

Oregon State University, Department of Chemistry

Chemistry 440 Hour exam 2, 18 November 2009

Name EXAM KEY

$$\Delta U = q_{by} - P_{ext}\Delta V$$

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

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

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

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

$$H = U + PV$$

$$A = U - TS$$

$$G = H - TS = \sum_i \mu_i n_i$$

$$C_v = \left(\frac{\partial U}{\partial T} \right)_V$$

$$C_p = \left(\frac{\partial H}{\partial T} \right)_P$$

$$\mu_{JT} = \left(\frac{\partial T}{\partial P} \right)_H$$

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

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

$$P_1 V_1^\gamma = P_2 V_2^\gamma; \quad T_2/T_1 = (V_1/V_2)^{\gamma-1} \quad \text{adiabatic process} \quad \gamma = C_p/C_v$$

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

$$\left(\frac{\partial P}{\partial T} \right)_{coex} = \frac{\Delta H}{T\Delta V}$$

problem 1	$\Delta U/(RT)$	$\Delta S/R$	$\Delta S_{env}/R$
(a)	0	$\ln 2$	$-\ln 2$
(b)	0	$\ln 2$	0
(c)	$3/10$	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 surroundings. Place your answers in the above box.

(a) The gas is expanded isothermally and reversibly from 10 to 20 L.

(b) The gas is expanded isothermally against zero pressure as the volume increases from 10 to 20 L.

(c) The gas is compressed adiabatically and reversibly until the temperature reaches $\frac{6}{5}T$. $C_v = \frac{3}{2}R$, $C_p = \frac{5}{2}R$

a) $\Delta U = 0 \Rightarrow dU = Tds - PdV = 0$
 $ds = \frac{P}{T}dV \rightarrow \Delta S = \int R dV/V = R \ln(V_2/V_1)$
 $\Delta S = R \ln(2), \Delta S_{env} = -R \ln(2)$

b) $\Delta U = 0, \Delta S = R \ln(2)$ same end pt as above
 but $\Delta U = 0 = q_{by} + \underset{0}{w_{on}} \Rightarrow q_{by} = 0,$
 ad $\Delta S_{env} = 0$

c) $\Delta U = C_v \Delta T = \frac{3}{2}R(\frac{1}{5}T) = \frac{3}{10}RT$
 $\Delta S = 0, \Delta S_{env} = 0$

2. (8 pts) Calculate the melting point of ice when it is exposed to a pressure of 101 bar. Assume that the density of ice is 0.90 g/cm^3 and that of liquid water is 1.00 g/cm^3 . $1 \text{ bar} = 10^5 \text{ Pa}$, and $\Delta S(L \rightarrow S) = -20 \text{ J/(K} \cdot \text{mole)}$.

$$\left(\frac{\partial P}{\partial T}\right)_{\text{coex}} = \frac{\Delta S}{\Delta V} \Rightarrow \Delta T = \frac{\Delta P \cdot \Delta V}{\Delta S}$$

$$\Delta V = V_L - V_S = \left(1.00 \frac{\text{cm}^3}{\text{g}} - \frac{1}{0.90} \frac{\text{cm}^3}{\text{g}}\right) * \frac{18 \text{ g}}{\text{mole}} * \left(\frac{1 \text{ M}}{10^2 \text{ cm}}\right)^3$$

$$= -0.10 * 18 * 10^{-6} \text{ m}^3 \approx -1.8 * 10^{-6} \text{ m}^3$$

$$\Delta T = \frac{[100 \text{ bar} * 10^5 \text{ Pa/bar}] [-1.8 * 10^{-6} \text{ m}^3]}{+20 \text{ J/K}} = -\frac{18}{20} \text{ K} \approx -1 \text{ K}$$

melting pt decreases by 1K, $T_m \approx 272 \text{ K}$.

3. (8 pts) The vapor pressure of a liquid obeys

$$\ln P = 20 - 12000/T \quad (1)$$

where the pressure is measured in units of bar and the temperature in Kelvin. Derive a numerical value of the normal boiling point temperature and ΔH .

normal boiling $P = 1 \text{ bar}$

$$\ln 1 = 0 = 20 - 12000/T_B$$

$$T_B = \frac{12,000}{20} = 600 \text{ K}$$

but

$$\left(\frac{\partial P}{\partial T}\right) = \frac{\Delta S}{\Delta V} = \frac{\Delta H}{RT/P} \rightarrow \left(\frac{\partial \ln P}{\partial P}\right) = \frac{\Delta H(L \rightarrow G)}{RT^2}$$

$$\frac{\partial}{\partial T} \left\{ 20 - \frac{12000}{T} \right\} = \frac{12000}{T^2} = \frac{\Delta H}{RT^2}$$

$$\therefore \Delta H(L \rightarrow G) = 12,000 R$$

4. (8 pts) The Helmholtz energy of a van der Waals fluid is given by

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

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

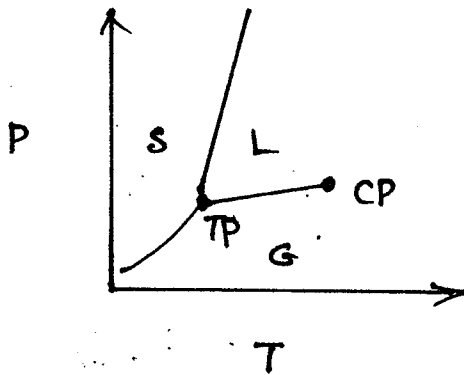
$$dA = -SdT - PdV$$

$$S = -\left(\frac{\partial A}{\partial T}\right)_V = nR \ln(V - nb) - \left(\frac{\partial f}{\partial T}\right)_V$$

$$P = -\left(\frac{\partial A}{\partial V}\right)_T = -\frac{an^2}{V^2} + \frac{nRT}{V - nb} \quad \text{vdW!}$$

5. (12 pts) Phase diagrams

- (3) (a) Plot P vs T for a single component system.
 (5) (b) Label the liquid, gas, solid phase regions, the critical point and the triple point.
 (4) (c) Given $A(n, T, V)$ at a fixed the temperature, what two simultaneous equations must be solved determine the densities at which two phases coexist?



$$P_L = P_G \Rightarrow -\left(\frac{\partial A}{\partial V}\right)_{T,n} = P$$

$$\mu_L = \mu_G \Rightarrow \left(\frac{\partial A}{\partial n}\right)_{T,V} = \mu$$

where $P_L = \text{function of } P_L, \text{ etc.}$

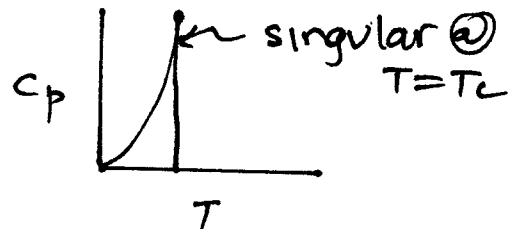
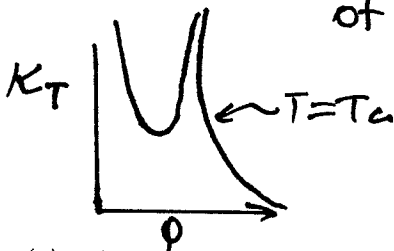
6. (14 pts) Big picture thermodynamics.

- (4) (a) Write the inequality that describes the criterium for all spontaneous changes that occur at constant T and V.

$$dA|_{T,V} \leq 0$$

- (6) (b) Define a second order transition and graph a function which best illustrates the behavior.

second order: singularity in the second deriv. of G, $(\partial^2 G / \partial T^2)$, or $(\partial^2 G / \partial P^2)$



- (4) (c) The inequality,

$$TdS \geq dq \quad (3)$$

can be adapted to conditions of constant T and P. When this is done, we have a condition for spontaneity. Derive that condition.

$$dg|_p = dH \quad \text{so}$$

$$TdS \geq dH \Rightarrow 0 \geq dH - TdS$$

at constant T,

$$dH - TdS = d[H - TS] = dG \quad \text{so}$$

$$0 \geq dG|_{T,P}$$

7. (32 pts) Derive or complete the indicated results. The starting point is any of the relations given on page 1. Show your work.

$$T \left(\frac{\partial S}{\partial T} \right)_V = ? \quad (4)$$

$$dU = Tds - pdv = c_v dT + \left(\frac{\partial U}{\partial V} \right)_T dv$$

$$\therefore \left(\frac{\partial S}{\partial T} \right)_V = \frac{c_v}{T}$$

When is the following identity valid?

$$dS = -(V/T)dP \quad (5)$$

$$dH = Tds + vdp$$

if $H = \text{const}$, then $\left(\frac{\partial S}{\partial P} \right)_H = -\left(\frac{\partial V}{\partial T} \right)_P$ follows

$$\left(\frac{\partial A}{\partial P}\right)_T = \kappa_T PV \quad (6)$$

$$dA = -SdT - PdV$$

$$\left(\frac{\partial A}{\partial P}\right)_T = -P\left(\frac{\partial V}{\partial P}\right)_T = PV \left\{ -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T \right\} =$$

$$\left(\frac{\partial H}{\partial T}\right)_v = C_v + f(\alpha_P, \kappa_T, V) \quad (7)$$

Find f .

$$dH = d[U + PV] = C_v dT + \left(\frac{\partial U}{\partial V}\right)_T dV + PdV + VdP$$

$$\left(\frac{\partial H}{\partial T}\right)_v = C_v + V\left(\frac{\partial P}{\partial T}\right)_v = C_v + \frac{\alpha_P \cdot V}{\kappa_T}$$

$$\text{but } \left(\frac{\partial P}{\partial T}\right)_v = -\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P = \frac{\alpha_P}{\kappa_T}$$

\uparrow \uparrow
 $\frac{-1}{V\kappa_T}$ $V\alpha_P$

$$f = V\alpha_P / \kappa_T$$