1}{2F}\left[\Delta\overline{G}_{rxn,o} + RT\ln\frac{a_{Cu^{++}}^{II}}{a_{Cu^{++}}^{III}}\right]$$

Writing out $\Delta\overline{G}_{rxn,o}$, we find:

$$\Delta\overline{G}_{rxn,o} = \mu_{Cu^{++},o} + \mu_{Cu,o} - \mu_{Cu^{++},o} - \mu_{Cu,o} = 0$$

…the standard states of the components in each half of the battery are the same. This leaves for the EMF:

$$\Delta\phi = -\frac{RT}{2F}\ln\frac{a_{Cu^{++}}^{II}}{a_{Cu^{++}}^{III}} = -\frac{RT}{2F}\ln\frac{\gamma_{Cu^{++}}^{II}X_{Cu^{++}}^{II}}{\gamma_{Cu^{++}}^{III}X_{Cu^{++}}^{III}} = -\frac{RT}{2F}\ln\frac{X_{Cu^{++}}^{II}}{X_{Cu^{++}}^{III}}$$

The last equality is true because the activity coefficients are the same in the two copper solutions if they do not depend on concentration (the only difference between the solutions is the Cu concentration).

3. (8 points) Just as the Gibbs free energy is a smoothly varying function of temperature at constant pressure, the Helmholtz free energy is a smoothly varying function of temperature at constant volume. Draw a qualitative plot of the variation of the Helmholtz free energy of a stable, pure single-component material vs. temperature at constant volume (a simple material that is undergoing no phase transitions). Show why the slope and curvature have the qualitative values you chose. As a reminder, the Helmholtz free energy is defined as:

$$F \equiv U - TS$$

The shape of the F vs. T curve at constant volume is determined by the values of the slope and curvature:

$$slope = \left(\frac{\partial F}{\partial T}\right)_{V,n}$$

$$curvature = \left(\frac{\partial^2 F}{\partial T^2}\right)_{V,n}$$

We first determine the slope:

$$F \equiv U - TS$$

$$dF = dU - TdS - SdT$$

$$dF(T,V) = -PdV - SdT = \left(\frac{\partial F}{\partial V}\right)_T dV + \left(\frac{\partial F}{\partial T}\right)_V dT$$

$$\therefore \left(\frac{\partial F}{\partial T}\right)_V = -S$$

$$\left(\frac{\partial^2 F}{\partial T^2}\right)_V = -\left(\frac{\partial S}{\partial T}\right)_V$$

Because the heat capacity at constant volume is equal to $T\left(\frac{\partial S}{\partial T}\right)_V$, we have the curvature:

$$\left(\frac{\partial^2 F}{\partial T^2}\right)_V = -\left(\frac{\partial S}{\partial T}\right)_V = -\frac{C_V}{T}$$

Since entropy is always positive, the slope of the curve must be negative, and likewise, since C_V and T are always positive, the curvature must be negative. Thus, our Helmholtz free energy curve is a replica of the Gibbs free energy shape: