Chemistry 440 Hour exam

EXAM KEY

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$$R \simeq 8\ J/(K \cdot mol) \simeq 0.08\ L \cdot atm/(K \cdot mol)$$

$$1\ bar = 10^5\ Pa \qquad 1\ bar = 1.0\ atm$$

$$\Delta U = q_{by} + w_{on} = q_{by} - \int P_{ext} dV$$

$$H = U + PV$$

$$C_v = \left(\frac{\partial U}{\partial T}\right)_V$$

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

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H$$

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial P}\right)_T$$

$$\alpha_P = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

$$P_1 V_1^\gamma = P_2 V_2^\gamma, \qquad T_1 \bar{V}_1^{\gamma-1} = T_2 \bar{V}_2^{\gamma-1} \qquad \text{adiabatic process } \gamma = \frac{C_p}{C_v} \qquad \gamma - 1 = \frac{R}{C_v}$$

$$Z = \frac{P}{\rho RT} = 1 + B_2\rho + B_3\rho^2 + \cdots \qquad \rho = \frac{n}{V}$$

$$P = \frac{\rho RT}{1 - b\rho} - a\rho^2 \qquad \text{vdW equation}$$

1. (12 pts) A van der Waals fluid has a density such that the compressibility factor satisfies $Z = 2$. (a) If the van der Waals a and b parameters are $a = 0$ and $b = 20 \ cm^3/\text{mole}$, then what is the molar density of the fluid in units of moles/cm^3. (b) What is the packing fraction for this fluid given that $b = 4v_0$, where v_0 the molar volume of matter.

a)
$$Z = \frac{1}{1-b\rho} = 2 \implies b\rho = \frac{1}{2}$$

$$\rho = \frac{1}{2b} = \frac{1}{2(20 \, cm^3/\text{mole})} = \frac{1}{40} \frac{\text{mole}}{cm^3}$$

b)
$$b\rho = 4v_0 \rho = \frac{1}{2} \implies \rho v_0 = \frac{1}{8} = \text{packing fraction}$$

2. (10 pts) Derive the isothermal compressibility, $\kappa_T(\rho)$, for a fluid obeying

$$Z(\rho) = 1 + B_2\rho \qquad (1)$$

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial P}\right)_T$$

$$Z = \frac{P}{\rho RT} = 1 + B_2\rho \quad \text{or} \quad P = \rho RT[1 + B_2\rho]$$

$$P = RT[\rho + B_2\rho^2], \quad \left(\frac{\partial P}{\partial \rho}\right)_T = RT[1 + 2B_2\rho]$$

and

$$\kappa_T = \frac{1}{\rho RT[1 + 2B_2\rho]}$$

3. One mole of nitrogen gas ($C_v = \frac{5}{2}R$) with an initial temperature of 300 K expands reversibly from an initial volume of 1 L to 10 L. Place the answers, all in units of K, in the Table.

	.....$\Delta H/R$.....	.....$\Delta U/R$.....	.. ...q_{by}/R.....	.....w_{by}/R.....
(a)	O	O	$300 \ln(10)$	$300 \ln(10)$
(b)	-630 K	-450	O	450 K

(a) (12 pts) Calculate the entries in the Table if the process is isothermal.

$$\Delta H = \Delta U = O$$
$$\Delta U = q_{by} - \int P dV = q_{by} - RT \ln(V_2/V_1)$$
$$\frac{q_{by}}{R} = \frac{w_{by}}{R} = T \ln\left(\frac{V_2}{V_1}\right) = 300 \ln(10)$$

(b) (12 pts) Calculate the entries in the Table if the process is adiabatic. Hint: $(1/10)^{(2/5)} \simeq 0.4$

$$q_{by} = O, \quad \Delta U = -W_{by} = C_V \Delta T$$
$$\Delta H = C_P \Delta T$$

need ΔT:
$$T_2 = T_1 \left(\frac{V_1}{V_2}\right)^{R/C_V} = T_1 \left(\frac{1}{10}\right)^{2/5} = 0.4 T_1$$

$T_2 = (0.4)(300 K) = 120$ K   and $\Delta T = 120 - 300 = -180$ K

$$\frac{\Delta U}{R} = \frac{5}{2}(-180 K) = -5.90 K = -450 K$$

$$\frac{\Delta H}{R} = \frac{7}{2}(-180 K) = -7.90 K = -630 K$$

(c) (6 pts) In which of the two expansions does the gas do the most work and why?

Isothermal process does the most work since energy is being supplied to the system.

4. (10 pts) Prove that $C_p = C_v + R$ for one mole of an **ideal gas**, stating all assumptions and starting from the definition of the enthalpy.

$$H = U + PV = U + RT$$

$$dH = dU + RdT$$

$C_p dT \quad\quad C_v dT$

and $\quad C_p dT = C_v dT + RdT$

or $\quad C_p = C_v + R$

5. (18 pts) Finite differences.

(a) Molecular nitrogen has a Joule-Thomson coefficient of $\mu_{JT} = 0.2$ K/bar at 300K. What pressure differential is needed to cause a 10 K drop in temperature?

$$\Delta T = -10 \text{ K}$$

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H, \qquad \Delta P = \frac{\Delta T}{\mu_{JT}} = \frac{-10 \text{ K}}{0.2 \text{ K/bar}} = -50 \text{ bar}$$

(b) When 200 J of energy are supplied to 2.0 moles of Ar under conditions of constant pressure, its temperature rises by 5 K. What are the molar heat capacities, C_v and C_p for Ar in units of R?

$$\Delta H = C_p \Delta T = 100 \text{ J/mole}$$

$$C_p = \frac{100 \text{ J/mole}}{5 \text{ K}} = 20 \frac{\text{J}}{\text{K·mole}}$$

$$R = 8 \text{ J/K·mole}, \qquad \frac{C_p}{R} = \frac{20}{8} = 2.5$$

$$C_p = C_v + R \implies \frac{C_v}{R} = 1.5$$

6. (12 pts) The enthalpy per mole $\bar{H}$ of a model fluid is given by

$$\bar{H}(T, P) = cT - a\frac{P}{RT} \qquad (2)$$

Derive: C_p, $\left(\frac{\partial H}{\partial P}\right)_T$ and μ_{JT} if a, c are constants.

$$C_p = \left(\frac{\partial H}{\partial T}\right)_P = c + \frac{aP}{RT^2}$$

$$\left(\frac{\partial H}{\partial P}\right)_T = -\frac{a}{RT}$$

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H = -\left(\frac{\partial H}{\partial P}\right)_T \left(\frac{\partial T}{\partial H}\right)_P = \frac{a/RT}{c + aP/RT^2} = \frac{a}{cRT + aP/T}$$

7. (8 pts) Show that
$$dq_{rev} = dH - VdP$$

starting from the First Law of Thermodynamics for a reversible process.

$$dU = dq_{rev} - PdV$$

$$dH = dU + d(PV) = dU + PdV + VdP$$

$$dH = dq_{rev} + VdP$$

$$\text{or } dq_{rev} = dH - VdP$$

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