

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

Useful Constants:

- 1 Newton=1 N= 1 kg m s⁻²
- 1 Joule=1J=1 N m=1 kgm²/s²
- 1 Pascal=1Pa=1N m⁻²
- 1atm=101325 Pa
- 1L=0.001m³
- Universal Gas Constant R=8.31 J K⁻¹ mol⁻¹=0.0821L atm K⁻¹mol⁻¹
- Avagadro's Number N_A=6.024x10²³ mol⁻¹

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.

Answer: 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.

(74 words)

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 $S=k_B \ln W$.

Answer: For a system at equilibrium the equations of mechanics ($F=Ma$) are time reversible. The motions of gas molecules at equilibrium have no preferred direction. In contrast, the entropy of an isolated system increases from initial to final state as the system increases the number of microstates W . The direction forward in time for an irreversible process is the direction that produces an entropy increase.

Question 1.3 An ideal gas expands isothermally into a vacuum. Which of the following are zero or non-zero: q , w , ΔU , ΔS . Explain.

Answer: Because the expansion process is isothermal $\Delta U=0$. Expansion into a vacuum does no work because $P_{\text{ext}}=0$. Then $q=-w=0$. But expansion into a vacuum is irreversible to $q_{\text{irrev}}=0$. Therefore $\Delta S>0$.

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

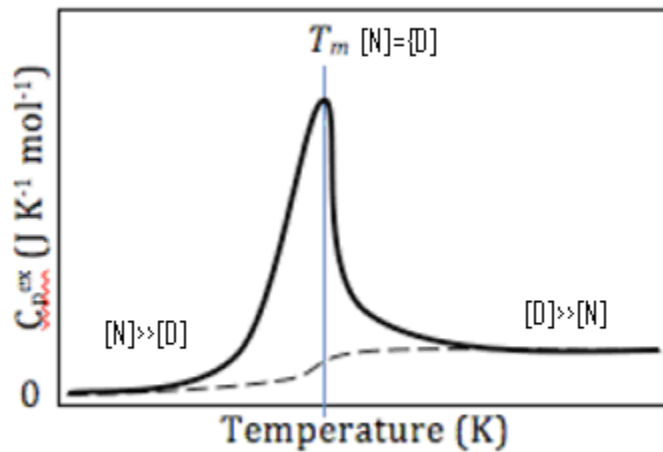
Answer: A system is displaced from its initial state by application of an infinitesimal force. The system is allowed to re-equilibrate before further application of the force. Thus the system’s path consists of a sequence of equilibrium states separated by these small displacements and any step can be reversed by application of an infinitesimal force. The equation of state is valid along a reversible path. (64 words).

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.

Answer:



The heat capacity of D is larger than N because the unstructured form has more degrees of freedom (motions, hydration sites, etc.) that can absorb heat. At T_m D and N are equally stable and together with the large number of partially structured forms that exist at this temperature, have the greatest capacity to absorb heat.

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.

Answer: We can answer this question using the following construction. For an ideal gas $dU = \delta q + \delta w \Rightarrow nC_V dT = \delta q - PdV$. Then the heat is: $\delta q = nC_V dT + PdV$ and we

further define $\frac{\delta q}{T} = \frac{nC_V}{T} dT + \frac{P}{T} dV$. How if the process is irreversible $P = P_{ext}$. We get:

$$\frac{\delta q_{irrev}}{T} = CdT + \frac{P_{ext}}{T} dV$$

$$\therefore \frac{\partial}{\partial V} \left(\frac{nC_V}{T} \right)_T = 0 \text{ and } \frac{\partial}{\partial T} \left(\frac{P_{ext}}{T} \right)_V = -\frac{P_{ext}}{T^2}$$

And this is not an exact differential.

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.

Answer: At constant pressure the heat transferred is equivalent to the enthalpy $q_p = \Delta H = mC\Delta T$. There if ΔT must be limited in order to avoid scorching the clothing the mass m must be made as large as practical to maximize the heat transfer.

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.

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 incorrectly assumes 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.

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.

Many students interpreted this question to be a request for a mathematical proof for $\left(\frac{\partial U}{\partial V}\right)_T = \frac{an^2}{V^2}$. If this was done by using the relationship $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$ and the v.d. Waals equation of state, I gave full credit.

But what I had hoped for was some physical reasoning. 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 parametrized by a . Therefore $\left(\frac{\partial U}{\partial V}\right)_T = \frac{an^2}{V^2}$ and there is no dependence on b .

Problem 2.4 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. $R=8.314 \text{ JK}^{-1}\text{mol}^{-1}$. 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 , ΔU and ΔS if one mole of an ideal monatomic gas initially at $T=400\text{K}$ and $P=1 \text{ atm}$ expands adiabatically and reversibly until $P=0.5 \text{ atm}$

$$\left(\frac{T_2}{T_1}\right)^{C_V} = \left(\frac{V_1}{V_2}\right)^R = \left(\frac{T_1 P_2}{T_2 P_1}\right)^R \rightarrow T_2 = T_1 \left(\frac{P_2}{P_1}\right)^{R/C_V+R} = (400\text{K}) \left(\frac{0.5}{1.0}\right)^{2/5} = 303\text{K}$$

$$\therefore \Delta U = w = nC_V\Delta T = (1) \left(\frac{3}{2}\right) (8.31\text{JK}^{-1}\text{mol}^{-1})(303\text{K} - 400\text{K}) = -1209\text{J}$$

$$q_{rev} = 0 \therefore \Delta S = 0$$

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 100K to 500K at constant pressure, calculate the molar enthalpy change of the gas.

Solution:

$$\begin{aligned} \Delta H &= \int_{T_1}^{T_2} C_p(T) dT = \int_{100}^{500} \left(22.66 + 4.381 \times 10^{-2} \frac{T}{\text{K}} - 1.0835 \times 10^{-4} \frac{T^2}{\text{K}^2} \right) dT \\ &= 22.66(500 - 100) + \frac{4.381 \times 10^{-2}}{2} (500^2 - 100^2) - \frac{1.0835 \times 10^{-4}}{3} (500^3 - 100^3) \\ &= 9064 + 5257 - 4479 = 9842\text{J} \end{aligned}$$

Problem 3.3 In this problem, you can choose which two (one accepted) 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) $\left(\frac{\partial H}{\partial P}\right)_T$.

$$C_p - C_v = TV \frac{\beta^2}{\kappa}$$

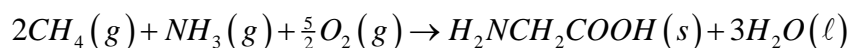
$$\therefore C_v = C_p - TV \frac{\beta^2}{\kappa} = 75.3 \text{ JK}^{-1} \text{ mol}^{-1} - (300 \text{ K}) (18.1 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}) \frac{(3.04 \times 10^{-4} \text{ K}^{-1})^2}{4.46 \times 10^{-10} \text{ m}^2 \text{ N}^{-1}} = 74.17 \text{ JK}^{-1} \text{ mol}^{-1}$$

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

$$\left(\frac{\partial H}{\partial P} \right)_v = -TV\beta + V = -(300 \text{ K}) (18.1 \times 10^{-6} \text{ m}^3) (3.04 \times 10^{-4} \text{ K}^{-1}) + 18.1 \times 10^{-6} \text{ m}^3$$

$$= (18.1 \times 10^{-6} \text{ m}^3) (1 - 0.09) = 16.44 \times 10^{-6} \text{ m}^3$$

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



The table below shows **entropy (change to enthalpy)** values at for T=298K and heat capacity values for each reaction component.

Substance	ΔH_f^0 (kJ mol ⁻¹)	C_p^0 (JK ⁻¹ mol ⁻¹)
CH ₄ (g)	-74.6	35.7
NH ₃ (g)	-45.9	35.1
O ₂ (g)		29.4
H ₂ O(g) → (l)	-285.8	75.3
glycine (s)	-537.2	99.2

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

$$\Delta H_{rxn}^0 = 3\Delta H_f^0(\text{H}_2\text{O}, \ell) + \Delta H_f^0(\text{glycine}, s) - \Delta H_f^0(\text{NH}_3, g) - 2\Delta H_f^0(\text{CH}_4, g)$$

$$= 3(-285.8 \text{ kJ}) + (-537.2 \text{ kJ}) - (-45.9 \text{ kJ}) - 2(-74.6 \text{ kJ})$$

$$= -1199.5 \text{ kJ} \approx -1.20 \times 10^3 \text{ kJ}$$

$$\Delta C_p^0 = 3\Delta C_p^0(\text{H}_2\text{O}, \ell) + \Delta C_p^0(\text{glycine}, s) - \Delta C_p^0(\text{NH}_3, g) - 2\Delta C_p^0(\text{CH}_4, g)$$

$$= 3(75.3 \text{ JK}^{-1}) + (99.2 \text{ JK}^{-1}) - (35.1 \text{ JK}^{-1}) - 2(35.7 \text{ JK}^{-1})$$

$$= 219 \text{ JK}^{-1}$$

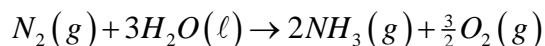
$$\therefore \Delta H_{rxn}(310 \text{ K}) = \Delta H_{rxn}^0 + \Delta C_p^0 \Delta T = -1.20 \times 10^3 \text{ kJ} + (219 \text{ JK}^{-1})(310 \text{ K} - 298 \text{ K})$$

$$= -1.20 \times 10^3 \text{ kJ} + (0.219 \text{ kJ})(12 \text{ K}) = -1.199 \times 10^3 \text{ kJ}$$

Note hardly any change to within 3 significant figures. This is typical of enthalpies...which are pretty insensitive to small temperature changes.

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 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
$H_2O(g) \rightarrow (l)$	70.0	75.3
$NH_3(s)$	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 $T=330K$.

$$\begin{aligned} \Delta S_{rxn}^0 &= 2S_f^0(NH_3, g) + \frac{3}{2}S_f^0(O_2, g) - S_f^0(N_2, g) - 3S_f^0(H_2O, \ell) \\ &= 2(192.8JK^{-1}) + \frac{3}{2}(205.2JK^{-1}) - (191.6JK^{-1}) - 3(70.0JK^{-1}) = 291.8JK^{-1} \end{aligned}$$

$$\begin{aligned} \Delta C_p^0 &= 2C_p^0(NH_3, g) + \frac{3}{2}C_p^0(O_2, g) - C_p^0(N_2, g) - 3C_p^0(H_2O, \ell) \\ &= 2(35.1JK^{-1}) + \frac{3}{2}(29.4JK^{-1}) - (29.1JK^{-1}) - 3(75.3JK^{-1}) = -141JK^{-1} \end{aligned}$$

$$\begin{aligned} \therefore \Delta S_{rxn}(330K) &= \Delta S_{rxn}^0(298K) + \Delta C_p^0 \ln\left(\frac{330}{298}\right) \\ &= 291.8JK^{-1} - 141JK^{-1} \ln(1.11) = 277JK^{-1} \end{aligned}$$

Now for the enthalpy of the surroundings: $\Delta S_{surr} = \frac{\Delta H_{surr}}{T_{surr}} = \frac{-\Delta H_{rxn}}{T_{surr}}$

See Table in Problem 3.4 for heats of formation (noted during exam)

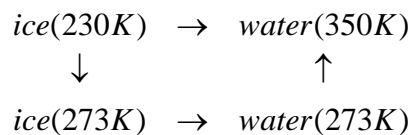
$$\begin{aligned} \Delta H_{rxn}^0 &= 2\Delta H_f^0(NH_3, g) + \frac{3}{2}\Delta H_f^0(O_2, g) - \Delta H_f^0(N_2, g) - 3\Delta H_f^0(H_2O, \ell) \\ &= 2\Delta H_f^0(NH_3, g) - 3\Delta H_f^0(H_2O, \ell) \\ &= 2(-45.9kJ) - 3(-285.8kJ) = 765.6kJ \end{aligned}$$

$$\Delta S_{surr} = \frac{-\Delta H_{rxn}}{T_{surr}} = -\frac{765800J}{330K} = -2321JK^{-1}$$

$$\Delta S_{universe} = \Delta S_{surr} + \Delta S_{rxn} = -2321JK^{-1} + 277JK^{-1} = -2044JK^{-1}$$

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 ΔS , the enthalpy change ΔH 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.

Solution: Designate a three-step path from water ice at $T=230K$ to liquid water at $T=350K$:



$$\text{Step 1: } \Delta H_1 = nC_p^{ice} \Delta T = (1mole)(37.7J / K \cdot mole)(273K - 230K) = 1621J$$

$$\Delta S_1 = nC_p^{ice} \ln\left(\frac{T_{final}}{T_{initial}}\right) = (1mole)(37.7J / K \cdot mole) \ln\left(\frac{273}{230}\right) = 6.46J / K$$

$$\text{Step 2: } \Delta H_2 = (1mole)\Delta H_{fusion} = (1mole)(6010J / mole) = 6010J$$

$$\Delta S_2 = \frac{\Delta H_2}{T_{fusion}} = \frac{6010J}{273K} = 22.0J / K$$

$$\text{Step 3: } \Delta H_3 = nC_p^{liquid} \Delta T = (1mole)(75J / K \cdot mole)(350K - 273K) = 5775J$$

$$\Delta S_3 = nC_p^{liquid} \ln\left(\frac{T_{final}}{T_{initial}}\right) = (1mole)(75J / K \cdot mole) \ln\left(\frac{350}{273}\right) = 18.63J / K$$

$$\text{Totals: } \Delta H_T^{water} = \Delta H_1 + \Delta H_2 + \Delta H_3 = 13,406J$$

$$\Delta S_T^{water} = \Delta S_1 + \Delta S_2 + \Delta S_3 = 47.09J / K$$

$$\Delta S \text{ for Surroundings: } \Delta H_{surr} = -\frac{\Delta H_{sys}}{T_{surr}} = -\frac{13406J}{350K} = -38.30JK^{-1}$$

ΔS for Universe:

$$\Delta S_{universe} = \Delta S_{surroundings} + \Delta S_{water} = -38.30J / K + 47.09J / K = 8.79J / K$$

