Chemistry 440 Hour exam

Name : .....EXAM KEY.....................

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25 October 2013

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

$$1 \ bar = 10^5 \ Pa \simeq 1 \ atm$$

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

$$H = E + PV$$

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

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

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

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

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

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

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

1. Provide the equation(s) and define the terms.

   (a) (6 pts) State the First Law of Thermodynamics as it applies to the *universe* and to the *system* (two equations).

   $$\Delta E_{universe} = \Delta E_{sys} + \Delta E_{surr} = 0$$
   the energy of the universe is conserved

   whereas

   $$\Delta E_{sys} = q_{by} + W_{on},$$
   ΔE_{sys} changes because of heat absorbed or work done on the system.

   (b) (4 pts) Define an adiabatic process in terms of the restriction it implements in the First Law (one equation).

   $$q_{by} = 0$$

   (c) (6 pts) Define the conditions for the critical point of a single component fluid (two equations). Use either density or volume as a variable.

   $$\left(\frac{\partial P}{\partial \rho}\right)_T = \left(\frac{\partial^2 P}{\partial \rho^2}\right)_T = 0 \quad \text{or equivalently,} \quad \left(\frac{\partial P}{\partial V}\right)_T = \left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0$$

2. (8 pts) The enthalpy per mole $\bar{H}$ of a model fluid is given by

$$\bar{H}(T,P) = aT + cTP^2 \tag{1}$$

Derive $\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H$ if a and c are constants.

$$\left(\frac{\partial T}{\partial P}\right)_H = -\left(\frac{\partial T}{\partial H}\right)_P \left(\frac{\partial H}{\partial P}\right)_T \quad \text{cyclic rule}$$

$$\left(\frac{\partial H}{\partial T}\right)_P = a + cP^2, \quad \left(\frac{\partial H}{\partial P}\right)_T = 2cTP$$

$$\therefore \quad \mu_{JT} = \frac{-2cTP}{a + cP^2}$$

3. (10 pts) The van der Waals equation, without allowance for attractive forces, is given by

$$P = \frac{\rho RT}{1 - \rho b} \tag{2}$$

For CS_2, the van der Waals b parameter is $b \simeq 0.040$ L/mole and the molar mass is roughly 80 g/mole.

a) If the mass density of liquid carbon disulfide is 1.2 g/mL, what is its molar density in moles/L?

$$1.2 \frac{g}{cm^3} \times \frac{1000 \, cm^3}{L} \times \frac{1 \, mole}{80 \, g} = \frac{1200}{80} \frac{moles}{L} = 15 \frac{moles}{L}$$

b) What is the lowest molar density (moles/L) at which Eq(2) fails?

when $1 - b\rho = 0$, vdW eqn fails, or

$$\rho \geq 1/b = 1/0.040 = 25 \, moles/L$$

4. (6 pts) For a specific material, the Joule-Thomson coefficient is found to be $\mu_{JT} = -1.25$ mK/bar. Does the temperature increase or decrease and by how much when the pressure drop is 1 kbar in a Joule-Thomson expansion?

$$\mu_{JT} = -1.25 \frac{mK}{bar}$$

$$\Delta T = \mu_{JT} \Delta P, \quad \Delta P = -10^3 \, bar$$

$$\Delta T = -1.25 \frac{mK}{bar} \times (-10^3 \, bar) = 1.25 \, K$$

heats on expansion

5. Consider a fluid whose equation of state obeys

$$P = \rho RT \left(1 + b\rho + (b\rho)^2\right) - a\rho^2; \qquad \rho = n/V \qquad (3)$$

where a and b are constant. Derive:

(a) (10 pts) $B_2(T), B_3(T)$, the second and third virial coefficients, respectively;

$$\frac{P}{\rho RT} = Z = 1 + b\rho + (b\rho)^2 - \frac{a}{RT}\rho$$

$$\therefore \quad B_2 = b - a/RT$$
$$B_3 = b^2$$

(b) (8 pts) and the dependence of total derivative of $E(T,\rho)$, namely $dE(T,\rho)$ on ρ and T. Use

$$\left(\frac{\partial E}{\partial \rho}\right)_T = \frac{\left(P - T\left(\frac{\partial P}{\partial T}\right)_V\right)}{\rho^2} \qquad (4)$$

$$dE = C_V dT + \left(\frac{\partial E}{\partial \rho}\right)_T d\rho$$

but, $\quad T\left(\frac{\partial P}{\partial T}\right)_V = \rho RT\left\{1 + b\rho + (b\rho)^2\right\}$ so that

$$P - T\left(\frac{\partial P}{\partial T}\right)_V = -a\rho^2 \quad \text{and} \quad \left(\frac{\partial E}{\partial \rho}\right)_T = -a$$

so that $\qquad dE = C_V dT - a\, d\rho$

$$\text{can not determine } C_V \text{ with the information given}$$

6. (18 pts) One mole of argon (assumed to be an ideal gas with $\bar{C}_v = \frac{3}{2}R$) is compressed reversibly from an initial state at 300K and a volume of e L to a final state whose volume is 1 L. Calculate $\Delta E, w_{on}$ and q_{by}. First, consider an *ISOTHERMAL* process and second, an *ADIABATIC* process. Place the answers in the Table.

	.....$\Delta E/R$.....	.....w_{on}/R.....	.....q_{by}/R.....
(a) isothermal	0	$+300\ K$	$-300\ K$
(b) adiabatic	$450(e^{2/3}-1)$	$450(e^{2/3}-1)$	0

a) Isothermal process

$$\Delta E = 0 = q_{by} + w_{on} = q - \int_{V_1}^{V_2} P\,dV$$

$$\therefore q_{by} = \int_{V_1}^{V_2} \frac{RT}{V}\,dV = RT\ln(V_2/V_1)$$

$$q_{by}/R = 300\,K\,\ln(1/e) = -300K$$

$$w_{on} = -q_{by}$$

b) Adiabatic, $q = 0$

$$\Delta E = C_v \Delta T = w_{on}$$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1} \qquad \text{but}\qquad \gamma = \frac{C_p}{C_v} = \frac{5/2}{3/2} = 5/3$$

$$\gamma - 1 = 2/3$$

$$\frac{T_2}{T_1} = \left(\frac{e}{1}\right)^{2/3} = e^{2/3}$$

$$T_2 = 300\,e^{2/3}$$

$$\Delta T = 300(e^{2/3}-1)\,K$$

$$C_v = \frac{3}{2}R \qquad \therefore \qquad \frac{C_v \Delta T}{R} = \frac{3}{2}\cdot 300\,(e^{2/3}-1)$$

$$\frac{\Delta E}{R} = 450\,(e^{2/3}-1)$$

7. (8 pts) Prove that

$$\alpha_P = \left(\frac{\partial P}{\partial T}\right)_V \kappa_T \tag{5}$$

starting with the definition of α_P.

$$\alpha_P = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = -\frac{1}{V}\underbrace{\left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V}_{\text{cyclic rule}} = \kappa_T \left(\frac{\partial P}{\partial T}\right)_V$$

8. (8 pts) Determine if dq_{by}/T^2 is an exact differential for an ideal gas which undergoes a reversible process. Assume that C_v is independent of T.

$$dE = C_v dT = dq - PdV = dq - \frac{nRT\,dV}{V}$$

so $\quad dq_{rev} = C_v dT + nRT\,dV/V$

$$\frac{dq_{rev}}{T^2} = \frac{C_v}{T^2} dT + \frac{nR}{T}\frac{dV}{V} \qquad \text{4 pts to get here.}$$

If exact, then $\left(\frac{\partial}{\partial V}\left(\frac{C_v}{T^2}\right)\right)_T = \left(\frac{\partial}{\partial T}\left(\frac{nR}{TV}\right)\right)_V$

$$\uparrow_0 \qquad = -\frac{nR}{VT^2} \qquad \text{not true}$$

$\therefore$ not exact

9. (8 pts) $dE(S, V)$ is an exact differential, where S is the entropy and T is the absolute temperature. If

$$dE(S, V) = TdS - PdV \qquad (6)$$

then by the condition of exactness

$$\left(\frac{\partial T}{\partial V}\right)_S = \cdots -\left(\frac{\partial P}{\partial S}\right)_V \qquad (7)$$

✓

−2 pts /first error

2nd error ⟹ no credit

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