

Chemistry 440 Hour exam

EXAM.....KEY.....

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16 November 2012

$$\begin{aligned}\Delta U &= q_{by} - P_{ext}\Delta V \\ dU(S, V, n_i) &= TdS - PdV + \sum_i \mu_i dn_i \\ H &= U + PV; \quad A = U - TS; \quad G = H - TS = \sum_i \mu_i n_i \\ C_v &= \left(\frac{\partial U}{\partial T}\right)_V; \quad C_p = \left(\frac{\partial H}{\partial T}\right)_P \\ \mu_{JT} &= \left(\frac{\partial T}{\partial P}\right)_H; \quad \alpha_P = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P \\ \kappa_T &= -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T \\ P_1 V_1^\gamma &= P_2 V_2^\gamma \quad \text{adiabatic process } \gamma = C_p/C_v \\ 1 \text{ bar} &= 10^5 \text{ Pa} \quad 1 \text{ L} = 10^{-3} \text{ m}^3\end{aligned}$$

	$\dots \frac{\Delta U}{RT} \dots$	$\dots \frac{\Delta S}{R} \dots$	$\dots \frac{(\Delta S)_{env}}{R} \dots$
Process a	0	$\ln 2$	$-\ln 2$
Process b	0	$\ln 2$	0
Process c	$\frac{3}{10}$	0	0

1. (18 pts) Calculate $\frac{\Delta U}{RT}$, $\frac{\Delta S}{R}$ and $\frac{\Delta S_{env}}{R}$ for the following processes which involve one mole of an ideal gas at an initial temperature T . Here *env* denotes the environment or the surroundings. To receive credit, place answers in the table.

- The gas is expanded isothermally and reversibly from 15 to 30 L.
- The gas is expanded isothermally against zero pressure as the volume increases from 15 to 30 L.
- The gas is compressed adiabatically and reversibly until its temperature reaches $\frac{6}{5}T$. Note $C_v = \frac{3}{2}R$, $C_p = \frac{5}{2}R$.

a) $\Delta U = 0 = q_{by} - w_{by} = q_{by} - \int P dV \Rightarrow \frac{q_{by}}{T} = \frac{RT}{T} \int \frac{dV}{V}$
 so $\Delta S = R \ln(30/15) = R \ln 2$, $\Delta S_{env} = -R \ln 2$

b) same ΔU , ΔS as before
 $\Delta S_{env} = 0$

c) adiabatic $\Rightarrow \Delta S = 0$
 reversible

$$\Delta U = C_v \Delta T = \frac{3}{2}R \left(\Delta T = \frac{6}{5}T - T \right) = \frac{3}{2}R \left(\frac{1}{5}T \right)$$

$$\Delta U/RT = 3/10$$

2. (10 pts) Complete the identity,

$$d \ln V = a dT + b dP \quad a = ?, b = ? \quad (1)$$

where a, b are expressed in terms of $\alpha_P, \kappa_T, C_v, C_p$ etc.

$$dV = \left(\frac{\partial V}{\partial T} \right)_P dT + \left(\frac{\partial V}{\partial P} \right)_T dP$$

$$\frac{dV}{V} = \alpha_P dT - \kappa_T dP = d \ln V$$

$$a = \alpha_P, \quad b = -\kappa_T$$

3. (24 pts) Derive the following starting from dU, dH, dG or dA .

$$\left(\frac{\partial S}{\partial P} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_P \quad (2)$$

$$dG = -SdT + VdP \quad \nearrow \text{Maxwell relation}$$

$$\frac{C_v}{T} = \left(\frac{\partial S}{\partial T} \right)_V \quad (3)$$

$$dU = C_v dT + \left(\frac{\partial U}{\partial V} \right)_T dV = Tds - PdV$$

$$\therefore @ \text{ const } V, \quad \frac{C_v}{T} = \left(\frac{\partial S}{\partial T} \right)_V$$

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T \left(\frac{\partial V}{\partial T}\right)_P \quad (4)$$

$$dH = Tds + vdp$$

$$\left(\frac{\partial H}{\partial P}\right)_T = V + T \left(\frac{\partial S}{\partial P}\right)_T \leftarrow \text{Maxwell from 3}$$

$$\left(\frac{\partial S}{\partial P}\right)_T = - \left(\frac{\partial V}{\partial T}\right)_P$$

$$\therefore \left(\frac{\partial H}{\partial P}\right)_T = V - T \left(\frac{\partial V}{\partial T}\right)_P$$

4. (8 pts) For the set of all processes conducted at constant T and V, equilibrium is attained when (a) ~~A~~ for the system is (b) ... ~~minimized~~

Fill in (a) with A, U, G, H or S. Fill in (b) with *minimized, maximized, left unchanged.*

5. (8 pts) The Helmholtz energy of a fluid is given by

$$A(n, V, T) = -a \frac{n^2}{V} - nRT \ln(V - nb) + f(T) \quad (5)$$

where a and b are constants and $f(T)$ is a function of temperature. Determine the pressure of the fluid.

$$dA = -SdT - PdV$$

$$P = - \left(\frac{\partial A}{\partial V} \right)_T = \frac{nRT}{V - nb} - a \left(\frac{n}{V} \right)^2$$

6. (8 pts) Calculate the change in Gibbs energy in Joules when 40 g of liquid ethanol (mass density of 0.80 g/cm^3) experiences a pressure increase of 20 bar.

$$dG = VdP, \quad \Delta G = V \cdot \Delta P$$

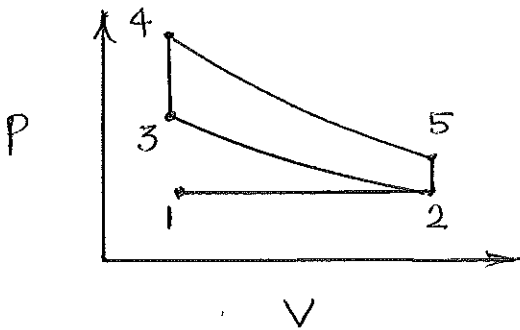
$$V = 40 \text{ g} \times \frac{1 \text{ cm}^3}{0.80 \text{ g}} \times \left(\frac{1 \text{ m}}{10^2 \text{ cm}} \right)^3 = 50 \times 10^{-6} \text{ m}^3$$

$$\Delta G = 20 \text{ bar} \times \frac{10^5 \text{ Pa}}{\text{bar}} \times 50 \times 10^{-6} \text{ m}^3 = 1000 \times 10^{-1} \text{ J}$$

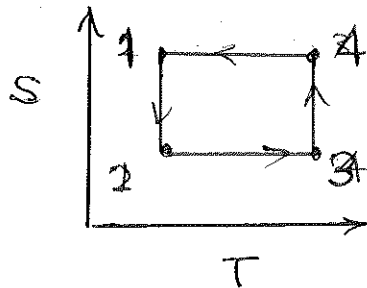
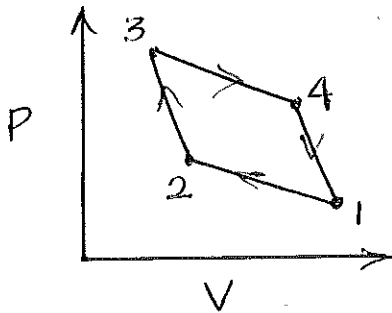
$$\text{or } \Delta G = 100 \text{ J}$$

7. (8 pts) Shown below is a plot of the Otto cycle in the P,V plane. Describe the real world significance of the following (mention q and w):

- step 3 → 4 oxidation of fuel, $q_{in} > 0$
- step 4 → 5 power step, generate work



8. (16 points) Also shown is the Carnot cycle as represented in the P,V plane. (a) Label the steps 1 → 2 and 2 → 3 citing the conditions applicable to the expansion or compression. (b) Replot the Carnot cycle in the S,T plane (the x-axis is T and the y-axis is S), labeling points 1...4 in accord with that of part (a). The explicit shape of the cycle is important.



- a) 1 → 2 isothermal compression
 2 → 3 adiabatic compression.

for the process with the indicated arrows

which has the larger entropy state 1 or 2?
 Along the isothermal path

$$\Delta S = R \ln(V_2/V_1)$$

$V_1 > V_2 \therefore$ state 1