

3.012 Quiz 1 Thermodynamics Solutions

10.12.05

100 points total

3.012

Fall 2005

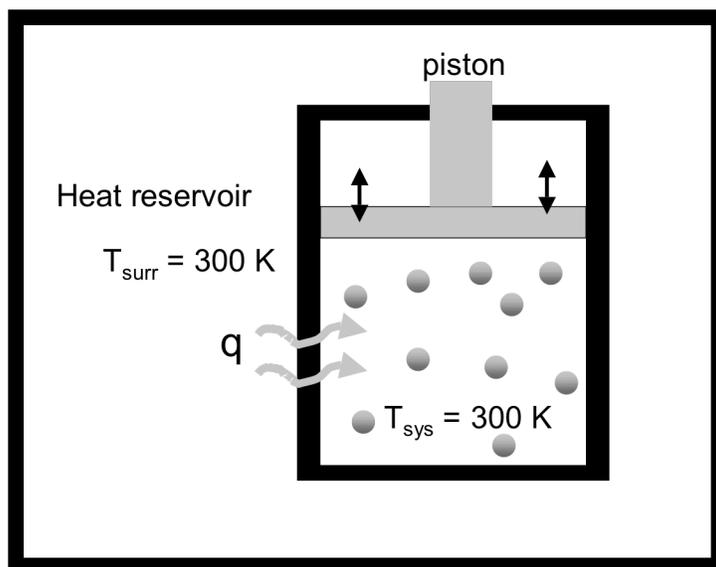
NAME: _____

Physical Constants:

Gas constant: $R = 8.3144 \text{ J/mole-K} = 0.082057 \text{ L-atm/mole-K}$

Thermodynamics. (2 problems, 50 points total).

1. (20 points total) **Analyzing an isothermal process.** Consider the process described schematically below. One mole of an ideal gas is confined in a rigid cylinder in a volume of 1 L by a movable frictionless piston on top; the piston is free to move in response to changes in the system. The system is placed inside a confined heat reservoir, and the combination of the system + the heat reservoir can be considered isolated. The heat reservoir is capable of transferring heat without changing its temperature significantly (think of it as a very large water bath). A quantity of 10 kJ of heat transfers from the heat reservoir into the system. During this process, the temperature of the system and heat reservoir are constant at 300K. Answer the questions below about this process.



- a. (3 points) What is the internal energy change in the gas?

The internal energy of an ideal gas depends only on temperature and the number of molecules. Thus, $\Delta U = 0$ for this isothermal process.

- b. (4 points) What happens to the piston once the heat is absorbed by the gas? Calculate the work done on the piston, and state whether this is work done **on** the gas or work done **by** the gas.

In order to maintain a constant temperature, the heated gas will expand against the piston. We calculate the work that will be done using the first law: Since the internal energy change in the process is zero, we have:

$$\Delta U = 0 = q + w$$
$$\therefore w = -q = -10 \text{ kJ}$$

Since this work is negative, it indicates that work is done by the gas on the piston.

c. (8 points) What is the final state (pressure and volume) of the gas?

The temperature remains constant. The volume change is determined from the calculation of the reversible work:

$$dw = -PdV$$

$$w = -10,000J = -\int_{V_i}^{V_f} PdV = -\int_{V_i}^{V_f} \frac{nRT}{V} dV = -nRT \ln\left(\frac{V_f}{V_i}\right)$$

$$-10,000J = -(1\text{mole})(8.3144 \frac{J}{\text{mole} \cdot K})(300K) \ln\left(\frac{V_f}{1L}\right)$$

$$\therefore V_f = 55.1L$$

The pressure is determined from the ideal gas law:

$$PV = nRT$$

$$P_f = \frac{nRT}{V_f} = \frac{(1\text{mole})(0.082057 \frac{L \cdot atm}{K \cdot mole})(300K)}{(55.1L)} = 0.447atm$$

Note that because of the ideal gas law, the pressure cannot remain constant if the system is isothermal and changing its volume.

d. (5 points) Using the second law, show that this process is reversible.

The second law states that the entropy of the universe does not change in a reversible process. Mathematically:

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surr} = 0$$

For the present isothermal process, the entropy changes are:

$$\Delta S_{system} = \frac{q_{rev}}{T_{system}} = \frac{-w}{T_{system}} = \frac{10,000J}{(300K)} = 33.3 \frac{J}{K}$$

$$\Delta S_{reservoir} = \frac{-q_{rev,system}}{T_{reservoir}} = \frac{-10,000}{300K} = -33.3 \frac{J}{K}$$

$$\therefore \Delta S_{universe} = 0$$

2. (30 points total) **The Thermodynamics of nanoparticle-based cancer therapy.** Recently, a novel anti-cancer therapy has been developed at Rice University, based on the design of nanomaterials that become rapidly superheated in response to illumination with laser light. The therapy is illustrated below: Amorphous silica nanoparticles with diameters of ~ 100 nm are coated with a very thin (~ 10 nm thick) shell of gold. When irradiated by an infrared laser ($\lambda \sim 800$ nm), which passes through normal tissues with almost no absorption, the particles absorb the light and efficiently convert it to heat, and thus are rapidly heated to very high temperatures. This heating response is being exploited to kill tumor cells, by injecting the nanoparticles into a tumor (see the figure), and illuminating for a few minutes with an infrared laser. Normal tissues and tumors are at 37°C , but if tumor cells are heated to $\sim 45^\circ\text{C}$, they are killed.

Let's carry out a simplified thermodynamic analysis of the requirements for this process. Suppose we can approximate a local 1 cm^3 region of tumor and healthy tissue to be isolated from the surrounding tissue and environment outside the body. We inject 100 mg of nanoshells into the tissue and irradiate for 60 seconds with the infrared laser. As a first-order approximation, let's assume the tissue, which is $>70\%$ water, is comprised of pure water. Use the physical data for the system given below to answer the following questions:

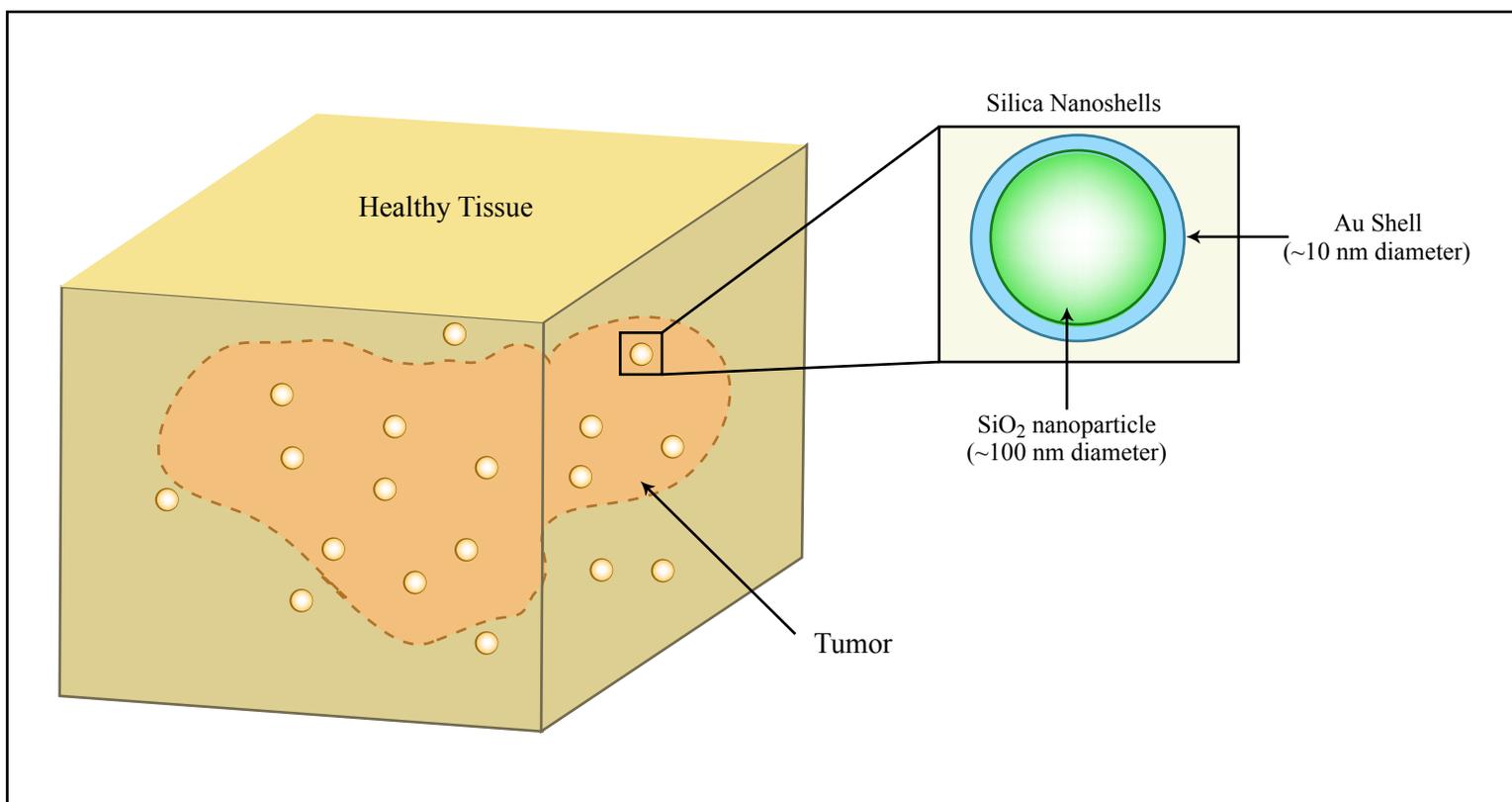


Figure by MIT OCW.

Data for SiO_2 (amorphous solid):

Molecular weight = 60.1 g/mole

Data for H_2O (liquid):

Molecular weight = 18 g/mole

- a. (3 points) What is the implication of assuming that the tissue volume + nanoparticles are an isolated system? Explain in 1-2 sentences.

No heat, work, or mass transfers between the system and its surroundings if the system is isolated.

- b. (15 points) Suppose that the nanoshells are heated quickly enough that no heat transfer between the particles and tissue occurs until after the laser is turned off, i.e., the nanoshells start at some temperature (clearly, greater than 37°C!) induced by the laser, and then exchange heat with the local tissue to reach thermal equilibrium. In order to heat the 1 cm³ region of tissue from its starting temperature of 37°C to 45°C, to what temperature would the nanoshells need to be initially heated by the laser? Neglect the presence of the gold shell for this calculation– consider that the nanoparticles are composed of pure silica.

Once the nanoshells are heated by the laser, they will pass heat into the surrounding tissue until the tissue and particles come to thermal equilibrium. Because the system is isolated, the only heat exchange which can occur is directly between the particles and the tissue. Therefore we state mathematically that any heat leaving the particles enters the surrounding tissue:

$$q_{tissue} = -q_{SiO_2}$$

$$\Delta H_{tissue} = -\Delta H_{SiO_2}$$

We know what final temperature we want the tissue to reach. We are making the approximation that the tissue is just water, which gives us:

$$\int_{310K}^{318K} n_{H_2O} \bar{C}_{p,H_2O} dT = - \int_{T_i}^{318K} n_{SiO_2} \bar{C}_{p,SiO_2} dT$$

$$n_{H_2O} = (1cm^3) \left(\frac{1g}{cm^3} \right) \left(\frac{mole}{18g} \right) = 0.056 moles$$

$$n_{SiO_2} = (0.1g) \left(\frac{mole}{60.1g} \right) = 1.66 \times 10^{-3} moles$$

$$(0.056) \left(75.31 \frac{J}{mole \cdot K} \right) (318 - 310K) = -(1.66 \times 10^{-3} moles) \left(44.5 \frac{J}{mole \cdot K} \right) (318K - T_i)$$

$$T_i = 773K$$

- c. (4 points) Calculate the entropy change in the silica particles during the process of cooling them into thermal equilibrium with the tissue after laser heating.

During the cooling process, we have:

$$\Delta S_{SiO_2} = \int_{773}^{318} n_{SiO_2} \frac{\bar{C}_{p,SiO_2}}{T} dT = (1.66 \times 10^{-3} \text{ moles}) \left(44.5 \frac{J}{\text{mole} \cdot K} \right) \ln \left(\frac{318K}{773K} \right) = -0.066 \frac{J}{K}$$

- d. (4 points) Is your result from part (c) in conflict with the second law? Explain why or why not.

This result is not in conflict with the second law, because the second law only dictates the behavior of the system + surroundings – the entire universe. A decrease in entropy in part of the system is perfectly acceptable in a spontaneous process if it is offset by a larger gain in entropy elsewhere.

- e. (4 points) The nanoshells start at 37°C before laser irradiation, and are then heated to the temperature you determined in part (b) by the laser. Will the volume change in the nanoparticles induced by this heating process be more than 1%? Explain your answer with a calculation. (You may neglect the effect of the gold shell and the surrounding tissue for this estimate- consider the nanoparticles are pure silica and can freely expand against the surrounding tissue).

The volume change for the heating process is:

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

$$\alpha dT = \frac{dV}{V}$$

$$\alpha \Delta T = \ln \left(\frac{V_f}{V_i} \right)$$

$$(1.2 \times 10^{-6} K^{-1})(773 - 310K) = \ln \left(\frac{V_f}{V_i} \right)$$

$$\therefore \frac{V_f}{V_i} = 5.56 \times 10^{-4}$$

...a change of only 0.06%.

Bonding. (2 problems, 50 points total).

1) **Lithium ions [8 questions, a) to h)]:** Lithium is the third element of the periodic table (following hydrogen and helium) and it has 3 protons in the nucleus. We'll discuss in this problem Li^{++} (i.e. the doubly-ionized lithium ion, with only one electron around the nucleus), Li^+ (the singly-ionized lithium, with two electrons around the nucleus), and Li (the neutral ion, with three electrons around the nucleus).

a. What is the stationary Schroedinger equation for the single electron in Li^{++} ?

$$-\frac{\hbar^2}{2m_e} \nabla^2 \psi(\vec{r}) - \frac{3e^2}{4\pi\epsilon_0 r} \psi(\vec{r}) = E \psi(\vec{r})$$

b. What is the ground-state energy for that electron (specify your units) ?

$$E_n \text{ (FOR THE HYDROGENOID SERIES)} = -\frac{Z^2}{n^2} R_y = -9 R_y = -\frac{9}{Z} \text{ a.u.}$$

c. Determine the wavelength of a photon that is able to excite that electron from the ground state to the first excited state (you can use the International System for the units of measure, given below, or atomic units – in atomic units the speed of light c is 137.036, Planck's constant $\hbar=1$, Bohr radius is 1, and the mass of the electron is 1).

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

$$\Delta E = E_{\text{FINAL}} - E_{\text{INITIAL}} = -\frac{9}{4} R_y - (-9 R_y) = 6.75 R_y = 3.375 \text{ a.u.}$$

$$\lambda = \frac{hc}{\Delta E} = \frac{2\pi \cdot 137.036}{3.375} = 255.12 \text{ a.u.} = (255.12 \cdot 0.529177 \cdot 10^{-10}) \text{ m} = 1.35 \cdot 10^{-8} \text{ m}$$

- d. Now let's consider Li^+ . The Li^+ ion has two electrons, exactly as neutral Helium. Which will be the largest atom, Li^+ or He? Explain why.

He WILL BE LARGER THAN Li^+ .

IN Li^+ THE 3 PROTONS ATTRACT THE 2 ELECTRONS CLOSER TO THE NUCLEUS.

- e. The two electrons in Li^+ will screen and repel each other. How can we write two one-particle Schrodinger equations (also called the Hartree equations) that take into account self-consistently this mutual screening? Can you explain what are the differences with the single equation you wrote in point a.?

THE SCHR. EQ. FOR ELECTRON 1 WILL INCLUDE THE REPULSION FROM ELECTRON 2, AND VICEVERSA:

$$1) -\frac{\hbar^2}{2m} \nabla^2 \psi_1 - \frac{3e^2}{4\pi\epsilon_0 r} \psi_1 + \frac{e^2}{4\pi\epsilon_0} \int \frac{|\psi_2(\vec{r}')|^2}{|\vec{r}-\vec{r}'|} d\vec{r}' = E \psi_1$$

$$2) -\frac{\hbar^2}{2m} \nabla^2 \psi_2 - \frac{3e^2}{4\pi\epsilon_0 r} \psi_2 + \frac{e^2}{4\pi\epsilon_0} \int \frac{|\psi_1(\vec{r}')|^2}{|\vec{r}-\vec{r}'|} d\vec{r}' = E \psi_2$$

THIS IS THE ADDITIONAL, SCREENING TERM

1) AND 2) MUST BE ITERATED (I.E. SOLVED ITERATIVELY) TO SELF CONSISTENCY

- f. Finally, let's suppose we add an electron to Li^+ . What will be the potential that this electron feels when it is very far away from the ion?

VERY FAR AWAY THE ELECTRON WILL SEE ONE POSITIVE CHARGE (3 PROTONS + 2 ELECTRONS)

$$V(\vec{r}) = -\frac{e^2}{4\pi\epsilon_0 r}$$

- g. Once this third electron reaches the lowest energy level available to him, where will it be? Specify the quantum numbers n, l, m . Why doesn't it go into a $1s$ level?

IT WILL GO INTO A $2s$ STATE:

$$n=2, l=0, m=0, m_s = \pm \frac{1}{2}$$

THE STATES WITH $(1, 0, 0, \frac{1}{2})$ AND $(1, 0, 0, -\frac{1}{2})$ ARE ALREADY FILLED, AND SO BY PAULI PRINCIPLE IT NEEDS TO GO INTO $2s$.

- h. The ionization potential of hydrogen is 0.5 Hartree = 1 Rydberg = 13.6 eV; this is the energy needed to strip away an electron from hydrogen. Will the ionization potential of Li (i.e. the energy needed to remove the third electron, in order to obtain Li^+) be greater, smaller, or equal to the case of hydrogen? Explain why.

THE I.P. FOR Li WILL BE SMALLER.

WHILE THE $2s$ ELECTRON FEELS 3 PROTONS ONLY PARTIALLY SCREENED BY TWO ELECTRONS, IT IS ALSO (DUE TO "REPULSIVE" ORTHOGONALITY FROM $1s$) IN THE $2s$ STATE, MUCH LESS BOUND THAN THE $1s$, AND THIS LAST EFFECT WINS.

- 2) **The scanning tunneling microscope [5 questions, a) to e)]:** A fairly accurate picture of the potential at the surface of a metal is given below – an electron with an energy between 0 and V_0 would be classically confined to the left side.

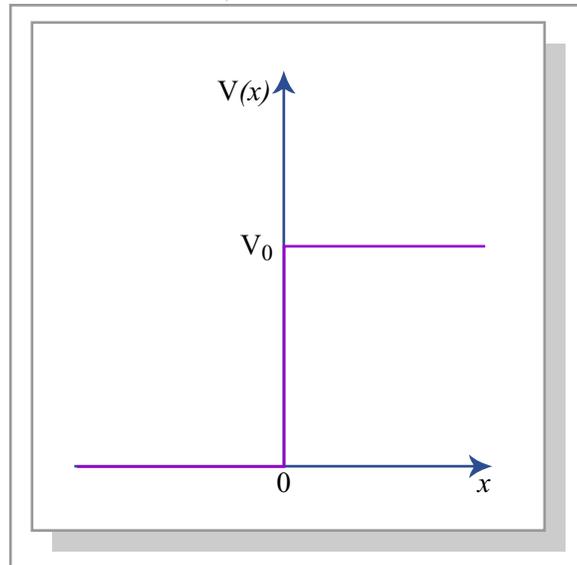


Figure by MIT OCW.

- a. Write out the Schroedinger equation for this one-dimensional case, both for $x < 0$ and for $x > 0$.

$$x < 0 : -\frac{\hbar^2}{2m} \nabla^2 \psi(x) = E \psi(x)$$

$$x > 0 : -\frac{\hbar^2}{2m} \nabla^2 \psi(x) + V_0 \psi(x) = E \psi(x)$$

- b. What are the eigenfunctions of the Schroedinger equation on the left side, for eigenvalues E that are between 0 and V_0 ? What are the eigenfunctions of the Schroedinger equation on the right side, for eigenvalues E that are between 0 and V_0 ? Discuss this analytically, not graphically.

$$x < 0 : A \sin kx + B \cos kx, \text{ OR EQUIVALENTLY } A e^{ikx} + B e^{-ikx}, \text{ ARE THE EIGENFUNCTIONS}$$

$$x > 0 : \underbrace{A e^{kx}}_{\text{THIS DIVERGES AT } x \rightarrow \infty; \text{ UNPHYSICAL}} + B e^{-kx} \quad k = \frac{1}{\hbar} \sqrt{(V_0 - E) 2m}$$

- c. Draw in the graph below an eigenfunction corresponding to an eigenvalue E somewhere between 0 and V_0 (draw it so that it covers all the interval $-\infty < x < \infty$ and is continuous at $x=0$)

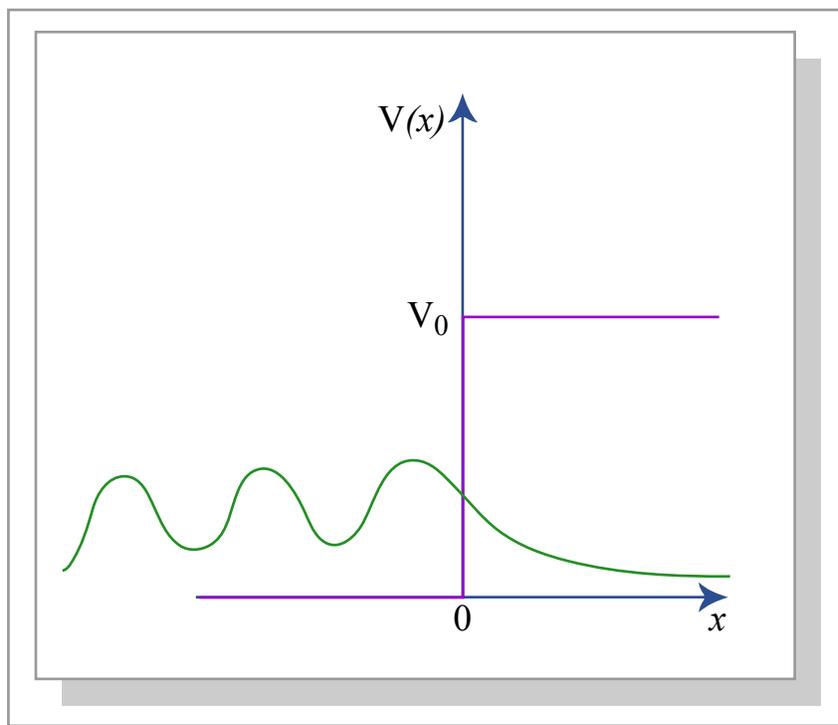


Figure by MIT OCW.

- d. Explain how the scanning tunneling microscope works, and how it relates to the picture above.

THE SHARP TIP OF THE STM PICKS UP THE ELECTRONS FROM THE SURFACE WITH A PROBABILITY (I.E. CURRENT) THAT CHANGES EXPONENTIALLY WITH THE DISTANCE FROM $x=0$. THE ELECTRON HAS A FINITE (BUT DECAYING) PROBABILITY OF TUNNELING BEYOND THE BARRIER AT $x=c$

- e. What would happen if V_0 were to become larger and larger?

$$k = \frac{1}{\hbar} \sqrt{(V_0 - E) 2m} \quad \text{WOULD BECOME LARGER,}$$

I.E. THE EXPONENTIAL TAIL OF THE WAVE FUNCTION WOULD DECAY FASTER.

$V_0 \rightarrow +\infty$, ELECTRON CONFINED $x < 0$