Chemistry 440 Hour exam 2

EXAM KEY

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\begin{aligned}
1\ bar &= 10^5\ Pa \qquad 1\ L = 0.001\ m^3 \\
\Delta E &= q_{by} - P_{ext}\Delta V \\
dE(S,V,n_i) &= TdS - PdV + \sum_i \mu_i dn_i \\
H &= E + PV \\
A &= E - TS \\
G &= H - TS = \sum_i \mu_i n_i \\
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; \quad T_2/T_1 = (V_1/V_2)^{\gamma-1} \quad \text{adiabatic process} \quad \gamma = C_p/C_v \\
H &= -T^2\left(\frac{\partial (G/T)}{\partial T}\right)_P
\end{aligned}
$$

1. (16 pts) First and Second Law and phase transitions

(a) State the First and Second Laws of thermodynamics (for the universe and for the system) using equations.

$\Delta E_{uni} = 0$, $\Delta E_{sys} = q_{by} + W_{on}$ 1st law

$\Delta S_{uni} \geq 0$, $\Delta S_{sys} \geq q_{by}/T$ 2nd law

inequality sign for irreversible processes

(b) Express the Second Law in terms of a line integral around a closed path, using the irreversible heat, q and T.

$\oint dq/T \leq 0$

(c) Describe the behavior of $\left(\frac{\partial G}{\partial T}\right)_P$ and $\left(\frac{\partial G}{\partial P}\right)_T$ at a first order transition.

$dG = -SdT + Vdp$, $V = \left(\frac{\partial G}{\partial P}\right)_T$ and $S = -\left(\frac{\partial G}{\partial T}\right)_P$

both change discontinuously @ a first order transition

(d) Describe the behavior of $\left(\frac{\partial^2 G}{\partial T^2}\right)_P$ and $\left(\frac{\partial^2 G}{\partial P^2}\right)_T$ at a second order transition.

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_P = -\left(\frac{\partial S}{\partial T}\right)_P = -C_p/T$$

$$\left(\frac{\partial^2 G}{\partial p^2}\right)_T = \left(\frac{\partial V}{\partial P}\right)_T = -V K_T$$

both diverge @ the critical point.

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problem 2	$\Delta E/(RT_1)$	$\Delta S/R$
(a)	0	ln(2)
(b)	−3/4	−(1/2) ln 2

2. (12 pts) Consider the following expansion processes for one mole of a monatomic ideal gas at an initial temperature T_1, whose volume changes from one to two liters. Please complete the Table for the following cases:

   (a) The gas is expanded isothermally and **irreversibly**.

   (b) The gas is expanded adiabatically and **irreversibly** until its final temperature reaches $\frac{1}{2}T_1$.

a) $\Delta E = 0$; $dS = \underbrace{\left(\frac{\partial S}{\partial T}\right)_V}_{C_V/T} \underbrace{dT}_{0} + \left(\frac{\partial S}{\partial V}\right)_T dV$

but $dA = -SdT - PdV$

so that $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

$dS = \left(\frac{\partial P}{\partial T}\right)_V dV$

$P = \frac{RT}{V}$, $\frac{\partial P}{\partial T} = \frac{R}{V}$ and

$dS = R\,dV/V \Rightarrow \Delta S = R\ln(V_2/V_1) = R\ln(2)$

b) $C_V = \frac{3}{2}R$, $\Delta E = C_V(T_2 - T_1) = \frac{3}{2}R\left(\frac{1}{2}T_1 - T_1\right) = -\frac{3}{4}RT_1$

$\frac{\Delta E}{RT_1} = -\frac{3}{4}$

From above $\Delta S = C_V \ln(T_2/T_1) + R\ln(V_2/V_1)$

$= \frac{3}{2}R\ln\left(\frac{1}{2}\right) + R\ln(2) = -\frac{1}{2}R\ln(2)$

$\frac{\Delta S}{R} = -\frac{1}{2}\ln(2)$

3. (12 pts) Consider two blocks of a metallic substance. Block A consists of two moles of material at temperature T_A, block B consists of one mole of the same material at temperature T_B. Derive the enthalpy change ΔH; the entropy change, ΔS; and the final equilibrium temperature, T_f when the two blocks are in thermal contact.

$$\Delta H = C_p(T_f - T_A)\cdot 2 + C_p(T_f - T_B) = 0$$

$$\therefore \ 2T_f - 2T_A + T_f - T_B = 0, \quad 3T_f = 2T_A + T_B$$

$$T_f = \frac{1}{3}(2T_A + T_B)$$

$$dS = C_p\, dT/T$$

$$\frac{\Delta S}{C_p} = 2\int_{T_A}^{T_f} dT/T + \int_{T_B}^{T_f} dT/T = 2\ln\left(\frac{T_f}{T_A}\right) + \ln\left(\frac{T_f}{T_B}\right)$$

$$\Delta S = C_p \ln\left(\frac{T_f^3}{T_A^2\, T_B}\right)$$

4. (8 pts) What is the change in the molar entropy of iron when the pressure is increased by 10^3 bar at a constant temperature? Given: $\alpha_P = 3\times10^{-3}\ K^{-1}$, $\bar{V} = 0.01\ m^3/mol$.

$$dS = \left(\frac{\partial S}{\partial P}\right)_T dP \qquad \text{but } dG = -SdT + VdP$$

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

$$\therefore \ \Delta S = -\left(\frac{\partial V}{\partial T}\right)_P \Delta P = -\bar{V}\alpha_p \Delta P$$

$$\Delta S = -0.01\ \frac{m^3}{mol} \times 3\times10^{-3}\ \frac{1}{K} \times 10^3\ bar \times 10^5\ \frac{Pa}{bar}$$

$$\Delta S = 3\times10^3\ \frac{Pa\cdot m^3}{K} = -3\times10^3\ J/K\cdot mol$$

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5. (8 pts) The pressure of a fluid in the vicinity of the critical point can be written as a power series

$$
\begin{aligned}
P &= P_c + \left(\frac{\partial P}{\partial T}\right)_V \Delta T + \tfrac{1}{2}\left(\frac{\partial^2 P}{\partial T^2}\right)_V (\Delta T)^2 + \left(\frac{\partial P}{\partial \rho}\right)_T \Delta\rho + \tfrac{1}{2}\left(\frac{\partial^2 P}{\partial \rho^2}\right)_T (\Delta\rho)^2 \\
&+ \tfrac{1}{6}\left(\frac{\partial^3 P}{\partial \rho^3}\right)_T (\Delta\rho)^3 + \left(\frac{\partial^2 P}{\partial T \partial \rho}\right)_{T,\rho} \Delta\rho\Delta T + \cdots
\end{aligned}
$$

where $\Delta\rho = \rho - \rho_c$, $\Delta T = T - T_c$. Select two derivatives that vanish or diverge at the critical point and label accordingly.

$$\left(\frac{\partial P}{\partial \rho}\right)_T = \left(\frac{\partial^2 P}{\partial \rho^2}\right)_T = 0$$ by def'n of the critical point

6. (32 pts) Derive the following identities using as a starting point any of the relations given on page 1.

$$\left(\frac{\partial P}{\partial T}\right)_G = \cdots$$

$$dG = -SdT + VdP = 0 \Rightarrow \left(\frac{\partial P}{\partial T}\right)_G = \frac{S}{V}$$

$$\left(\frac{\partial \mu}{\partial V}\right)_{T,n} = -\left(\frac{\partial P}{\partial n}\right)_{T,V}$$

$$dA = -SdT - PdV + \mu dn$$

$$\therefore \left(\frac{\partial \mu}{\partial V}\right)_{n,T} = -\left(\frac{\partial P}{\partial n}\right)_{T,V}$$

Determine the function f,

$$\left(\frac{\partial S}{\partial V}\right)_P = f(\alpha_P, \kappa_T, C_p, C_v, etc.)$$

$$\left(\frac{\partial s}{\partial V}\right)_P = \frac{\left(\frac{\partial s}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial T}\right)_P} = \frac{\frac{C_p}{T}}{V\alpha_p} = \frac{C_p}{TV\alpha_p}$$

Differentiate A/T to demonstrate that

$$E = -T^2 \left(\frac{\partial(A/T)}{\partial T}\right)_V$$

$$\left(\frac{\partial(A/T)}{\partial T}\right)_v = \underbrace{\left(\frac{\partial A}{\partial T}\right)_v}_{-S} \frac{1}{T} - \frac{A}{T^2} = -\frac{(TS + A)}{T^2} = -\frac{E}{T^2}$$

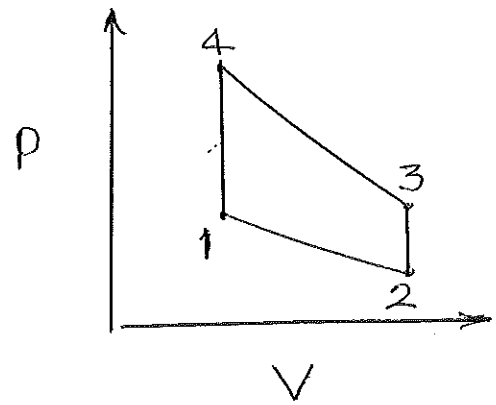
$$\therefore \quad E = -T^2 \left(\frac{\partial(A/T)}{\partial T}\right)_V$$

7. (12 pts) Shown is the idealized Stirling cycle: a two stroke version of the Otto cycle, which was discussed in class.

2pts (a) Indicate the direction of travel around the cycle by placing arrows on the diagram.

6 pts (b) Label the power stroke, the exhaust step, and the fuel oxidation step.

4pts (c) Calculate the *net* work performed by the working fluid in this cycle under the conditions that the appropriate steps are adiabatic and reversible.



a) direction of travel : $2 \rightarrow 1 \rightarrow 4 \rightarrow 3 \rightarrow 2$

b) power stroke $4 \rightarrow 3$

exhaust $3 \rightarrow 2$

oxidation $1 \rightarrow 4$

c) $\Delta E = \Delta E(4 \rightarrow 3) + \Delta E(2 \rightarrow 1) = \underbrace{q}_{0} - W_{by}$

$\therefore W_{by} = \Delta E(3 \rightarrow 4) + \Delta E(1 \rightarrow 2)$

$= C_v(T_4 - T_3) + C_v(T_2 - T_1)$

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