Chemistry 440 Hour exam

EXAM KEY

Department of Chemistry, Oregon State University

21 October 2009

\[ R \simeq 8 \, J/(K \cdot mol) \simeq 0.08 \, L \cdot atm/(K \cdot mol) \]

1 bar = 10^5 Pa \simeq 1 atm

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

\[ H = U + PV \]

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

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

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

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

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

\[ P_1V_1^{\gamma} = P_2V_2^{\gamma}, \quad T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1} \quad \text{for an adiabatic process;} \quad \gamma = \frac{C_p}{C_v} \]

\[ \frac{1}{1-x} \simeq 1 + x + x^2 + x^3 + \cdots \]

\[ Z = \frac{P}{\rho RT} = 1 + B_2\rho + B_3\rho^2 + \cdots \quad \rho = \frac{n}{V} \]
1. Provide the equation(s) and define terms.

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

\[ \Delta U_{\text{univ}} = \Delta U_{\text{sys}} + \Delta U_{\text{surr}} = 0 \quad \text{Total energy of the universe is conserved} \]

\[ \Delta U_{\text{sys}} = q_{\text{sys}} + w_{\text{sys}} \quad \text{The change in internal energy of the system is the sum of the heat absorbed + work done on the sys.} \]

(b) (2 pts) Define an adiabatic process in terms of the thermodynamic variables of the system (one equation).

\[ q_{\text{sys}} = 0 \]

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

\[ \left( \frac{\partial P}{\partial V} \right)_T = \left( \frac{\partial^2 P}{\partial V^2} \right)_T = 0 \quad \text{or} \quad \left( \frac{\partial^2 P}{\partial T \partial V} \right)_T = 0 \]

2. (10 pts) The internal energy per mole \( \bar{U} \) of a model fluid is given by

\[ \bar{U}(\rho, T) = \bar{C}_vT - a\rho \quad (1) \]

Derive \( \frac{\partial T}{\partial \rho} \) if \( \bar{C}_v \) and \( a \) are constants.

\[ dU = C_v dT - a d\rho = 0 \]

\[ \therefore \left( \frac{\partial T}{\partial \rho} \right)_U = \frac{a}{C_v} \]
3. (10 pts) The van der Waals equation, without allowance for attractive forces, is given by

\[ P = \frac{nRT}{V - nb} \] (2)

For \( CS_2 \), \( b \approx 0.040 \) L/mole, and its molecular weight 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?

\[
\frac{1.2 \text{ g}}{\text{mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{1 \text{ mole}}{80 \text{ g}} = \frac{1200}{80} = 15 \text{ moles/L}
\]

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

\[
V - nb = 0, \quad \frac{n}{V} = \frac{1}{b} = \frac{1}{0.040 \text{ L/mole}} = 25 \text{ mol/L}
\]

4. (10 pts) A Joule-Thomson coefficient has a value, \( \mu_{JT} = -1.25 \text{ mK/bar} \). Does the temperature increase or decrease and by how much when the pressure drop is 1 kbar?

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

\[
\Delta T = \mu_{JT} \Delta P
\]

\[
= (-1.25 \text{ mK/bar}) \times (10^3 \text{ bar})
\]

\[
\Delta T = +1.25 \text{ K}
\]

\( T \) increases
5. Consider a fluid whose equation of state obeys

\[ P = \rho RT (1 + b\rho) - a\rho^2; \quad \rho = n/V \] (3)

where \( a \) and \( b \) are constant. Derive:

(a) (12 pts) \( B_2(T), B_3(T) \), the second and third virial coefficients, respectively;

\[ Z = \frac{P}{\rho RT} = 1 + b\rho - \frac{a\rho}{RT} = 1 + B_2\rho + B_3\rho^2 + \cdots \]

\[ B_2 = b - \frac{a}{RT} \]

\[ B_3 = 0 \]

(b) (6 pts) and the dependence of \( dU(T, V) \) on \( V \), note

\[ \left( \frac{\partial U}{\partial V} \right)_T = T \left( \frac{\partial P}{\partial T} \right)_V - P \] (4)

\[ \left( \frac{\partial P}{\partial V} \right)_T = \rho R (1 + b\rho) \]

so

\[ \left( \frac{\partial U}{\partial V} \right)_T = \rho RT (1 + b\rho) - \left\{ \rho RT (1 + b\rho) - a\rho^2 \right\} \]

\[ = a\rho^2 \]

\[ dU = a\rho^2 dV = a\left( \frac{n}{V} \right)^2 dV \]
6. (12 pts) One mole of argon (assumed to be an ideal gas) is compressed reversibly from 1 L to 1 L at 300 K. Calculate $\Delta U$, $w_{on}$ and $q_{by}$. First, consider an ISOTHERMAL process and second, an ADIABATIC process.

<table>
<thead>
<tr>
<th></th>
<th>$\Delta U$ (kJ)</th>
<th>$w_{on}$ (kJ)</th>
<th>$q_{by}$ (kJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) isothermal</td>
<td>0</td>
<td>2.4</td>
<td>-2.4</td>
</tr>
<tr>
<td>(b) adiabatic</td>
<td>$C_V \Delta T$</td>
<td>$C_V \Delta T$</td>
<td>0</td>
</tr>
</tbody>
</table>

\[ a) \quad dU = 0 = q_{by} - \int_{V_1}^{V_2} P dV = q_{by} - RT \int_{V_1}^{V_2} \frac{dV}{V} \]

\[ W_{by} = -w_{on} = RT \ln \left( \frac{V_2}{V_1} \right) = RT \left[ \ln 1 - \ln e \right] = -RT \]

\[ q_{by} = W_{by} = -RT \]

\[ w_{on} = RT = 8 \frac{J}{K} \cdot 300 K = 2.4 kJ \]

\[ b) \quad \Delta U = C_V \Delta T = q_{by} + w_{on} = w_{on} \]

For Ar, $C_V = \frac{3}{2} R$

\[ \frac{T_2}{T_1} = \left( \frac{V_1}{V_2} \right)^{\gamma - 1} \quad \gamma \approx \frac{C_P}{C_V} - 1 = \frac{R}{C_V} = \frac{2}{3} \]

\[ T_2 = T_1 \cdot \left( \frac{e}{1} \right)^{\frac{2}{3}} \]

\[ \Delta T = T_2 - T_1 = T_1 \cdot \left( e^{\frac{2}{3}} - 1 \right) \]

\[ C_V \Delta T = \frac{3}{2} RT_1 \left[ e^{\frac{2}{3}} - 1 \right] = \frac{3}{2} \cdot 8 \frac{J}{K} \cdot 3000 \cdot \left[ e^{\frac{2}{3}} - 1 \right] \]

\[ C_V \Delta T = 3.6 kJ \left[ e^{\frac{2}{3}} - 1 \right] = w_{on} \]
7. (10 pts) Prove that

\[ \alpha_P = \left( \frac{\partial P}{\partial T} \right)_V \kappa_T \]

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

\text{cyclic rule}

8. (10 pts) Determine if \( dq_{rev} \) is an exact differential for an ideal gas which undergoes a reversible process.

\[ dU = C_v \, dT = dq_{rev} - P \, dv \]

\[ dq_{rev} = C_v \, dT + P \, dv \]

\[ \Rightarrow \left( \frac{\partial C_v}{\partial T} \right)_T = \left( \frac{\partial P}{\partial T} \right)_V = \frac{\partial}{\partial T} \left( \frac{RT}{V} \right) = \frac{R}{V} \]

\[ \Rightarrow dq_{rev} \text{ is not exact} \]

9. (10 pts) \( dU(S,V) \) is an exact differential, where \( S \) is the entropy and \( T \) is the absolute temperature. If

\[ dU(S,V) = T \, dS - P \, dV \]

then by the condition of exactness

\[ \left( \frac{\partial T}{\partial V} \right)_S = - \left( \frac{\partial P}{\partial S} \right)_V \]