Problem Set 4B (due 9PM Monday , 1/30/12)
Consider these Practice Problems for the Exam Monday
See the last page for the Cover page to the Fist Exam Monday

Q1). Define Euler's Criterion for Exactness. Explain how this rule is relevant to the field of thermodynamics. Cite one example.

Q2) Explain the concept of reversibility as it applies to thermodynamic pathways.

Q3) An ideal monatomic gas with initial temperature T_1 expands adiabatically into a vacuum thereby doubling its volume. Student A predicts that the change in the gas temperature is $\Delta T = T_1\left(2^{-2/3}-1\right)$ while Student B predicts that ΔT=0. Explain each student's reasoning. Which student is correct? Justify your answer.

Q4) . The van der Waals equation of state is $\left(P+\frac{an^2}{V^2}\right)(V-nb)=nRT$. The parameter a is due to attractive forces between molecules of the gas. The parameter b is due to repulsive forces, and represents the amount of the total volume that is occupied by a mole of gas molecules. In the internal energy equation $dU=\left(\frac{\partial U}{\partial T}\right)_V dT+\left(\frac{\partial U}{\partial V}\right)_T dV$, where $\left(\frac{\partial U}{\partial V}\right)_T=\frac{an^2}{V^2}$ for a van der Waals gas. Explain why $\left(\frac{\partial U}{\partial V}\right)_T$ depends on a, but does not depend on b.

4a) Show by calculation (using the T.EoS.) that this the above identities are correct.

4b) Explain by physical reasoning involving the meanings of a and b that this should be correct.

Q5) The Principal of Equipartition states that for every degree of mechanical freedom possessed by a molecule a factor of R/2 is contributed to the heat capacity C_V, where R is the universal gas constant, i.e. R=8.314 $JK^{-1}mol^{-1}$. Therefore, a monatomic gas with three degrees of translational freedom has C_V=3R/2, while a diatomic gas with has seven degrees of freedom and therefore has a heat capacity of C_V=7R/2. Consider the table of heat capacities C_P at T=298.15K taken from the back of your text:

Gas	Helium	Nitrogen	Oxygen	Neon	Hydrogen	Argon
C_P ($JK^{-1}mol^{-1}$	20.79	29.13	29.38	20.79	28.84	20.79

Which of these gases has a heat capacity that is predicted by the Principle of Equipartition? Explain your reasoning and account for any discrepancies. Assume the gases behave ideally.

Q6) Calculate q, w, ΔU and ΔH if one mole of an ideal monatomic gas initially at T=400K and P=1 atm expands adiabatically and reversibly until P=0.5 atm

Q7). For water at T=300K and P=1 Bar, The heat capacity $C_P = 75.3\text{JK}^{-1}\text{mol}^{-1}$, the coefficient of thermal expansion $\beta = 3.04\times10^{-4}K^{-1}$ and the isothermal compressibility $\kappa = 4.46\times10^{-10}m^2N^{-1}$. At T=300K the molar volume of water is $V_m = 18.1\times10^{-6}\text{m}^3\text{mol}^{-1}$. Calculate these three quantities for water at T=300K and P=1atm :

1) C_V

2) $\left(\frac{\partial U}{\partial V}\right)_T$

3) $\left(\frac{\partial H}{\partial P}\right)_T$

Q8) Consider a Hookean spring, with spring constant, k, that has mass m on it that extends it to length ℓ from the fully relaxed length. In the first step (from state 1 to state 2), a mass of $M = 2m$ is added to the mass on the spring.

a) How much work does the environment do on the spring to extend the spring?

b) How much heat is transferred?

c) What is the minimum amount of work needed to extend the spring the same distance?

d) Now in step 2, from state 2 back to state 1, the extra mass (mass $M = 2m$) is removed from the spring, and the spring returns to its original extension length ℓ, how much work did the spring do?

e) Verify for these two transformations that the reversible work and the irreversible work are related as $w_{rev} \le w_{Irr}$

f) What do texts (and people) mean when they say your get more work from a system doing the work reversibly when the above inequality looks like just the opposite?

Q9) Compare reversible isothermal work with reversible adiabatic work. Assume both processes begin at the same state 1, $P_1V_1 = nRT_1$ for both processes. In both cases assume the work stops when the pressure of the state 2 is $P_2 = \frac{1}{3}P_1$, for an ideal monatomic gas.

a) Find the ratio of $\frac{w_{rev}^{Adiabatic}}{w_{rev}^{Isothermal}}$ and explain how this shows which process generates more work.

b) What is the physical basis for the one type of reversible work being able to do more work than the other over the same pressure interval?

Useful information and equations:

Law IA: $\Delta U = q + w$

Law IB:
$U = U(T, V)$

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

$H = U + PV$

Heat Capacity

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P$$

Work:

$w = -P_{ext} dV$

$w = mgh = F_g h$

$g = 10 \text{ m/sec}^2$

$w = VIdt$

Kinetic Energy: $\varepsilon = \dfrac{mv^2}{2}$

Isothermal Reversible work:

$$w = -nRT \ln\left(\frac{V_f}{V_i}\right)$$

$PV = Const$

Adiabatic Reversible work: $w = -PdV$

$$P\left(V^{\gamma}\right) = Const; \quad \text{where } \gamma = \frac{C_{P,m}}{C_{V,m}}$$

Thermodynamic Equations of State

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P$$

Hook's law spring:

$F_s = k_s \ell \qquad E = \frac{1}{2} k_s \ell^2$

I.G. EoS (and other IG relations)

$PV_m = RT$

$\Delta U = C_V \Delta T$

Van der Waals gas EoS

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^{\ 2}}$$

Cyclic rule:

$$\left(\frac{dx}{dy}\right)_z \left(\frac{dz}{dx}\right)_y \left(\frac{dy}{dz}\right)_x = -1$$

Calculus Rules:

$$\frac{d(yz)}{dx} = z\frac{d(y)}{dx} + y\frac{d(z)}{dx}$$

$$\frac{dx}{dz} = \frac{dy}{dz}\frac{dx}{dy}$$

$$\Delta Z = \int_{x_i}^{x_f} \left(\frac{\partial Z}{\partial x}\right)_y dx$$

Gas Constant:

$R = 8.3 J / mol - K$

$R = 0.082 L - Atm / mol - K$

$R \cdot 300K = 2.5 kJ / mol$

$100J \approx 1L - Atm$

$1Atm \approx 1bar = 10^5 \, Pa$

$T(K) = T(C) + 273.15$

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

$N = 6.022 \cdot 10^{23} \, molecules/mole$

The mean is often quite low on these exams. If you are having difficulty, don't freak out.
Many parts of problems can be done independently, so if you get stuck, see if you can do another section.
The questions are not arranged in order of difficulty.
Show your work throughout, always write down the equations you are using before substituting in numerical values and always show units for computed quantities. Show the analytical results of derivatives and integrals before substituting numbers. You do not need to compute the final number if you do not want to but show where the numbers you are given can be used.