Chemistry 440 Final exam

Department of Chemistry, Oregon State University, Corvallis, OR 97331
(Dated: 4 December 2006)

\[ R = \frac{8 \text{J}}{(\text{K} \cdot \text{mol})} = 0.08 \text{L} \cdot \text{atm}/(\text{K} \cdot \text{mol}) \]

\[ 1 \text{bar} = 10^5 \text{Pa} \]

\[ \Delta U = q_{ab} - p_{ext} \Delta V \]

\[ dU(S,V,\{n_i\}) = T dS - P dV + \sum_i \mu_i d\mu_i \]

\[ dH(S,P,\{n_i\}) = T dS + V dP + \sum_i \mu_i d\mu_i \]

\[ dA(T,V,\{n_i\}) = -S dT - P dV + \sum_i \mu_i d\mu_i \]

\[ dG(T,P,\{n_i\}) = -S dT + V dP + \sum_i \mu_i d\mu_i \]

\[ n d\mu(T,V) = -S dT + V dP \]

\[ H = U + PV \]

\[ A = U - TS \]

\[ G = H - TS = \sum_i \mu_i n_i \]

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

\[ \left( \frac{\partial H}{\partial F} \right)_T = V - T \left( \frac{\partial V}{\partial T} \right)_P ; \]

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

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

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

\[ \Delta G^o = -RT \ln K(T) \]

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

\[ F = 2 + C - P \]
1. (39 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.

1st LAW: Energy of the universe is conserved, $\Delta U(\text{uni}) = 0$

Energy of the system changes if the system absorbs heat or if work is done on the system,

$\Delta U = q_{by} + w_{on}$

2nd LAW: The entropy of the universe increases in all spontaneous processes. For the system, changes in the entropy exceed $dq/T$

$\frac{ds}{dt} > \frac{dq}{T}$ Equal signs depict reversible processes.

(b) (6 pts) Prove that the Helmholtz energy of the system decreases for all spontaneous processes that occur at constant $T$ and $V$.

$Tds > dq$, if $V$ is constant

$dU = dq_v$

$Tds > dU \Rightarrow dU - Tds \leq 0$

and at constant $T$,

$d(U - Ts) \leq 0$ or

$dA|_{T,V} \leq 0$
(c) (15 pts) Express the derivatives of $A$ in the series expansion in terms of variables of state, compressibilities, expansion coefficients, heat capacities, etc.

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

$$dA = -SdT - pdV$$

\begin{align*}
\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 = \frac{1}{\kappa_T} V \\
\left( \frac{\partial^2 A}{\partial T^2} \right)_V &= -\left( \frac{\partial S}{\partial T} \right)_V = -CV, \quad \left( \frac{\partial}{\partial T} \left( \frac{\partial A}{\partial V} \right) \right)_V = -\left( \frac{\partial p}{\partial V} \right)_T = \frac{\alpha_p}{\kappa_T}
\end{align*}

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

$$V \kappa_T = -\left( \frac{\partial V}{\partial p} \right)_T$$

(d) (6 pts) Select a derivative of $A(T, V)$ that has a critical anomaly and discuss. Likewise, select the derivative that behaves discontinuously at a first order transition and elaborate.

1st order discontinuity $S$ behaves discontinuously at a transition

2nd order transition $CV$ diverges, although

$$\left( \frac{\partial^2 A}{\partial V^2} \right) \to 0.$$
2. (16 pts) Reversible Cycles for ideal gases.

(a) Draw a Carnot cycle in the $P, V$ plane that has two isothermal steps (at temperatures $T_1 < T_2$) and two adiabatic steps. Show that $\Delta U = 0$ for the cycle.

(b) Plot $S$ vs. $V$ for a cycle consisting of two adiabatic steps and two constant volume heating/cooling steps. Show that $\Delta S = 0$ for this process.

\[
\Delta U = \Delta U(A \rightarrow B) + \Delta U(B \rightarrow C) + \Delta U(C \rightarrow D) + \Delta U(D \rightarrow A)
\]

\[
\text{isothermals } \Rightarrow \Delta U = C_V \Delta T = 0
\]

\[
\Delta U = C_V (T_1 - T_2) + C_V (T_2 - T_1) = 0
\]

\[
B \rightarrow C \quad D \rightarrow A
\]

\[
\Delta S = \Delta S(A \rightarrow B) + \Delta S(B \rightarrow C) + \Delta S(C \rightarrow D) + \Delta S(D \rightarrow A)
\]

\[
\text{adiab, reversible } \Rightarrow \Delta S = 0
\]

\[
\Delta S = C_V \ln\left(\frac{T_{\text{fin}}}{T_{\text{init}}}\right)
\]

\[
\Delta S = C_V \ln\left(\frac{T_C}{T_B}\right) + C_V \ln\left(\frac{T_A}{T_D}\right) = C_V \ln\left(\frac{T_A T_C}{T_B T_D}\right)
\]

But

\[
\frac{T_B}{T_A} = \left(\frac{V_A}{V_B}\right)^{\gamma - 1} = \left(\frac{V_{\text{small}}}{V_{\text{large}}}\right)^{\gamma - 1}, \quad \frac{T_B}{T_C} = \left(\frac{V_{\text{large}}}{V_{\text{small}}}\right)^{\gamma - 1}
\]

\[
\therefore \frac{T_B T_D}{T_A T_C} = 1 \quad \text{and} \quad \text{vanishes}
\]

\[
\Delta S = 0
\]
3. (28 pts) Provide numerical values in the above table for water at the designated conditions. Note that $C_p = 70 \text{ J/(K mole)}$, $\kappa_T = 5 \times 10^{-5} \text{ bar}$, $\alpha_P = 6 \times 10^{-4} \text{ K}^{-1}$, $K_f = 2 \text{ K/(mol/kg)}$, $\rho(\text{liq}) = 1.0 \text{ g/cm}^3$, $\rho(\text{ice}) = 0.9 \text{ g/cm}^3$, $\Delta S(\text{liq} \rightarrow \text{solid}) = -20 \text{J/(K mole)}$.

Calculate the change in

(a) volume when the temperature is increased by 10K at a fixed pressure of 1 bar;
(b) melting point when we apply a pressure 10 kbar
(c) volume when we apply a pressure of 10 kbar at 300K
(d) melting point when we add one mole of non-dissociating solute to one kg of water
(e) enthalpy change when the temperature increase by 10 K
(f) chemical potential if the pressure increases by 10 kbar
(g) osmotic pressure when 1 mole of solute is added to make a one molar solution at 300K.

\[
\begin{array}{|c|c|}
\hline
\text{a, } \Delta V/V & 6 \times 10^{-3} \\
\hline
\text{b, } \Delta T & -0.1 \\
\hline
\text{c, } \Delta V/V & -0.5 \\
\hline
\text{d, } \Delta T & 2 \text{ K} \\
\hline
\text{e, } \Delta H/\text{mole} & 700 \text{ J} \\
\hline
\text{f, } \Delta \mu/\text{V} & 10^4 \text{ bar} = 10^9 \text{ Pa} \\
\hline
\text{g, } \Pi & 24 \text{ atm} \\
\hline
\end{array}
\]

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

(b) $\frac{\Delta P}{\Delta T} = \frac{\Delta S}{\Delta V} = \frac{-20 \text{ J}}{(0.9 \text{ g}) \times 18 \text{ g} \times 1 \text{ mol} \times (10^{-3} \text{ cm})^3} = \frac{-20 \text{ J}}{2 \times 10^{-6}}$

(c) $\kappa_T = -\frac{1}{V} \frac{\partial^2 V}{\partial P^2} \bigg|_T \Delta V = -K_T \Delta P = -5 \times 10^{-5} \text{ bar} \times 10 \times 10^3 \text{ bar} = -0.5$

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

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

(f) $\left(\frac{\Delta \mu}{\Delta P}\right) = \frac{\Delta V}{V} \Rightarrow \Delta \mu/\Delta P = 10 \text{ kbar} = 10^9 \text{ Pa}$

(g) $\Pi = C \cdot R \cdot T = (1 \text{ mole}) \left(0.08 \text{ L atm/mol K} \cdot \text{K} \right) \times 300 = 24 \text{ atm}$
4. (40 pts) Prove or derive the following.

(a) Prove

\[ p \left( \frac{\partial \mu}{\partial \rho} \right)_T = \left( \frac{\partial p}{\partial \rho} \right)_T \]  

\[ dG = d(\eta u) = n du + \mu d\eta = -S dT + v dp + \mu d\eta \]

\[ n du = -S dT + v dp \quad \text{const} \ T \Rightarrow \]

\[ n du = v dp \quad \Rightarrow \quad n \left[ \frac{\partial u}{\partial p} \right]_T = v \left[ \frac{\partial \rho}{\partial p} \right]_T \]

\[ \sigma \rho \left[ \frac{\partial u}{\partial T} \right] = \left[ \frac{\partial \rho}{\partial T} \right] \]

(b) Prove

\[ \left( \frac{\partial H}{\partial F} \right)_T = V - T \left( \frac{\partial V}{\partial T} \right)_p \]

\[ dh = T ds + v dp \quad \Rightarrow \quad \left[ \frac{\partial H}{\partial T} \right]_p = V + T \left[ \frac{\partial s}{\partial T} \right]_p \]

\[ \left[ \frac{\partial V}{\partial T} \right]_p = - \left[ \frac{\partial s}{\partial T} \right]_p \]

\[ \left[ \frac{\partial H}{\partial T} \right]_p = V - T \left[ \frac{\partial s}{\partial T} \right]_p \]

(c) Evaluate \( \left( \frac{\partial H}{\partial T} \right)_p \) for a fluid obeying

\[ P = \frac{RT}{V - nb}, \quad V - nb = \frac{RT}{P} \]

\[ V = \eta b + \frac{nRT}{\rho} \]

\[ \left[ \frac{\partial V}{\partial T} \right]_p = \frac{nR}{P} \quad \Rightarrow \quad \left[ \frac{\partial H}{\partial T} \right]_p = \frac{n b + nRT}{P} - \frac{RT}{P} = nb \]
(d) The internal energy obeys

\[ dU(T, V) = C_v dT + a(T, V) dV \]  

Express \( a(T, V) \) in terms of \( P, T \) and \( V \) for an arbitrary material.

\[ a(T, V) = \frac{\partial U}{\partial V} \bigg|_T, \quad dU = T ds - PdV \quad \text{so} \]

\[ \frac{\partial U}{\partial V} = T \frac{\partial s}{\partial V} - P \]

\[ \Rightarrow a(T, V) = T \left( \frac{\partial P}{\partial V} \bigg|_T \right) - P \]

5. (18 pts) Binary mixtures.

(a) Sketch \( \mu(T, P) \) vs. \( T \) and \( \mu(T, P) \) vs. \( P \) for a pure substance with solid, liquid, and gas phases.

(b) Show graphically why the increase in boiling point is always much less than the decrease in freezing point.
6. (27 pts) The phase diagram below represents a 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
(b) LIQUID–LIQUID CRITICAL POINT
(c) AZEOTROPE
(d) BOILING POINT OF PURE B

Identify the phases present
(e) GAS PHASE
(f) LIQUID ↔ GAS
(g) LIQUID MIXTURE
(h) TWO SEPARATE LIQUID PHASES
(i) LIQUID ↔ SOLID PHASE
7. (18 pts) Express the following thermodynamic functions in SI units

(a) the entropy
\[ \frac{J}{K} \]

(b) the reversible heat
\[ J \]

(c) the adiabatic compressibility
\[ K_S = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_s = \frac{1}{\rho a} \]

(d) the Helmholtz energy
\[ J \]

(e) the heat capacity at constant pressure
\[ \frac{J}{K} \]

(f) the chemical potential
\[ \frac{J}{\text{mole}} \]

8. (14 pts) Equilibrium. If we were to measure the temperature dependence of an equilibrium constant and found that

\[ \ln K(T) = a_0 + a_1/T + a_2/T^2 \]

where \( a_0, a_1, a_2 \) are constants, what is the accompanying \( T \)-dependence of \( \Delta H \) and \( \Delta S \)? Hint: see front page.

\[ \Delta G = -RT \ln K = -RT \left( a_0 + a_1/T + a_2/T^2 \right) \]

\[ \Delta G = -R \left( a_0 T + a_1 + a_2/T \right) \]

But
\[ \Delta S = -\frac{\partial \Delta G}{\partial T} = R \left[ a_0 - a_2/T^2 \right] \]

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

\[ \Delta H = RT^2 \left[ -a_1/T^2 - 2a_2/T^3 \right] = -R \left[ a_1 + 2a_2/T \right] \]