Chemistry 440 Hour exam

EXAM KEY
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\begin{aligned}
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_1V_1^\gamma &= P_2V_2^\gamma, \qquad T_1\bar{V}_1^{\gamma-1} = T_2\bar{V}_2^{\gamma-1} \qquad \text{for an adiabatic process;}\ \gamma = \frac{C_p}{C_v}\\
\frac{1}{1-x} &\simeq 1 + x + x^2 + x^3 + \cdots\\
Z &= \frac{P}{\rho RT} = 1 + B_2\rho + B_3\rho^2 + \cdots \qquad \rho = \frac{n}{V}
\end{aligned}
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1. Provide an equation or two and define terms.

(a) (4 pts) State the First Law of Thermodynamics as it applies to the universe and to the system (two equations).

$\Delta E_{univ} = 0$ energy is conserved in the universe

$\Delta E_{sys} = q_{by} + W_{on}$

The energy of the system changes if it absorbs heat or if work is done to it.

(b) (2 pts) Define reversible work in terms of its thermodynamic variables (one equation).

$P_{external} = P_{system}$

$\therefore W_{by} = P_{sys} dV$

(c) (4 pts) Define the *two* conditions for a critical point of a single component fluid (two equations).

$\left(\frac{\partial P}{\partial \rho}\right)_T = \left(\frac{\partial^2 P}{\partial \rho^2}\right)_T = 0$ or the V-equivalent

2. (10 pts) The internal energy for one mole of a model fluid is given by

$$E(\rho, T) = \tfrac{3}{2}RT + gT^2 - a\rho \qquad \rho = n/V \tag{1}$$

Derive $\left(\frac{\partial T}{\partial \rho}\right)_E$ and $C_v(T)$ assuming that a, g are constants.

$C_V = \left(\frac{\partial E}{\partial T}\right)_V = \frac{3}{2}R + 2gT$

$dE = 0 = C_V dT - a d\rho$

$\therefore \left(\frac{\partial T}{\partial \rho}\right)_E = \frac{a}{C_V}$

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3. (12 pts) One mole of argon (assumed to be an ideal gas) is compressed from 10 L to 5 L at 300 K by two processes: a reversible isothermal compression; and a compression at a constant pressure equal to the final pressure of the gas. Calculate $\Delta E, w_{on}$ and q_{by}.

	...ΔE(kJ) ...	...w_{on} (kJ) ...	...q_{by} (kJ)...
(a) isothermal	0	2.4 ln 2	-2.4 ln 2
(b) constant P	0	2.4	-2.4

a) $\Delta E = 0 = q_{by} + W_{on}$, $W_{on} = -\int P dV = -nRT \ln(V_2/V_1)$

$W_{on} = RT \ln 2 = 8 \frac{J}{K} \cdot 300 \ln(2) = 2.4 \ln 2$ kJ

b) $\Delta E = 0$, $W_{on} = -P_{ext} \cdot (5-10) l$

$P_{ext} = \frac{nRT}{V} = \frac{0.08 \frac{l \cdot atm}{K} \cdot 300 K}{5 l} = 60 \times 0.08 = 4.8$ atm

$W_{on} = 4.8 \text{ atm} \cdot 5 l \times \frac{8 J}{0.08 l \cdot atm} = 2.4 \times 10^3 J$

$= 2.4$ kJ

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4. Quick math

(a) (8 pts) A block of iron at 1 bar is heated from 300K to 500K, what is the fractional change in volume given that $\alpha_P = 3 \times 10^{-5} K^{-1}$.

$$\alpha_p = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \rightarrow \frac{\Delta V}{V} = \alpha_p \cdot \Delta T$$

$$\frac{\Delta V}{V} = \left(3 \times 10^{-5} \frac{1}{K}\right)(200K) = 6 \times 10^{-3}$$

(b) (8 pts) When 720 J of energy are supplied to 3 moles of gaseous water in a closed container of fixed volume, the temperature increases by $10K$. What are C_v and C_p in units of R for gaseous water?

$$q_V = nC_V\Delta T, \quad 720J = 3 \cdot C_V \cdot 10K$$

$$C_V = 24 \frac{J}{K}, \quad C_V/R = 3$$

$$C_P/R = 4$$

(c) (8 pts) Calculate the heat of vaporization of water at 20° C and at 1 bar given that the heat capacity of water is 4J/(K· g) and the heat of vaporization is 2180 J/g at 100° C. Express your answer in J/g.

$$\Delta H(20°C) = C_p \Delta T + \Delta H(100°C)$$

$$= \frac{4J}{K \cdot g} \cdot 80K + 2180 \frac{J}{g} = 2500 \frac{J}{g}$$

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5. The proposed equation of state, Eq(2), has many advantages over the van der Waals equation,

$$P = \frac{\rho RT}{(1-\eta)^4} - a\rho^2 \qquad \eta = \rho v_o \tag{2}$$

particularly in its treatment of intermolecular repulsion. Here a is the van der Waals a-parameter and η the packing fraction.

(a) (8 pts) What is the second virial coefficient derived from Eq(2)? Note the series expansion given on page 1 of the exam.

$$\frac{P}{\rho RT} = Z = \frac{1}{(1-\eta)^4} - \frac{a\rho}{RT} = 1 + 4\eta - \frac{a\rho}{RT} = 1 + \left(4V_o - \frac{a}{RT}\right)\rho$$

$$B_2(T) = 4V_o - a/RT$$

(b) (8 pts) derive $(dE(T,\rho)/d\rho)_T$ using Eq(2) and

$$\left(\frac{\partial E}{\partial \rho}\right)_T = \frac{n}{\rho^2}\left(P - T\frac{\partial P}{\partial T}\right)_\rho \tag{3}$$

$$\left(\frac{\partial P}{\partial T}\right)_\rho = \frac{\rho R}{(1-\eta)^4} \Rightarrow P - T\frac{\partial p}{\partial T} = -a\rho^2 \quad \text{so}$$

$$\left(\frac{\partial E}{\partial \rho}\right)_T = -an$$

(c) (4 pts) The van der Waals a parameter represents molecular physics. What does it represent. If we increase a, does the internal energy increase or decrease?

a = measure of intermolecular attraction

If a increases, so does intermolecular attraction, and the energy decreases.

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6. Proofs

(a) (8 pts) Prove that $C_p - C_v = R$ for one mole of an ideal gas, starting from dE and the definition of H.

$$dH = d(E + PV) = C_v dT + d(RT) = (C_v + R)dT$$

for one mole of gas.

(b) (8 pts) Prove that

$$\alpha_P = \left(\frac{\partial P}{\partial T}\right)_V \kappa_T \tag{4}$$

starting from the definition of α_P on page 1.

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

(c) (8 pts) If

$$dJ(T,V) = \frac{E}{T^2}dT + \frac{P}{T}dV \tag{5}$$

then

$$\left(\frac{\partial E}{\partial V}\right)_T = \cdots \tag{6}$$

Supply the right hand side.

$$\left(\frac{\partial (E/T^2)}{\partial V}\right)_T = \left(\frac{\partial (P/T)}{\partial T}\right)_V = \frac{1}{T^2}\left(\frac{\partial E}{\partial V}\right)_T$$

$$\therefore \left(\frac{\partial E}{\partial V}\right)_T = T^2\left(\frac{\partial (P/T)}{\partial T}\right)_V$$

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