

Chemistry 440 Final exam

EXAM KEY

Department of Chemistry, Oregon State University

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$$H = U + PV \quad A = U - TS \quad G = H - TS = \sum_i \mu_i n_i$$

$$dU(S, V, \{n_i\}) = TdS - PdV + \sum_i \mu_i dn_i$$

$$dH(S, P, \{n_i\}) = TdS + VdP + \sum_i \mu_i dn_i$$

$$dA(T, V, \{n_i\}) = -SdT - PdV + \sum_i \mu_i dn_i$$

$$dG(T, P, \{n_i\}) = -SdT + VdP + \sum_i \mu_i dn_i$$

$$nd\mu(T, V) = -SdT + VdP$$

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = T \left(\frac{\partial S}{\partial T} \right)_V; \quad C_P = \left(\frac{\partial H}{\partial T} \right)_P$$

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

$$P_1 V_1^\gamma = P_2 V_2^\gamma; \quad \frac{T_2}{T_1} = \left(\frac{V_1}{V_2} \right)^{\gamma-1} = \left(\frac{P_2}{P_1} \right)^{(\gamma-1)/\gamma}; \quad \gamma = C_P/C_V$$

$$\Delta G^\circ = -RT \ln K(T)$$

$$H = -T^2 \left(\frac{\partial(G/T)}{\partial T} \right)_P; \quad U = -T^2 \left(\frac{\partial(A/T)}{\partial T} \right)_V$$

$$R = 8 \text{ J}/(\text{K} \cdot \text{mol}) = 0.08 \text{ L} \cdot \text{atm}/(\text{K} \cdot \text{mol}) \quad 1 \text{ bar} = 10^5 \text{ Pa}$$

1. (41 pts) The laws

- (a) (12 pts) State the First and Second Laws of Thermodynamics in terms of properties of the universe and next, in terms of properties of the system. Define the terms in the equations.

$$\Delta U_{\text{universe}} = \Delta U_{\text{surroundings}} + \Delta U_{\text{system}} = 0$$

energy is conserved in the universe,

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

whereas changes in the energy of the system arise from heat absorbed by the system + work done on it.

$$\Delta S_{\text{universe}} \geq 0$$

$$\Delta S_{\text{sys}} \geq q_{\text{by}}/T$$

The entropy of the universe increases ~~for~~ for spontaneous processes and the entropy change of the system exceeds (or is equal to, for reversible processes) the heat absorbed by the system.

- (b) (6 pts) Prove that the internal energy of the system decreases for all spontaneous processes that occur at constant S and V.

$$Tds \geq dq_{\text{by}} \quad \text{but} \quad dU = dq_{\text{by}} - P_{\text{ext}}dV$$

$$\therefore dq_{\text{by}} = dU + P_{\text{ext}}dV$$

$$Tds \geq dU + P_{\text{ext}}dV$$

@ cons S, V we have $0 \geq dU|_{S,V}$

\therefore a spontaneous process, subject to const S, V will decrease U.

- (c) (15 pts) Express the derivatives of A in the series expansion in terms of variables of state, compressibilities, expansion coefficients, heat capacities, etc.

$$A(T + \Delta T, V + \Delta V) = A(T, V) + \Delta V \left(\frac{\partial A}{\partial V} \right)_T + \frac{1}{2} (\Delta V)^2 \left(\frac{\partial^2 A}{\partial V^2} \right)_T \\ + \Delta T \left(\frac{\partial A}{\partial T} \right)_V + \frac{1}{2} (\Delta T)^2 \left(\frac{\partial^2 A}{\partial T^2} \right)_V + \Delta T \Delta V \left(\frac{\partial}{\partial V} \left(\frac{\partial A}{\partial T} \right)_V \right)_T$$

$$dA = -SdT - PdV$$

$$\therefore \left(\frac{\partial A}{\partial V} \right)_T = -P \quad \left(\frac{\partial A}{\partial T} \right)_V = -S$$

$$\left(\frac{\partial^2 A}{\partial V^2} \right)_T = - \left(\frac{\partial P}{\partial V} \right)_T = 1/V\kappa_T \quad \left(\frac{\partial^2 A}{\partial T^2} \right)_V = - \left(\frac{\partial S}{\partial T} \right)_V = -\frac{C_V}{T}$$

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T, \quad \kappa_T V = - \left(\frac{\partial V}{\partial P} \right)_T$$

$$\left(\frac{\partial^2 A}{\partial T \partial V} \right) = - \left(\frac{\partial P}{\partial T} \right)_V = \frac{\alpha_P}{\kappa_T}$$

$$\Delta A(T, V) = -P\Delta V - S\Delta T + \frac{1}{2} \frac{1}{V\kappa_T} (\Delta V)^2 - \frac{1}{2} \frac{C_V}{T} (\Delta T)^2 - \left(\frac{\partial P}{\partial T} \right)_V \Delta V \Delta T$$

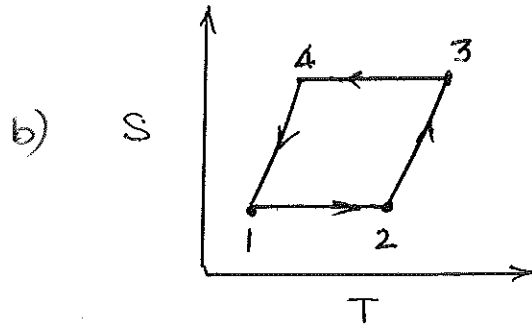
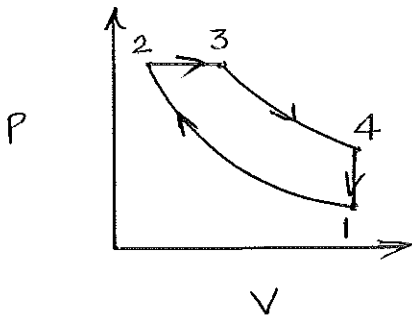
- (d) (8 pts) Select a derivative of $A(T, V)$ that has a critical anomaly. Likewise, select the derivative that behaves discontinuously at a first order transition.

$\left(\frac{\partial^2 A}{\partial T^2} \right)_V \sim C_V$ has a critical anomaly
 where $\left(\frac{\partial A}{\partial T} \right)_V$ is discontinuous at a first order transition

2. (16 pts) Shown in the $P - V$ diagram is the idealized Diesel cycle: steps $1 \rightarrow 2$ and $3 \rightarrow 4$ are adiabatic; $2 \rightarrow 3$ is the fuel injection/ignition step at constant pressure and $4 \rightarrow 1$ is the exhaust (and cooling) step at constant volume.

(a) Calculate the entropy change for an ideal gas in the $4 \rightarrow 1$ step. On the basis of your answer,

(b) plot S vs. T for the cycle. Be careful regarding the curvature of the lines in the plot.



$$a) \quad ds = \left(\frac{\partial s}{\partial T} \right)_V dT + \left(\frac{\partial s}{\partial V} \right)_T dV \leftarrow 0$$

$$\Delta S(4 \rightarrow 1) = C_V \int_{T_4}^{T_1} dT/T = C_V \ln(T_1/T_4) < 0$$

$$\therefore S(4) > S(1)$$

since V is constant, $P_1 \sim T_1$, $P_4 \sim T_4$

$$\text{and } \Delta S(4 \rightarrow 1) = C_V \ln(P_1/P_4) < 0$$

a, ΔT	-2 K
b, $\frac{\Delta V}{V}$	6×10^{-3}
c, ΔT	-100 K
d, $\frac{\Delta V}{V}$	-0.5
e, $\Delta H/\text{mole}$	700 J/mole
f, $\Delta\mu/\bar{V}$	10^8 Pa
g, Π	$2.4 \times 10^5 \text{ Pa}$ ← or 24 atm

3. (35 pts) Provide numerical values in the above table for water at the designated conditions. Note that

$$C_P = 70 \text{ J}/(\text{K mole}), \quad \kappa_T = 5 \times 10^{-5} \text{ bar}^{-1}, \quad \alpha_P = 6 \times 10^{-4} \text{ K}^{-1} \quad (1)$$

$$K_f = 2 \text{ K}/(\text{mol/kg}), \quad \rho(L) = 1.0 \text{ g}/\text{cm}^3, \quad \rho(S) = 0.9 \text{ g}/\text{cm}^3 \quad (2)$$

$$\Delta S(L \rightarrow S) = -20 \text{ J}/(\text{K mole}) \quad (3)$$

Calculate the change in

- melting point when we add one mole of non-dissociating solute to one kg of water
- volume when the temperature is increased by 10 K at a fixed pressure of 1 bar;
- melting point when we apply a pressure 10 kbar
- volume when we apply a pressure of 10 kbar at 300 K
- enthalpy change when the temperature is increased by 10 K
- chemical potential if the pressure increases by 10 kbar
- osmotic pressure of a one molar solution at 300 K.

$$(a) \Delta T = K_f m = 2 \text{ K}$$

$$(b) \frac{\Delta V}{V} = \alpha_P \Delta T = 6 \times 10^{-4} \frac{1}{\text{K}} \cdot 10 \text{ K} = 6 \times 10^{-3}$$

$$(d) \frac{\Delta V}{V} = -\kappa_T \Delta P = -5 \times 10^{-5} \frac{1}{\text{bar}} \cdot 10^4 \text{ bar} = -5 \times 10^{-1} = -0.5$$

$$(e) \Delta H = C_p \Delta T = \left(70 \frac{\text{J}}{\text{K} \cdot \text{mole}}\right) (10 \text{ K}) = 700 \text{ J/mole}$$

$$(f) d\mu = \bar{V} dp, \quad \frac{\Delta \mu}{\bar{V}} = \Delta P = 10^4 \text{ bar} \\ = 10^6 \text{ kPa} = 10^5 \text{ Pa}$$

$$(g) \pi = CRT = \left(\frac{1 \text{ mol}}{\text{l}}\right) (300 \text{ K}) \left(0.08 \frac{\text{l} \cdot \text{atm}}{\text{K} \cdot \text{mol}}\right) \\ = 2.4 \text{ atm} \sim 2.4 \text{ bar} \sim 2.4 \times 10^5 \text{ Pa}$$

$$(c) d\mu_L = d\mu_S = -\bar{S}dT + \bar{V}dp \quad \text{rearrange}$$

$$\Delta T = \left(\frac{\Delta V}{\Delta S}\right) \Delta P = \frac{\Delta V(S \rightarrow L)}{\Delta S(S \rightarrow L)} \Delta P$$

$$\Delta V(S \rightarrow L) = \left(1 - \frac{1}{0.9}\right) \frac{\text{cm}^3}{\text{g}} \times 18 \frac{\text{g}}{\text{mole}} \times \left(\frac{1 \text{ m}}{10^2 \text{ cm}}\right)^3 \\ = (18 - 20) \times 10^{-6} \text{ m}^3 = -2 \times 10^{-6} \text{ m}^3$$

$$\frac{\Delta V(S \rightarrow L)}{\Delta S(S \rightarrow L)} = \frac{2 \times 10^{-6} \text{ m}^3/\text{mol}}{20 \text{ J/K} \cdot \text{mole}} = 1 \times 10^{-7} \frac{\text{m}^3 \cdot \text{K}}{\text{J}}$$

$$\Delta T = \left(10^{-7} \frac{\text{m}^3 \cdot \text{K}}{\text{J}}\right) 10^4 \text{ bar} \times 10^5 \frac{\text{Pa}}{\text{bar}} = -10^2 \text{ K}$$

4. (30 pts) Prove or derive the following.

(a) Prove

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

$$dH = Tds + vdp$$

$$\left(\frac{\partial H}{\partial P}\right)_T = T \left(\frac{\partial s}{\partial P}\right)_T + v$$

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

but $dG = -sdt + vdp$
 $\therefore \left(\frac{\partial s}{\partial P}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_P$

(b) Evaluate $\left(\frac{\partial H}{\partial P}\right)_T$ and $\left(\frac{\partial T}{\partial P}\right)_H$ for a fluid obeying

$$P = \frac{nRT}{V - nb}, \quad C_v = \frac{3}{2}R \cdot n \quad (5)$$

using Eq(4).

$$\left(\frac{\partial v}{\partial T}\right)_P \Rightarrow dp = \left(\frac{\partial p}{\partial T}\right)_v dT + \left(\frac{\partial p}{\partial v}\right)_T dv$$

$$dp = \left(\frac{nRdT}{V - nb}\right) dT - \frac{nRT}{(V - nb)^2} dv = 0$$

$$\text{so } \left(\frac{\partial v}{\partial T}\right)_P = \frac{V - nb}{T}$$

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

Next,

$$\left(\frac{\partial T}{\partial P}\right)_H = - \left(\frac{\partial T}{\partial H}\right)_P \left(\frac{\partial H}{\partial P}\right)_T = - \frac{1}{C_p} \left(\frac{\partial H}{\partial P}\right)_T = - \frac{2}{5R \cdot n} n \cdot b = - \frac{2b}{5R}$$

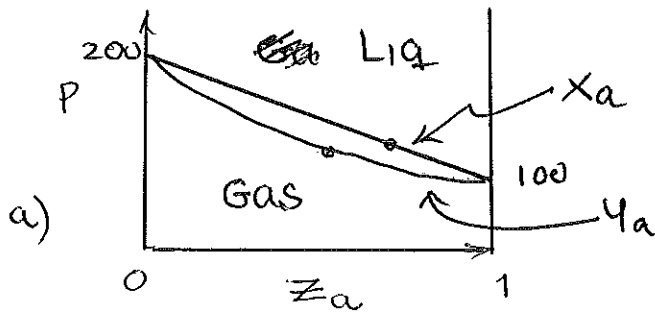
$$C_p = C_v + R = \frac{5}{2}R \cdot n$$

↑ should have an n here

5. (18 pts) Binary mixtures.

(a) Sketch P vs. z_a for a two component fluid with ideal liquid and gas phases, subject to $P_a^0 = 100$ kPa, $P_b^0 = 200$ kPa. Label the gas and liquid phases, and the coexistence region.

(b) If $x_a = \frac{2}{3}$, show that $y_a = \frac{1}{2}$.



b) If $x_a = \frac{2}{3}$, $P_a = P_a^0 x_a = \left(\frac{2}{3}\right) 100 \text{ kPa} = \frac{200}{3} \text{ kPa}$

$$x_b = \frac{1}{3}, \quad P_b = \left(\frac{1}{3}\right) (200 \text{ kPa}) = \frac{200}{3} \text{ kPa}$$

$$P_{\text{tot}} = P_a + P_b = \frac{400}{3} \text{ kPa}$$

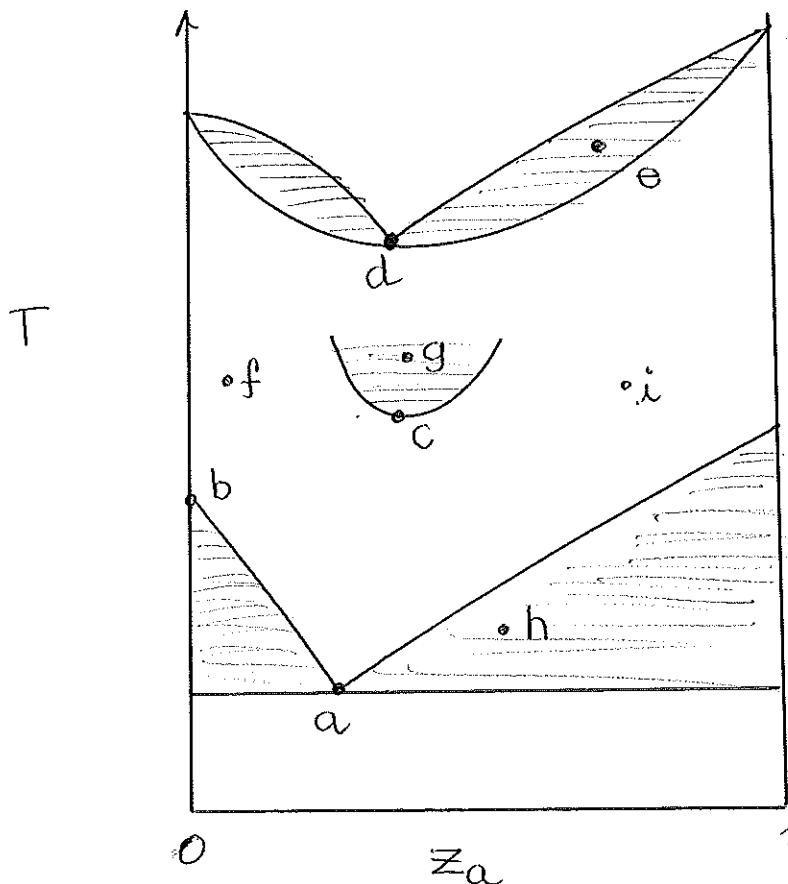
$$y_a = \frac{P_a}{P} = \frac{\left(\frac{200}{3}\right) \text{ kPa}}{\frac{400}{3} \text{ kPa}} = \frac{1}{2}$$

6. (27 pts) The phase diagram below represents a two component system with gas, liquid and solid phases. Shaded areas correspond to coexistence regions. The following points have special names attributed to them. Provide these terms:

- (a) eutectic pt.
- (b) ~~B~~ melting pt. of pure B.
- (c) ~~azeotrope~~ lower critical point
- (d) ... azeotrope

Identify the phases present

- (e) coexisting phases of L, G mixture
- (f) liquid mixture of A + B.
- (g) liquid mixture of two liquid phases, one rich in A one dilute in A
- (h) $A(s) \rightleftharpoons A(L), B(L)$
- (i) liquid mixture of A + B



7. (18 pts) Express the following thermodynamic quantities in SI units

(a) $S/(nR)$ unit less

(b) q_{rev}/T , J/K

(c) $\kappa_S \sim 1/p \sim 1/Pa$

(d) $A/T \sim R \sim J/K$

(e) $C_P T^2 \sim J \cdot K$

(f) $\mu/(RT) \sim$ unit less

8. (15 pts) If the temperature dependence of an equilibrium constant is

$$\ln K(T) = a_0 + a_1/T + a_2/T^2 \quad (6)$$

where a_0, a_1, a_2 are constants, what are the accompanying T-dependences of ΔH and ΔS ?

$$\Delta G = -RT \ln K,$$

$$\frac{\Delta G}{T} = -R \ln K$$

$$\Delta H = -T^2 \frac{\partial (\Delta G/T)}{\partial T} = +RT^2 \frac{\partial \ln K}{\partial T} = RT^2 \frac{\partial}{\partial T} \left(a_0 + \frac{a_1}{T} + \frac{a_2}{T^2} \right)$$

$$\Delta H = RT^2 \left(-\frac{a_1}{T^2} - \frac{2a_2}{T^3} \right) = -R \left(a_1 + \frac{2a_2}{T} \right) \quad (5)$$

$$\Delta G = \Delta H - T\Delta S, \quad \Delta S = \frac{(\Delta H - \Delta G)}{T}$$

$$\Delta S = -R \left(a_1 + \frac{2a_2}{T} \right) + RT \left(a_0 + \frac{a_1}{T} + \frac{a_2}{T^2} \right)$$

$$\Delta S = (RTa_0 - Ra_2/T) / T = Ra_0 - Ra_2/T^2 \quad (5)$$