Chemistry 440 Hour exam

EXAM KEY

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\[ R \simeq 8 \frac{J}{(K \cdot mol)} \simeq 0.08 \frac{L \cdot atm}{(K \cdot mol)} \]

1 bar = 10^5 Pa \quad 1 \text{ bar} \simeq 1 \text{ atm} \\
\Delta U = q_{by} + w_{on} = q_{by} - w_{by} = q_{by} - \int P_{ext} dV \\
H = U + PV \\
C_v = \left( \frac{\partial U}{\partial T} \right)_V \\
C_p = \left( \frac{\partial H}{\partial T} \right)_p \\
\mu_T = \left( \frac{\partial T}{\partial P} \right)_H \\
\kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T \\
\alpha_P = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p \\
P_1 V_1^\gamma = P_2 V_2^\gamma, \quad T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1} \quad \text{for an adiabatic process; } \gamma = \frac{C_p}{C_v} \]
1. (8 pts) Compare the molar volume (in cm$^3$) of liquid water (density = 1 g/cm$^3$) with that of its vapor at 1 atm and 127$^\circ$C. Assume water vapor is an ideal gas.

\[
\text{Liquid} \quad 18 \text{ g/mole} \times 1 \text{ cm}^3/\text{g} = 18 \text{ cm}^3/\text{mole}
\]

\[
\text{Gas} \quad PV = nRT, \quad \frac{V}{n} = \frac{RT}{P} = \left(0.08 \text{ L atm/mol K}\right)\left(\frac{1}{1 \text{ atm}}\right)400 \text{ K}
\]

\[
\frac{V}{n} = 32 \text{ L} = 32 \times 10^3 \text{ cm}^3/\text{mole}
\]

2. (8 pts) The thermal expansion coefficient of liquid water at 300K and at 1 bar is $2 \times 10^{-4} K^{-1}$. What is the fractional increase in volume of the ocean if the temperature of the ocean increases by 2 K?

\[
\alpha_p = \frac{1}{V} \left(\frac{dV}{dT}\right)_p \Rightarrow \frac{\Delta V}{V} = \alpha_p \Delta T = \left(2 \times 10^{-4} \frac{1}{K}\right)(2 \text{ K})
\]

\[
\frac{\Delta V}{V} = 4 \times 10^{-4}
\]

3. (8 pts) Calculate the heat of vaporization of water at 20$^\circ$C and at 1 bar given that $C_p$ of liquid water is 4J/(K·g) and the heat of vaporization is 2000 J/g at 100$^\circ$C. Express your answer in J/g.

\[
\Delta H = C_p \Delta T + \Delta H_{vap}(100^\circ \text{C}) = 4 \frac{\text{J}}{\text{K} \cdot \text{g}} \times \frac{80 \text{ K}}{\text{K} \cdot \text{g}} + 2000 \frac{\text{J}}{\text{g}}
\]

\[
\Delta H = 2320 \frac{\text{J}}{\text{g}} = \Delta H_{vap}(20^\circ \text{C})
\]
4. (24 pts) Consider a substance whose enthalpy obeys

\[ H(T, P) = \frac{5}{2} nRT + n^2 P^2 (b - \frac{c}{T}) \]  

(1)

where \( b \) and \( c \) are constants. Derive

a) \( \left( \frac{\partial H}{\partial b} \right)_T \); b) the inversion temperature; and c) the Joule-Thomson coefficient.

\[ a) \quad C_p = \left( \frac{\partial H}{\partial T} \right)_P = \frac{5}{2} nR + \frac{n^2 P^2 c}{T^2} \]

\[ \left( \frac{\partial C_p}{\partial P} \right)_T = \frac{2n^2 PC}{T^2} \]

\[ b) \quad \text{At the inversion temp,} \quad \left( \frac{\partial H}{\partial P} \right)_T = 0 \]

\[ \left( \frac{\partial H}{\partial P} \right)_T = 2n^2 P \left( b - \frac{c}{T} \right) = 0 \Rightarrow T_{in} = \frac{c}{b} \]

\[ c) \quad \mu_{JT} = -\left( \frac{\partial H}{\partial P} \right)_T \quad \frac{C_p}{C_p} = \frac{-2n^2 P (b - \frac{c}{T})}{\frac{5}{2} nR + \frac{n^2 P^2 c}{T^2}} \]
5. Equations of state.

(a) (8 pts) Graph an ideal gas equation and the critical isotherm on a plot of $P$ vs $\rho$, where $\rho = n/V$.

(b) (8 pts) A thermodynamic system obeys the equation of state,

$$\frac{P}{\rho RT} = 1 + b\rho - c\rho^2$$

where $b, c$ are positive constants. Does this system have a critical point? Prove your assertion.

\[ P = RT\left\{\rho + b\rho^2 - c\rho^3 \right\} \]

\[
\left. \frac{\partial P}{\partial \rho} \right|_T = 0 \Rightarrow 1 + 2b\rho - 3c\rho^2 = 0 \tag{1}
\]

\[
\left. \frac{\partial^2 P}{\partial \rho^2} \right|_T = 0 \Rightarrow 2b - 6c\rho = 0 \quad \therefore \rho_c = \frac{b}{3c} \tag{2}
\]

Substitute into Eq(1)

$$1 + 2b\left(\frac{b}{3c}\right) - 3c\left(\frac{b}{3c}\right)^2 = 1 + \frac{1}{3} \frac{b^2}{c} \neq 0$$

cannot satisfy requirement for a critical point. No c.p.
6. (24 pts) One mole of water vapor (assumed to be an ideal gas, $C_v = 3R$) is compressed from a volume of $V_1$ to a volume $V_2 = \frac{1}{8}V_1$ at an initial temperature of $T_1$.

What are the values of $\Delta H, \Delta U, w_{by}$ and $q_{by}$, in units of $RT_1$, (CIRCLE YOUR ANSWERS)

(a) first, when the compression is conducted adiabatically and reversibly, $q_{by} = 0$

$$\Delta H = C_p \Delta T, \quad \Delta U = C_v \Delta T = -W_{by}$$

so need $\Delta T$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1} \quad \gamma = \frac{C_p}{C_v} = \frac{4}{3}$$

$$\frac{T_2}{T_1} = 8^{1/3} = 2, \quad T_2 = 2T_1$$

$$\Delta H = 4R(2T_1 - T_1) = 4RT_1$$

$$\Delta U = 3R(2T_1 - T_1) = 3RT_1$$

$$W_{by} = -3RT_1$$

(b) and second, when the compression is conducted against a constant pressure (equal to the final pressure in the adiabatic process = $16P_1$). Heat is removed in the process such that the endpoint here is the same as the endpoint in the previous case.

$$\Delta H = 4RT_1, \quad \Delta U = 3RT_1$$

same as above

$$W_{by} = +P_{ext} \Delta V = +16P_1(\frac{1}{8}V_1 - V_1) = -14P_1V_1$$

$$W_{by} = -14RT_1$$

$$\Delta U = q_{by} - W_{by} = 3RT_1 = q_{by} + 14RT_1$$

$$q_{by} = -11RT_1$$
7. (12 pts) The Helmholtz energy $A = U - TS$ obeys

$$dA(T, V) = -SdT - PdV$$  \hspace{1cm} (3)

(a) Prove Eq(3) using the identity

$$dU(T, S) = TdS - PdV$$  \hspace{1cm} (4)

(b) Starting from the equation for $dA(T, V)$, complete the following

$$\left( \frac{\partial S}{\partial V} \right)_T = \ldots$$  \hspace{1cm} (5)

\[ a) \quad dA = dU - TdS - SdT = TdS - PdV = -SdT - PdV - TdS - SdT \]

\[ b) \quad \left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial P}{\partial T} \right)_V \quad \text{consequence of exactness} \]