Chemistry 304 - Section 111
The University of British Columbia
Midterm Examination
October 31, 2011

Time Limit: 50 min

Student Number: ______________________

Name (printed): ______________________

Signature: ______________________

Marks Distribution

Part	Marks	Grade Received
I	15	
II	10	
III	25	
Bonus	5	
Total	50	
Bonus	5	

INSTRUCTIONS

1. Please write all answers on the examination paper, and show full details of your solutions.
2. **Please read each question carefully.**
3. Please check that your examination contains pages numbered 1 through 7, and that you have a formula sheet at the end. This sheet may be detached during the exam, if you wish.
4. **Please use the back side of pages if you require more space for your responses.**

PART I: (15 marks total)

Indicate whether each of the following statements 1–4 is true or false and on the line underneath write one sentence to justify your choice. There will be no penalties for incorrect answers. Each correct answer with accompanying explanation is worth 3 marks.

1. For fixed N and V, the value of the canonical partition function Q increases when T increases.

   1) True   2) False

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2. The entropy of 1 mol of neon gas at $T = 298\,\mathrm{K}$ and $P = 1\,\mathrm{atm}$ is $232\,\mathrm{J\,K^{-1}}$. Thus, a system consisting of 5 neon atoms will have, under the same conditions, an entropy of $5(232/N_A)\,\mathrm{J\,K^{-1}}$ (N_A is Avogadro's number).

   1) True   2) False

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3. When the volume and number of particles are held fixed, the energies of the microstates of a system decrease when the temperature is lowered.

   1) True   2) False

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4. Mixing together 100 mL of water with 100 mL of methanol produces a solution with a volume of 200 mL.

   1) True   2) False

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5. Briefly describe the two basic postulates of statistical mechanics.

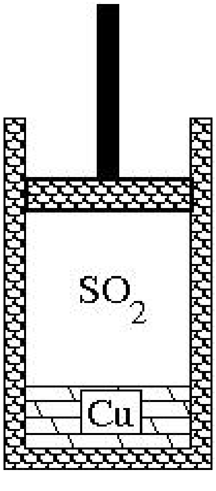
PART II (10 marks total)

Starting with equations from the attached formula sheet, derive the following expressions clearly indicating all steps in your reasoning:

$$\text{i)}\ \left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}\ , \quad \text{and} \quad \text{ii)}\ \left(\frac{\partial H}{\partial P}\right)_T = V(1-\alpha T)\ .$$

PART III (25 marks total)

Consider the apparatus to the right consisting of a cylinder fitted with a piston. The bottom of the cylinder contains 5 moles of solid copper shaped as a cylindrical plug. Above the plug are 3 moles of SO_2 gas. Treat the gas with the van der Waals equation of state with parameters $a = 6.71\,\mathrm{L^2\,atm\,mol^{-2}}$ and $b = 0.0579\,\mathrm{L\,mol^{-1}}$. The entire apparatus is surrounded by high grade thermal insulation. The gas and solid are initially equilibrated to a temperature of 300 K. The initial volume of the gas is 70 L.



The following thermodynamic data may be useful (assume all except $V_m(\mathrm{Cu})$ remain constant under all conditions)

$C_{P,m}(\mathrm{SO_2}) = 40.3\,\mathrm{J\,K^{-1}\,mol^{-1}}$, $C_{P,m}(\mathrm{Cu}) = 24.5\,\mathrm{J\,K^{-1}\,mol^{-1}}$,
$C_{V,m}(\mathrm{SO_2}) = 31.2\,\mathrm{J\,K^{-1}\,mol^{-1}}$, $\alpha(\mathrm{Cu}) = 51 \times 10^{-6}\,\mathrm{K^{-1}}$,
$\kappa(\mathrm{Cu}) = 0.740 \times 10^{-6}\,\mathrm{atm^{-1}}$, $V_m(\mathrm{Cu})(T = 300\,\mathrm{K}, 1\,\mathrm{atm}) = 7.11\,\mathrm{cm^3\,mol^{-1}}$.

1. In a reversible process, the piston is slowly pressed until the temperature of the gas reaches 1500 K. Assume SO_2 remains gaseous and does not decompose, and the copper plug doesn't change temperature or volume during this process. Calculate the final pressure of the gas (Answer: 1697 atm). Calculate w (in kJ), ΔU (in kJ), and ΔS (in $\mathrm{J\,K^{-1}}$) for the gas for this process. Recall for a van der Waals gas, $(\partial U/\partial V)_T = n^2a/V^2$.

2. After the compression in 1. the gas, at $T = 1500\,\mathrm{K}$, and copper plug, at $T = 300\,\mathrm{K}$, are allowed to equilibrate to the same temperature while the pressure is kept constant at 1697 atm. Calculate the final equilibrated temperature (Answer: 896 K).

3. In 2. the temperature of the solid copper plug changed from 300 K to 896 K all at a constant pressure of 1697 atm. Calculate w (in J), ΔV (in L), and ΔS (in $\mathrm{J\,K^{-1}}$) for the copper for this process. Assume the heat was added reversibly to the copper.

Bonus Question (5 marks total) **Answering this question is optional.**

Consider a system at fixed N, V, and T with 5 different energy levels. The energies and degeneracies of these levels are given in the table below, in which $\epsilon = 4.0 \times 10^{-21}$ J. If you wish, you may use the blank cells for intermediate calculations.

E_i	$\Omega(E_i)$			
0.5ϵ	1			
1.5ϵ	10			
3.0ϵ	1			

1. How many microstates does the system possess?
2. Calculate the average energy of the system when $T = 290\,\mathrm{K}$.

MATHEMATICAL RELATIONSHIPS

1. For the exact differential $dA = BdC + DdE$, $\left(\frac{\partial B}{\partial E}\right)_C = \left(\frac{\partial D}{\partial C}\right)_E$ (Euler)
2. $\left(\frac{\partial A}{\partial D}\right)_C = \left(\frac{\partial A}{\partial B}\right)_C \left(\frac{\partial B}{\partial D}\right)_C$ (Chain Rule)
3. $\left(\frac{\partial A}{\partial B}\right)_C \left(\frac{\partial B}{\partial A}\right)_C = 1$ or $\left(\frac{\partial A}{\partial B}\right)_C = \frac{1}{\left(\frac{\partial B}{\partial A}\right)_C}$ (Reciprocal Rule)
4. $\left(\frac{\partial A}{\partial C}\right)_B = -\left(\frac{\partial A}{\partial B}\right)_C \left(\frac{\partial B}{\partial C}\right)_A$ or $\left(\frac{\partial A}{\partial B}\right)_C \left(\frac{\partial B}{\partial C}\right)_A \left(\frac{\partial C}{\partial A}\right)_B = -1$ (Cyclic Rule)
5. $\left(\frac{\partial A}{\partial B}\right)_D = \left(\frac{\partial A}{\partial B}\right)_C + \left(\frac{\partial A}{\partial C}\right)_B \left(\frac{\partial C}{\partial B}\right)_D$

THERMODYNAMIC RELATIONSHIPS

Definitions: $H = U + PV$, $A = U - TS$, $G = H - TS$, $dw = -P_{\text{ext}}dV$, $dS = \frac{dq_{\text{rev}}}{T}$,
$C_P = \left(\frac{\partial H}{\partial T}\right)_P$, $C_V = \left(\frac{\partial U}{\partial T}\right)_V$, $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$, $\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$

Laws: $dU = dq + dw$, $TdS \geq dq$

Basic Equations: $dU = TdS - PdV$, $dA = -SdT - PdV$, $dH = TdS + VdP$,
$dG = -SdT + VdP$, $(dG)_{T,P} = dw_{\text{rev}}'$

Equations of State: $PV = nRT$, $d\ln V = \alpha dT - \kappa dP$, $\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$

STATISTICAL MECHANICAL EXPRESSIONS

NVT/Canonical Ensemble: $P(E_K) = e^{-\beta E_K}/Q$, $Q = \sum_K e^{-\beta E_K}$, $\beta = 1/kT$,
$q_i = \sum_{\varepsilon_i} e^{-\beta \varepsilon_i}$, $Q = \prod_i^N q_i$ (Distinguishable Particles),
$Q = \frac{q^N}{N!}$ (Indistinguishable Particles), $A = -kT\ln Q$,
$\bar{E} = \sum_K E_K P(E_K) = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_{N,V}$, $S = k\ln Q + \frac{\bar{E}}{T}$,
$S = -k\sum_K P(E_K)\ln P(E_K)$

NVE/Microcanonical Ensemble: $S = k\ln\Omega(E)$

SOLUTIONS

Multicomponent Sysytems: $dG = -SdT + VdP + \sum_i \mu_i dn_i$,
$G = \sum_i \mu_i n_i$ (constant T, P)

Raoult's Law: $P_i = P_i^* x_i$

Henry's Law: $P_i = k_i x_i$

Chemical Potential: $\mu_i = \mu_i^0 + RT\ln(P_i/P^0)$ (ideal gas),
$\mu_i(\text{soln}) = \mu_i^* + RT\ln a_i$ (rational system),
$\mu_i(\text{soln}) = \mu_i^0(\text{soln}) + RT\ln a_i$ (practical system),
$\bar{\mu}_i = \mu_i^0(\text{soln}) + RT\ln a_i + z_i F\phi$ (electrochemical potential)

CONSTANTS AND UNIT CONVERSIONS

$R = N_0 k = 0.082057\,\text{L atm mol}^{-1}\,\text{K}^{-1} = 8.3145\,\text{J mol}^{-1}\,\text{K}^{-1}$, $1\ \text{L atm} = 101.325\ \text{J}$,
$N_0 = 6.02214 \times 10^{23}\ \text{mol}^{-1}$ (Avogadro's number), $k = 1.38065 \times 10^{-23}\ \text{J K}^{-1}$,
$h = 6.626068 \times 10^{-34}\,\text{J s}$, $F = 96{,}485.3\ \text{C mol}^{-1}$, $1\ \text{volt} = 1\ \text{V} = 1\ \text{J C}^{-1}$