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 \\
dH(S,P,n_i) &= TdS + VdP + \sum_i \mu_i dn_i \\
dA(T,V,n_i) &= -SdT - PdV + \sum_i \mu_i dn_i \\
dG(T,P,n_i) &= -SdT + VdP + \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}
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problem 1	$\Delta H/(RT_1)$	$\Delta S/R$
(a)	0	ln(2)
(b)	−2	0

2. (12 pts) Consider the following processes which involves one mole of an ideal gas at an initial temperature T_1 and an initial volume of $V_1 = 1L$. Please complete the Table for the following cases:

   (a) The gas is expanded isothermally and **irreversibly** from one to two liters.

   (b) The gas is expanded adiabatically and reversibly until its temperature reaches $\frac{1}{2}T_1$. Note $C_v = 3R, C_p = 4R$.

a) $dS = \underbrace{\left(\frac{\partial S}{\partial T}\right)_V dT}_{0} + \underbrace{\left(\frac{\partial S}{\partial V}\right)_T}_{\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V}} dV$, $\quad \Delta S = R\ln(V_2/V_1)$

$= R\ln 2$

b) $\Delta H = C_p\Delta T = 4R\left(\frac{1}{2}T_1 - T_1\right) = -2RT_1$

1. (12 pts) Second Law and phase transitions

(a) State the Second Law of thermodynamics (first for the universe and second for the system).

$\Delta S_{uni} \geq 0$ the entropy of the universe increases for spontaneous processes

$\Delta S_{sys} \geq dq/T$

(b) Express the Second Law in terms of dq_{by}, T, dS.

$dS = dq_{by}/T$

reversible heat

(c) Name two thermodynamic properties that diverge at the gas-liquid critical point.

C_p (or C_v), κ_T

(d) Provide two quantities that change discontinuously at a phase transition of a single component fluid.

V, H (or S)

3. (18 pts) A solid at room temperature has a density of 8 g/cm^3, a molecular weight of 60 g/mole, $\kappa_T = 6 \times 10^{-12} Pa^{-1}$, $\alpha_P = 3 \times 10^{-5} K^{-1}$.

   (a) If the solid is exposed to a pressure increase of 100 bar, what is the change in the molar Gibbs energy (in J)?

   (b) What is the accompanying change in volume $\frac{\Delta V}{V}$? subject to the pressure increase of 100 bar at constant T?

   (c) If the temperature increases by 50 K, what is the accompanying change in volume $\frac{\Delta V}{V}$ at constant P?

(a) $dG = -SdT + VdP \rightarrow \Delta G = V\Delta P$

$$\Delta G = \frac{1\,cm^3}{8\,g} \times \frac{60\,g}{mole} \times \left(\frac{1\,M}{10^2\,cm}\right)^3 \times 100\,bar \times \frac{10^5\,Pa}{bar}$$

$$\Delta G = \frac{60}{8} \times \frac{10^7}{10^6} \frac{J}{mole} = 75\,J$$

(b) $$\frac{\Delta V}{V} = -\kappa_T \Delta P = -6 \times 10^{-12} \frac{1}{Pa} \times 10^2\,bar \times \frac{10^5\,Pa}{bar}$$

$$\frac{\Delta V}{V} = -6 \times 10^{-5}$$

(c) $$\frac{\Delta V}{V} = \alpha_P \Delta T = 3 \times 10^{-5} \frac{1}{K} * 50\,K = 150 \times 10^{-3}\,K$$

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4. (12 pts) The Gibbs energy of a fluid of N particles with a pressure P and temperature T is

$$G(N,P,T) = Nk_BT\ln\left(\frac{P\Lambda}{T^{5/2}}\right)$$

where Λ is a constant. Derive $S(N,P,T)$ and $\mu(N,P,T)$ for the fluid.

$$\mu = \left(\frac{\partial G}{\partial N}\right)_{T,P} = k_BT\ln(P\Lambda/T^{5/2})$$

$$S = -\left(\frac{\partial G}{\partial T}\right)_{P,N} = -Nk_B\ln\left(\frac{P\Lambda}{T^{5/2}}\right) - Nk_BT\frac{\partial}{\partial T}\left\{\ln(P\Lambda) - \frac{5}{2}\ln T\right\}$$

$$= \frac{5}{2}Nk_B - Nk_B\ln\left(\frac{P\Lambda}{T^{5/2}}\right)$$

5. (36 pts) Derive the following identities using as a starting point any of the relations given on page 1.

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

From $dG = -SdT + Vdp$

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

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

$dA = -SdT - PdV \Rightarrow (\partial A/\partial T)_V = -S$ and

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

$$\left(\frac{\partial E}{\partial P}\right)_T = V(aP - bT)$$

Express a and b as simply as possible in terms of $\alpha_P, C_v, C_p, \mu_{JT}, \kappa_T$.

$$dE = TdS - PdV$$

$$\left(\frac{\partial E}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T - P\left(\frac{\partial V}{\partial P}\right)_T = +PV\kappa_T - TV\alpha_P$$

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

$$= V\{P\kappa_T - \alpha_P T\}$$

$$a = \kappa_T$$

$$b = \alpha_P$$

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

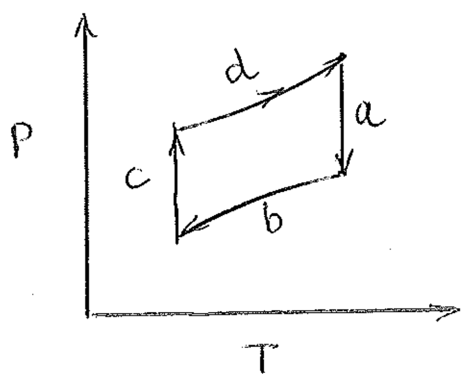
$$\frac{\partial}{\partial T}\left(\frac{A}{T}\right) = +\frac{1}{T}\{-SdT - PdV\} - \frac{1}{T^2}\{E - TS\}$$

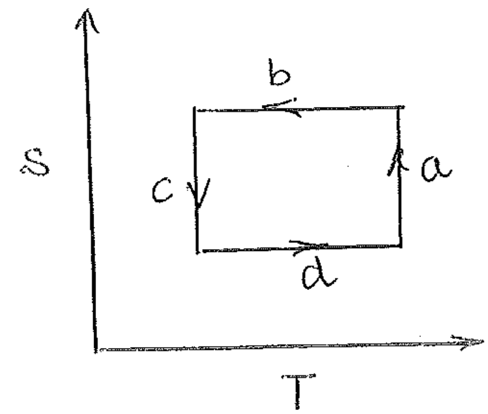
$$\left(\frac{\partial}{\partial T}\left(\frac{A}{T}\right)\right)_V = -E/T^2$$

6. (10 pts) The Carnot cycle consists of four steps:

- a) isothermal expansion $(T_1, P_1, V_1) \rightarrow (T_1, P_2, V_2)$;
- b) adiabatic expansion $(T_1, P_2, V_2) \rightarrow (T_2, P_3, V_3)$;
- c) isothermal compression $(T_2, P_3, V_3) \rightarrow (T_2, P_4, V_4)$; and
- d) an adiabatic compression $(T_2, P_4, V_4) \rightarrow (T_1, P_1, V_1)$.

Provide two graphs, P vs T and S vs T, labelling each step $a \cdots d$ for an ideal gas which is taken through the Carnot cycle.





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