

Enter Name, student ID, course (452 or 456) and answers in a Blue Book

**Useful Constants:**

- 1 Newton=1 N= 1 kg m s<sup>-2</sup>
- 1 Joule=1J=1 N m=1 kgm<sup>2</sup>/s<sup>2</sup>
- 1 Pascal=1Pa=1N m<sup>-2</sup>
- 1atm=101325 Pa
- 1L=0.001m<sup>3</sup>
- Universal Gas Constant R=8.31 J K<sup>-1</sup> mol<sup>-1</sup>=0.0821L atm K<sup>-1</sup>mol<sup>-1</sup>
- Avagadro's Number N<sub>A</sub>=6.024x10<sup>23</sup> mol<sup>-1</sup>

All answers must be in MKS units (i.e. units of meters, seconds, kilograms, Joules, Pascals etc.)

Helpful math relationships:

1)  $\frac{dax^n}{dx} = anx^{n-1}$ ; a is a constant, n is a positive or negative number

2)  $\int x^n dx = \frac{x^{n+1}}{n+1} dx + c$  where c is a constant and  $n \neq -1$

3)  $\int \frac{dx}{x} = \ln x + c$  where c is a constant

4)  $\ln(xy) = \ln x + \ln y$ ;  $\ln\left(\frac{x}{y}\right) = \ln x - \ln y$ ;  $x \ln y = \ln y^x$

**Part 1 (18 points) Answer THREE out of the following SIX questions. Limit definitions to less than 200 words. Use equations where helpful or required, but detailed calculations are not necessary.**

**Question 1.1.** Define Euler's Criterion for Exactness. Explain how this rule is relevant to the field of thermodynamics.

**Question 1.2.** The entropy has been defined as "time's arrow". Explain this definition using thermodynamic reasoning. Utilize in your argument the statistical interpretation of entropy  $S=k_B \ln W$ .

**Question 1.3** An ideal gas expands isothermally into a vacuum. Which of the following are zero or non-zero: q, w,  $\Delta U$ ,  $\Delta S$ . Explain.

**Question 1.4** Explain the concept of reversibility as it applies to thermodynamic pathways.

**Question 1.5:** Assume a protein denatures with a melting temperature of  $T_m=330\text{K}$ .

Sketch the differential scanning calorimetry data i.e.  $\frac{dq_p}{dT}$  vs.  $T$  starting with a temperature  $T_1 \ll 330\text{K}$  to a temperature  $T_2 \gg 330\text{K}$ . Indicate the regions of the data where the structured form N is most stable, where the unstructured form D is most stable and where the D and N forms are in 1:1 equilibrium. Explain the appearance of the data.

**Question 1.6:** Explain why the entropy is defined as  $\Delta S = \frac{q_{rev}}{T}$ . Why must the  $q$  be

transferred reversibly. You can show equations in your explanation. You do not have to do numerical calculations.

**Part 2: (20 points) Answer TWO of the FOUR questions. Answers longer than 200 words are acceptable. Equations may be used to illustrate your points but numerical calculations are not required. Physical reasoning based on thermodynamic principles is recommended.**

**Problem 2.1** In the days before the invention of permanent press fabrics and electric irons, clothing was pressed using flat iron plates with wooden handles. These original “irons” were heated to moderate temperature to avoid scorching the clothing. These irons were extremely heavy, even though it was known at the time that the heat, not the weight of the iron is what smoothed out the clothing. Explain why irons were made so heavy.

**Problem 2.2** 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.

**Problem 2.3.** 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  $b$ . Hint: This can be answered with a calculation but physical reasoning involving the meanings of  $a$  and  $b$  can also be used.

**Problem 2.4** 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.  $R=8.314 \text{ JK}^{-1}\text{mol}^{-1}$ . There is an old rule or “guideline” called the Law of Dulong and Petit that states that the heat capacity  $C_V$  of an

atomic crystal (e.g. Cu or Fe) approached 3r at high temperature. Using the Principle of Equipartition, explain the Law of Dulong and Petit.

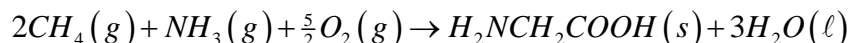
**Part 3 (30 points) Answer TWO of the following FOUR questions.**

**Problem 3.1** Calculate  $q$ ,  $w$ ,  $\Delta U$  and  $\Delta S$  if one mole of an ideal monatomic gas initially at  $T=400\text{K}$  and  $P=1\text{ atm}$  expands adiabatically and reversibly until  $P=0.5\text{ atm}$

**Problem 3.2)** The molar heat capacity at constant pressure (units of  $\text{JK}^{-1}\text{mol}^{-1}$ ) for a certain gas is given by  $C_p = 22.66 + 4.381 \times 10^{-2} \frac{T}{\text{K}} - 1.0835 \times 10^{-4} \frac{T^2}{\text{K}^2}$ . If the gas increases its temperature from  $100\text{K}$  to  $500\text{K}$  at constant pressure, calculate the molar enthalpy change of the gas.

**Problem 3.3** In this problem, you can chose which two out of three derivatives to evaluate. For water at  $T=300\text{K}$  and  $P=1\text{ atm}$ , 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 one of the following three quantities for water at  $T=300\text{K}$  and  $P=1\text{atm}$ : 1)  $C_v$ ; 2)  $\left(\frac{\partial U}{\partial V}\right)_T$ ; 3)  $\left(\frac{\partial H}{\partial P}\right)_T$ .

**Problem 3.4** The amino acid glycine is produced in bacteria by the reaction of ammonia and methane:



The table below shows entropy values at for  $T=298\text{K}$  and heat capacity values for each reaction component.

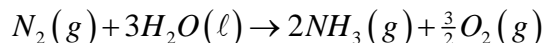
Substance	$\Delta H_f^0$ ( $\text{kJmol}^{-1}$ )	$C_p^0$ ( $\text{JK}^{-1}\text{mol}^{-1}$ )
$\text{CH}_4(g)$	-74.6	35.7
$\text{NH}_3(g)$	-45.9	35.1
$\text{O}_2(g)$		29.4
$\text{H}_2\text{O}(g)$	-285.8	75.3
glycine (s)	-537.2	99.2

Calculate the enthalpy change for this reaction at  $T=310\text{K}$ . Assume all heat capacities are constant between  $298\text{K}$  and  $310\text{K}$ .

**Part 4 (32 points) Perform ONE out of the TWO multi-step calculations**

**Problem 4.1** Nitrogen is necessary in organisms for the synthesis of proteins and nucleic acids. Even though nitrogen is abundant in earth's atmosphere as  $\text{N}_2$  gas, the diatomic gas

cannot be metabolized by most organisms. Only a few types of nitrifying bacteria can convert  $N_2$  to nitrogen-containing compounds that can be metabolized by plants and animals. Such compounds are called “fixed nitrogen” compounds. The simplest form of fixed nitrogen is ammonia  $NH_3$ . A possible synthesis of ammonia in bacteria is the following hydrolysis mechanism:



Substance	$S_f^0 (JK^{-1}mol^{-1})$	$C_p^0 (JK^{-1}mol^{-1})$
$N_2(g)$	191.6	29.1
$O_2(g)$	205.2	29.4
$H_2O(g)$	70.0	75.3
$NH_3(g)$	192.8	35.1

Calculate at  $T=330K$ : a) the entropy change for the production of ammonia in bacteria, b) the entropy change of the surroundings, and c) the entropy change of the universe. Assume all heat capacities are constant between  $T=298K$  and  $T=330K$ .

**Problem 4.2** 18 grams of water ice at 230 K are placed in thermal contact with a large heating block maintained at a temperature of 350 K. Calculate the entropy change  $\Delta S$ , the enthalpy change  $\Delta H$  of the water, when 18 grams of water ice at 230 K are converted to liquid water at 350K. Also calculate the entropy change of the heating block as a result of this process and the entropy change of the universe as a result of this process. For ice  $C_p=37.7 J/K$ . For liquid water  $C_p=75 J/K$ . For water  $\Delta H_{fusion}=6.01 kJ/mole$ . Assume the density of ice is 0.92 gm/mL and approximately constant between 230K and 273K. The density of liquid water is 1 gm/mL at 273K and approximately constant up to 350K. Assume only P-V work occurs. The external pressure is 1 atm.