

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

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

A differential, $M(x, y)dx + N(x, y)dy$ is exact if there exist a function $Z(x, y)$ such that

$$dZ = \left(\frac{\partial Z}{\partial x} \right)_y dx + \left(\frac{\partial Z}{\partial y} \right)_x dy = M(x, y)dx + N(x, y)dy .$$

The criterion for exactness is

therefore $\frac{\partial M}{\partial y} = \frac{\partial N}{\partial x} = \frac{\partial^2 Z}{\partial x \partial y}$. The path integrals of exact differentials are dependent only

on the initial and final states of the path, not on the details of the path itself. Differentials of state functions are exact so when integrated over specific paths, the state function change is dependent only on the definitions of the initial and final states. Lots of examples; the coolest one is to show the dependence of the heat capacity (C_v) on volume.

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

For now reversibility means that all changes from one state to the next are infinitesimal and incremental. At any point in a multistep process the change can be done in either direction and with an infinitesimal amount of work or heat or energy or any such combination of the three. In practice, for our purposes the internal pressure of a gas is always equal to (or infinitesimally different from) the external pressure. For the springs the change in length is done by adding or removing infinitesimally small masses.

Later we will discuss: The equations of mechanics ($F=Ma$) are time reversible. This means they are as valid going forward in time as going backwards. In contrast, the entropy of an isolated system increases from initial to final state, or remains the same. The final state is understood to be reached later in time, so moving toward the final state is marked by increased entropy. The reversal of mechanics in an isolated system, which in turn would decrease the entropy is not impossible, but is nevertheless a highly improbable event.

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 $\Delta T = T_1 (2^{-2/3} - 1)$ while Student B predicts that $\Delta T=0$. Explain each student's reasoning. Which student is correct? Justify your answer.

Answer: The ideal gas expands adiabatically into a vacuum. Adiabatic so $q=0$. If it expands into a vacuum no work is done because $P_{\text{ext}}=0$. Therefore, $\Delta U = nC_V\Delta T = q + w = 0$. Therefore $\Delta T=0$. Student B is correct. Student A assumes incorrectly that the expansion is reversible and adiabatic. Student A uses the relationship: $\left(\frac{T_2}{T_1}\right)^{C_V} = \left(\frac{V_1}{V_2}\right)^R = \left(\frac{1}{2}\right)^R$ which is derived in turn from $dU = nC_V dT = PdV$ and the ideal gas law $P=RT/V$. But the work is zero, so Student A has used the wrong equation to describe an irreversible expansion accompanied by no work.

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.

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

$$T\left(\frac{\partial P}{\partial T}\right)_V = \frac{RT}{V_m - b}$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P = \frac{RT}{V_m - b} - \left\{\frac{RT}{V_m - b} - \frac{a}{V_m^2}\right\}$$

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

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

The parameter b represents the excluded volume of one mole of gas. Therefore the free volume is $V-b$. If the free volume changes we have $\Delta V = V_2 - b - (V_1 - b) = V_2 - V_1$. This means that the excluded volume is a constant and when you calculate the change ΔU with a volume change ΔV the excluded volume correction cancels. On the other hand a volume change will change internuclear interactions parameterized by a . Therefore

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{an^2}{V^2} \text{ and there is no dependence on } b.$$

Q5) The Principle 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. $R=8.314 \text{ JK}^{-1}\text{mol}^{-1}$. 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 $T=298.15\text{K}$ taken from the back of your text:

Gas	Helium	Nitrogen	Oxygen	Neon	Hydrogen	Argon
$C_P (\text{JK}^{-1}\text{mol}^{-1})$	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.

Answer: He, Ne, and Ar are monatomic gases and their molar heat capacities are all $C_V = C_P - R = 20.79 \text{ JK}^{-1}\text{mol}^{-1} - 8.31 \text{ JK}^{-1}\text{mol}^{-1} = 12.48 \text{ JK}^{-1}\text{mol}^{-1} \approx 3R/2$

The monatomic gases therefore obey the equipartition principle.

Nitrogen, oxygen and hydrogen are diatomic gases and their heat capacities are

$$C_V = C_P - R = 29.00 \pm 0.4 \text{ JK}^{-1}\text{mol}^{-1} - 8.31 \text{ JK}^{-1}\text{mol}^{-1} = 20.69 \pm 0.4 \text{ JK}^{-1}\text{mol}^{-1} \approx 5R/2$$

The diatomic gases have heat capacities about R less than predicted by the equipartition principle. This results because at $T=298\text{K}$ the two vibrational degrees of freedom do not absorb heat and so the vibrational heat capacity is zero instead of R . If you included this in your reasoning, that is fine too, and note that with this understanding even the diatomic gasses are indeed obeying equipartition but not populating vibronic levels because they are too high in energy.

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

$$\left(\frac{T_2}{T_1}\right)^{\frac{C_V}{R}} = \left(\frac{P_2}{P_1}\right) \rightarrow T_2 = T_1 \left(\frac{P_2}{P_1}\right)^{nR/C_P} = (400\text{K}) \left(\frac{0.5}{1.0}\right)^{2/5} = 303\text{K}$$

$$\therefore \Delta U = w = nC_V\Delta T = (1) \left(\frac{3}{2}\right) (8.31 \text{ JK}^{-1}\text{mol}^{-1}) (303\text{K} - 400\text{K}) = -1.2 \text{ kJ}$$

$$\therefore \Delta H = nC_P\Delta T = (1) \left(\frac{3}{2} + 1\right) (8.31 \text{ JK}^{-1}\text{mol}^{-1}) (303\text{K} - 400\text{K}) = -2.0 \text{ kJ}$$

$$q = q_{rev} = 0$$

Q7). For water at $T=300\text{K}$ and $P=1 \text{ Bar}$, The heat capacity $C_p = 75.3 \text{ JK}^{-1}\text{mol}^{-1}$, the coefficient of thermal expansion $\beta = 3.04 \times 10^{-4} \text{ K}^{-1}$ and the isothermal compressibility

$\kappa = 4.46 \times 10^{-10} \text{ m}^2 \text{ N}^{-1}$. At $T=300\text{K}$ the molar volume of water is $V_m = 18.1 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$. Calculate these three quantities for water at $T=300\text{K}$ and $P=1\text{atm}$:

1) C_V

$$C_p - C_v = T \left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial V}{\partial T} \right)_P = -T \left(\frac{\partial P}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P^2 = TV \frac{\beta^2}{\kappa}$$

$$\therefore C_v = C_p - TV \frac{\beta^2}{\kappa} = 75.3 \text{ JK}^{-1} \text{ mol}^{-1} - (300\text{K}) (18.1 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}) \frac{(3.04 \times 10^{-4} \text{ K}^{-1})^2}{4.46 \times 10^{-10} \text{ m}^2 \text{ N}^{-1}} = 74.17 \text{ JK}^{-1} \text{ mol}^{-1}$$

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

$$\left(\frac{\partial U}{\partial V} \right)_V = \frac{\beta}{\kappa} T - P = \frac{3.04 \times 10^{-4} \text{ K}^{-1}}{4.46 \times 10^{-10} \text{ m}^2 \text{ N}^{-1}} (300\text{K}) - 101325 \text{ Pa} = 2.04 \times 10^8 \text{ Pa} - 1.01 \times 10^5 \text{ Pa} \approx 2.04 \times 10^8 \text{ Pa}$$

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

$$\begin{aligned} \left(\frac{\partial H}{\partial P} \right)_V &= -TV\beta + V = -(300\text{K})(18.1 \times 10^{-6} \text{ m}^3)(3.04 \times 10^{-4} \text{ K}^{-1}) + 18.1 \times 10^{-6} \text{ m}^3 \\ &= (18.1 \times 10^{-6} \text{ m}^3)(1 - 0.09) = 16.44 \times 10^{-6} \text{ m}^3 \end{aligned}$$

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?

$$mg = kl \quad \text{or} \quad 3mg = k3l$$

$$w = Fdh = 3mg * 2l = 6mgl = 6(kl^2)$$

b) How much heat is transferred?

$$\Delta E = q + w$$

$$+4(kl^2) = q + 6(kl^2)$$

$$q = -2(kl^2)$$

The system wasted work and so 2 units of energy were discarded as heat, out to the environment (The process is exothermic).

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

The minimum work is the reversible work, which is the energy stored in the system

$$w_{\text{reversible}} = \Delta E = \frac{1}{2}k(3l)^2 - \frac{1}{2}k(l)^2 = +4(kl^2)$$

- 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?

$$mg = kl \quad \text{or} \quad 3mg = k3l$$

$$w = F \cdot dh = mg \cdot (-2l) = -2mgl = -2(kl^2)$$

- e) Verify for these two transformations that the reversible work and the irreversible work are related as $w_{\text{rev}} \leq w_{\text{irr}}$

For expansion or extension the environment did 6 units of work vs 4 units for the reversible case, and for compression (or relaxation) the system did -2 units of work vs the reversible case where it would do -4 units. In the extension case the $4 < 6$, and the compression case $-4 < -2$. So in both cases $w_{\text{rev}} < w_{\text{irr}}$.

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

You get work out of a machine only when it does work, and then the work is negative, so the case where $-4 < -2$ applies, and the system would have done -4 units of work reversibly but did only -2 units of work, so the system did less work. Or in other mathematical words $|-4| > |-2|$ shows the reversible process gives more work than the irreversible process.

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 $\frac{w_{\text{rev}}^{\text{Adiabatic}}}{w_{\text{rev}}^{\text{Isothermal}}}$ and explain how this shows which process generates more work.

$$w_{rev}^{Isothermal} \quad \Delta T = 0$$

$$w = -\int P dV \quad n = -nRT \ln\left(\frac{V_2}{V_1}\right) = +nRT_1 \ln\left(\frac{P_2}{P_1}\right) = -nRT_1 \ln 3$$

$$w = -nRT_1 \cdot 1.1$$

$$w_{rev}^{Adiabatic} \quad q = 0$$

$$w = \Delta U = C_V \Delta T = \frac{3}{2} nRT_1 \left(\frac{T_2}{T_1} - 1\right)$$

$$C_V dT = -nR \frac{T}{V} dV \quad c = \frac{3}{2} \frac{C_V}{nR} = \frac{3}{2}$$

$$c \frac{dT}{T} = \frac{dV}{V} \Rightarrow c \ln\left(\frac{T_2}{T_1}\right) = -\ln\left(\frac{V_2}{V_1}\right) = -\ln\left(\frac{T_2 P_1}{T_1 P_2}\right)$$

$$(c+1) \ln\left(\frac{T_2}{T_1}\right) = -\ln(3) \Rightarrow \left(\frac{T_2}{T_1}\right) = \left(\frac{1}{3}\right)^{\frac{2}{5}} = 0.6444$$

$$w = \frac{3}{2} nRT_1 (0.6444 - 1) = -nRT_1 \cdot 0.533$$

Having done each problem separately the ratio is about 1/2

$$\frac{w_{rev}^{Adiabatic}}{w_{rev}^{Isothermal}} = 0.49$$

- 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?

So for this example the adiabatic work is only about 1/2 that of the isothermal work. This happens because adiabatic work can only be done at the expense of the internal energy of the gas. The gas temperature must drop to do the work. However the isothermal gas the internal energy of the gas does not get used to do the work. The work is done through energy taken from the surroundings and that temperature does not drop. So of course the system can do more work for the same pressure ratio. In the isothermal case the volume

expansion ratio is directly proportional to the pressure drop: $\left(\frac{V_2}{V_1}\right) = \left(\frac{P_1}{P_2}\right) = 3$. So the

mass is lifted $\Delta V = 2V_1$. But in the adiabatic case, the volume ratio is not as large

because $\left(\frac{V_2}{V_1}\right) = \left(\frac{P_1}{P_2}\right) \cdot \left(\frac{T_2}{T_1}\right) = 3 \cdot 0.644$ or $\Delta V = (3 \cdot 0.644 - 1)V_1 = 0.933V_1$, so the volume

expansion for the adiabatic case is 1/2 of the isothermal value, so the work is approximately the same proportion (and this is approximate, because it does not take into account the integral nature of the work).

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:

$w = -P_{ext} dV$

$w = mgh = F_g h$

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

$w = VI dt$

Kinetic Energy: $\mathcal{E} = \frac{mv^2}{2}$

Isothermal Reversible work:

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

$PV = \text{Const}$

Adiabatic Reversible work: $w = -PdV$

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

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:

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

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:

$R = 8.3 \text{ J / mol} - \text{K}$

$R = 0.082 \text{ L} - \text{Atm / mol} - \text{K}$

$R \cdot 300 \text{ K} = 2.5 \text{ kJ / mol}$

$100 \text{ J} \approx 1 \text{ L} - \text{Atm}$

$1 \text{ Atm} \approx 1 \text{ bar} = 10^5 \text{ Pa}$

$T(\text{K}) = T(\text{C}) + 273.15$

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

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

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

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.