# Chemistry 304 - Midterm Solutions - 2011

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

   $Q = \sum_i e^{-\beta E_i}$, as $T \uparrow$, $\beta \downarrow$, and $e^{-\beta E_i} \uparrow$ so $Q \uparrow$.

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]

   Entropy is only defined for macroscopic systems. 5 atoms is too small to be macroscopic.

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]

   The energy of a microstate depends only on $N$ and $V$ and is independent of temperature.

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]

   The partial molar volumes of water and methanol change with concentration so volume is not conserved.

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

a) Thermodynamic quantities correspond to ensemble averages over all the microstates in a system. These averages are the same as those obtained by averaging quantities in time.

b) The probability the system is in a particular microstate depends only upon the energy of the microstate, so that microstates with the same energy have equal probabilities.

PART II (10 marks total)

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

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

i) From $dH = TdS + VdP$ one obtains by dividing by $dT$ and taking $P$ constant

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

Identifying the partial derivative of $H$ with $C_P$ then gives the final result

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

ii) From $dH = TdS + VdP$ one obtains by dividing by $dP$ and taking $T$ constant

$$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V\ .$$

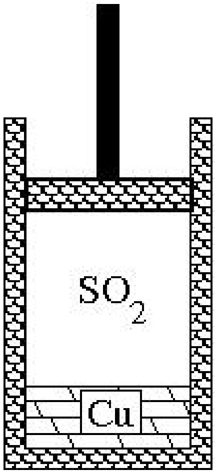
Using the Maxwell relation from $dG = -SdT + VdP$ gives

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

Combining this with the previous result gives

$$\left(\frac{\partial H}{\partial P}\right)_T = T(-\alpha V) + V = V(1-\alpha T)\ .$$

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)

$C_{P,m}(\mathrm{SO_2}) = 40.3\,\mathrm{J\,K^{-1}\,mol^{-1}}$, $C_{P,m}(\mathrm{Cu}) = 24.5\,\mathrm{J\,K^{-1}\,mol^{-1}}$,
$C_{V,m}(\mathrm{SO_2}) = 31.2\,\mathrm{J\,K^{-1}\,mol^{-1}}$, $\alpha(\mathrm{Cu}) = 51\times10^{-6}\,\mathrm{K^{-1}}$,
$\kappa(\mathrm{Cu}) = 0.740\times10^{-6}\,\mathrm{atm^{-1}}$, $V_m(\mathrm{Cu})(T = 300\,\mathrm{K}, 1\,\mathrm{atm}) = 7.11\,\mathrm{cm^3\,mol^{-1}}$.

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), $\Delta U$ (in kJ), and $\Delta S$ (in $\mathrm{J\,K^{-1}}$) for the gas for this process. Recall for a van der Waals gas, $(\partial U/\partial V)_T = n^2a/V^2$.

The process is reversible and adiabatic (apparatus is surrounded by thermal insulation) so $dq = 0$, $q = 0$, $\Delta S = 0$, and $w = \Delta U$. Starting from the equation $dw = dU$ and substituting expressions for the pressure of a van der Waals gas and for $dU$ gives

$$\begin{aligned}
dw &= dU \\
-PdV &= C_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \\
-\left[\frac{nRT}{V-nb} - \frac{n^2a}{V^2}\right] dV &= C_V dT + \frac{n^2a}{V^2} dV \\
-\frac{nRT}{V-nb} dV &= C_V dT \\
\frac{dV}{V-nb} &= -\frac{C_V}{nR}\frac{dT}{T} \\
\ln\left(\frac{V_2-nb}{V_1-nb}\right) &= -\frac{C_{V,m}}{R}\ln\left(\frac{T_2}{T_1}\right) \\
V_2 - nb &= (V_1-nb)\left(\frac{T_2}{T_1}\right)^{-C_{V,m}/R} .
\end{aligned}$$

Substituting the values $C_{V,m} = 31.2\,\mathrm{J\,K^{-1}\,mol^{-1}}$, $b = 0.0579\,\mathrm{L\,mol^{-1}}$, $T_1 = 300\,\mathrm{K}$, $T_2 = 1500\,\mathrm{K}$, $n = 3\,\mathrm{mol}$, and $V_1 = 70\,\mathrm{L}$ gives $V_2 - nb = 0.1664\,\mathrm{L}$ and $V_2 = 0.340\,\mathrm{L}$. Plugging this volume into the van der Waals equation with $T = 1500\,\mathrm{K}$ gives the final pressure of the gas to be 1697 atm.

The value of $\Delta U$ is calculated using the general formula so that

$$\begin{aligned}
dU &= C_V dT + \frac{n^2a}{V^2} dV \\
\Delta U &= C_V \Delta T + n^2a\left(\frac{1}{V_1} - \frac{1}{V_2}\right) .
\end{aligned}$$

Substituting in the values $C_V = 3\,\mathrm{mol}\times 31.2\,\mathrm{J\,K^{-1}\,mol^{-1}}$, $\Delta T = 1200\,\mathrm{K}$, $a = 6.71\,\mathrm{L^2\,atm\,mol^{-2}}$, $V_1 = 70\,\mathrm{L}$ and $V_2 = 0.340\,\mathrm{L}$ gives $\Delta U = 94.4\,\mathrm{kJ}$.

In summary: $\Delta S = 0$, $w = \Delta U = 94.4\,\mathrm{kJ}$.

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).

   The process is isobaric so $dq_P = dH = C_P dT$ and $q_P = C_P \Delta T$. The heat lost by the gas is gained by the solid copper. Casting this equation into mathematics and letting $T$ be the final equilibrated temperature gives

$$\begin{aligned} q_P(gas) &= -q_P(solid) \\ C_P(\mathrm{SO_2})(T - 1500) &= -C_P(\mathrm{Cu})(T - 300) \\ T[C_P(\mathrm{SO_2}) + C_P(\mathrm{Cu})] &= 300[C_P(\mathrm{Cu}) + 5C_P(\mathrm{SO_2})] \\ T &= 300\frac{C_P(\mathrm{Cu}) + 5C_P(\mathrm{SO_2})}{C_P(\mathrm{SO_2}) + C_P(\mathrm{Cu})} \ . \end{aligned}$$

   Substituting the values $C_P(\mathrm{Cu}) = 5\,\mathrm{mol} \times 24.5\,\mathrm{J\,K^{-1}\,mol^{-1}} = 122.5\,\mathrm{J\,K^{-1}}$ and $C_P(\mathrm{SO_2}) = 3\,\mathrm{mol} \times 40.3\,\mathrm{J\,K^{-1}\,mol^{-1}} = 120.9\,\mathrm{J\,K^{-1}}$ gives $T = 896\,\mathrm{K}$.

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), $\Delta V$ (in L), and $\Delta S$ (in $\mathrm{J\,K^{-1}}$) for the copper for this process. Assume the heat was added reversibly to the copper.

   In 1. we are told to assume the copper plug does not change volume when the pressure increases from 1 atm to 1697 atm, so the initial volume of the copper plug at $T = 300\,\mathrm{K}$ and $P = 1697\,\mathrm{atm}$ is taken to be the same as it was at $T = 300\,\mathrm{K}$ and $P = 1\,\mathrm{atm}$, that is $V_1 = nV_m = 5\,\mathrm{mol} \times 7.11\,\mathrm{cm^3\,mol^{-1}} = 35.55\,\mathrm{cm^3} = 0.03555\,\mathrm{L}$. The process of heating the copper plug to $T = 896\,\mathrm{K}$ is isobaric so the equation of state $d\ln V = \alpha dT - \kappa dP$ gives

$$\begin{aligned} d\ln V &= \alpha dT \\ \ln\left(\frac{V_2}{V_1}\right) &= \alpha \Delta T \\ V_2 &= V_1 e^{\alpha \Delta T} \ . \end{aligned}$$

   Substituting the values $\alpha = 51 \times 10^{-6}\,\mathrm{K^{-1}}$, $\Delta T = 896 - 300 = 596\,\mathrm{K}$, and $V_1 = 0.03555\,\mathrm{L}$ gives $V_2 = 0.03665\,\mathrm{L}$ so $\Delta V = 1.10 \times 10^{-3}\,\mathrm{L}$.
   The external pressure is constant so the work is given by

$$w = -P_{ext}\Delta V = -1697\,\mathrm{atm} \times 1.10 \times 10^{-3}\,\mathrm{L} = -1.867\,\mathrm{L\,atm} = -189\,\mathrm{J} \ .$$

   Because the process is isobaric and reversible, $dq_{rev} = dq_P = dH = C_P dT$, so the entropy is calculated as

$$\begin{aligned} dS &= \frac{dq_{rev}}{T} = C_P \frac{dT}{T} \\ \Delta S &= C_P \ln\left(\frac{T_2}{T_1}\right) \\ &= 5\,\mathrm{mol} \times 24.5\,\mathrm{J\,K^{-1}\,mol^{-1}} \times \ln\left(\frac{896\,\mathrm{K}}{300\,\mathrm{K}}\right) \\ &= 134\,\mathrm{J\,K^{-1}} \ . \end{aligned}$$

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

Consider a system at fixed $N$, $V$, and $T$ with 3 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.

| $E_i$ | $\Omega(E_i)$ | $e^{-\beta E_i}$ | $\Omega(E_i)e^{-\beta E_i}$ | $P_i$ |
|---|---|---|---|---|
| $0.5\epsilon$ | 1 | 0.6065 | 0.6065 | 0.2101 |
| $1.5\epsilon$ | 10 | 0.2231 | 2.231 | 0.7728 |
| $3.0\epsilon$ | 1 | 0.04979 | 0.04979 | 0.01725 |

1. How many microstates does the system possess?

   Adding all the degeneracies gives the total number of states as 12.

2. Calculate the average energy of the system when $T = 290\,\mathrm{K}$.

   At $T = 290K$, $\beta\epsilon = 1.0$ so that the factors $e^{-\beta E_i}$ are simplified and are listed in the table for each energy. Adding the values of $\Omega(E_i)e^{-\beta E_i}$ together gives $Q = 2.887$. This can be used to evaluate the microstate probabilities, $P_i = \Omega(E_i)e^{-\beta E_i}/Q$, and are listed in the table. The average energy is then

$$\overline{E} = \sum_{i=1}^{3} E_i P_i = (0.5 \times 0.2101 + 1.5 \times 0.7728 + 3.0 \times 0.01725)\epsilon = 1.32\epsilon = 5.28 \times 10^{-21}\ \mathrm{J}$$