Chemistry 440 Final exam

EXAM KEY

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

dH(S,P,n_i) = TdS + V dP + \sum_i \mu_i d n_i, \quad H = U + PV

dA(T,V,n_i) = -SdT - PdV + \sum_i \mu_i d n_i, \quad A = U - TS

dG(T,P,n_i) = -SdT + V dP + \sum_i \mu_i d n_i, \quad G = U + PV - TS = \sum_i \mu_i n_i

C_v = \left( \frac{\partial U}{\partial T} \right)_V \quad 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_T = \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; \quad \text{adiabatic process}

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

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

\ln \left( \frac{K(T_2)}{K(T_1)} \right) \approx \frac{\Delta H}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)

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

F = 2 + C - P

R = 8.314 \text{J/(k}\cdot\text{mole)}
1. (20 pts) State the First and Second laws of Thermodynamics as they apply to the
system and to the universe. Use prose and equations.

1st law. The energy of the universe is conserved

\[ \Delta U_{\text{univ}} = 0 \]

whereas the energy of the system changes when heat flows into the system \( \mathcal{Q} \) and/or
work is done by the system,

\[ \Delta U = Q_{\text{in}} - W_{\text{sys}} \]

2nd law: The entropy of the universe increases
in spontaneous processes, \( \Delta S_{\text{univ}} > 0 \)
and entropy changes in the system are bounded
by \( ds \geq d\mathcal{Q}/T \)

2. (10 pts) Prove that the Helmholtz energy decreases for all spontaneous processes that
occur at fixed \( T \) and \( V \). Start with the entropy based statement of the Second law.

\[ ds \geq d\mathcal{Q}/T \]

if \( V \) is fixed,

\[ dU = d\mathcal{Q} - P_{\text{ext}} dV \rightarrow dq \]

so

\[ ds \geq dU/T \]

or

\[ 0 \geq d[U-TS] \bigg|_{T,V} = dA \bigg|_{T,V} \]
3. (12 pts) Consider a system with two components, A and B, and two phases, liquid L and gas G.

(a) What is the phase rule variance (F) of the system?
(b) What are the relationships that exist between the intensive variables?

\[ F = 2 \]

- \( T \) is uniform, \( T_L = T_G \)
- \( P \) is uniform, \( P_L = P_G \)
- Chemical potentials are uniform: \( \mu_A, L = \mu_A, G \)
- \( \mu_B, L = \mu_B, G \)

4. (10 pts) Reversible adiabatic and reversible isothermal compressions are performed on an ideal gas (monatomic, diatomic) starting from the state point \( P_1, V_1, T_1 \). At the end of the compression, both systems have a final pressure of \( P_2 = 2P_1 \). Show that \( (\Delta H)_{\text{adiabatic}} > (\Delta H)_{\text{isothermal}} \).

For an isothermal process, \( \Delta T = 0 \Rightarrow \Delta H \nu_0 = 0 \)

For the adiabatic process,

\[
\frac{T_2}{T_1} = \left( \frac{P_2}{P_1} \right)^{(\gamma-1)/\gamma} = \left( \frac{2}{1} \right)^{(\gamma-1)/\gamma} > 1
\]

\[ \Delta H_{\text{adiab}} = C_p (T_2 - T_1) > 0 \]

\[ \therefore \Delta H_{\text{adiab}} > \Delta H_{\text{iso}} \]
5. (30 pts) Derive

(a) the entropy derivative \( \left( \frac{\partial S}{\partial V} \right)_T \)

(b) the Joule coefficient, \( \left( \frac{\partial T}{\partial V} \right)_U \)

(c) and the volume derivative of the heat capacity, \( \left( \frac{\partial C_V}{\partial V} \right)_T \)

for fluid obeying

\[ P = \frac{nRT}{V} - a \left( \frac{n}{V} \right)^2 \]

where \( a \) is a constant.

a) \[ dA = -SdT - PdV \quad \Rightarrow \quad \left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial P}{\partial T} \right)_V = \frac{nR}{V} \]

b) \[ \left( \frac{\partial T}{\partial V} \right)_U = - \left( \frac{\partial T}{\partial U} \right)_V \frac{\partial U}{\partial V} = - \frac{1}{C_V} \left( \frac{\partial U}{\partial V} \right)_T \]

\[ dU = TdS - PdV \quad \Rightarrow \quad \left( \frac{\partial U}{\partial V} \right)_T = \frac{T(\partial S}{\partial V)}_T - P = \frac{nRT}{V} - \left[ \frac{nRT}{V} - a \phi^2 \right] \]

\[ \left( \frac{\partial U}{\partial V} \right)_T = a(n/V)^2 \]

and \[ \left( \frac{\partial T}{\partial V} \right)_U = -a \phi^2 \frac{1}{C_V} \]

\( \phi = n/V \)

c) If \( \left( \frac{\partial U}{\partial V} \right)_T = a \phi^2 \), then \( \left( \frac{\partial}{\partial T} \left( \frac{\partial U}{\partial V} \right)_T \right)_V = \left( \frac{\partial C_V}{\partial V} \right)_T = 0 \)

since we can change the order of differentiation.
6. (6 pts) Given

\[ C_P = C_V + T \left( \frac{\partial V}{\partial T} \right)_P \left( \frac{\partial P}{\partial T} \right)_V \]

select the proper response

(a) \( C_P > C_V \) for all materials;
(b) \( C_P < C_V \) for all materials;
(c) no general rule exists regarding \( C_P \) and \( C_V \);
(d) generally \( C_P \) and \( C_V \) are so similar that differences can be ignored.

\[ C_P - C_V = T \left( \frac{1}{V} \frac{\partial V}{\partial T} \right)_P \left( \frac{\partial P}{\partial T} \right)_T \left( \frac{\partial V}{\partial T} \right)_P \]

\[ = TV \left( \alpha_p \right)^2 \frac{1}{\kappa_T} > 0 \quad \Rightarrow \quad C_P > C_V \]

7. (10 pts) Derive

\[ dS(T, P) = \frac{C_P}{T} dT - \alpha_p V dP \]

starting from any equation given on page 1.

\[ dS = \left( \frac{\partial S}{\partial T} \right)_P dT + \left( \frac{\partial S}{\partial P} \right)_T dP \]

\[ dH = T dS + V dP \]

\[ dG = V dP - S dT \]

and

\[ (\frac{\partial H}{\partial T})_P = C_P = T \left( \frac{\partial S}{\partial T} \right)_P \]

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

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

\[ \left( \frac{\partial S}{\partial T} \right)_P = C_P / T \]

Insert into \( dS \)
8. (16 pts) In Hildebrand’s theory of Regular solutions, the Gibbs energy of mixing, $\Delta G_{mix}$, and the vapor pressure of component 1, $P_1$, are

$$
\Delta G_{mix} = G(T, P, n_1, n_2) - [n_1\mu_1(T, P) + n_2\mu_2(T, P)] \\
= n(wx_1x_2 + RT(x_1\ln x_1 + x_2\ln x_2)) \\
P_1 = x_1P^0_1e^{wx^2_2/RT}
$$

where all the terms have their usual meaning.

(a) Derive $\Delta H_{mix}$ and the Henry’s law constant $k_H$ for component 1.

$$
\Delta H = -T^2 \frac{\partial}{\partial T} \left( \frac{G(T)}{T} \right) = -T^2 \frac{\partial}{\partial T} \left( \frac{nwx_1x_2}{T} \right) = nwx_1x_2 \\
P_1 = x_1k_{H1}, \quad k_{H1} = P^0_1\exp(W/RT) = \lim_{x_2 \to 0} \left[ P^0_1e^{wx^2_2/RT} \right]
$$

(b) Plot $P_1$ vs $x_1$ for an ideal liquid mixture and for a fluid with the non-ideal corrections inherent in Hildebrand’s theory. Indicate the Raoult’s law and Henry’s law regimes on the non-ideal $P_1$ vs. $x_1$ plot.

9. (10 pts) Liquid mercury occupies $8 \times 10^{-8}$ m$^3$/g whereas the solid occupies $7 \times 10^{-8}$ m$^3$/g at its melting point of $-33^\circ$C. The heat of vaporization is 10 J/g. Calculate the melting point when the pressure is increased by 1000 bar (= 10$^8$ Pa).

$$
\left( \frac{\partial P}{\partial T} \right) = \frac{\Delta H}{T\Delta V}, \quad \Delta T = \frac{T \cdot \Delta P \cdot \Delta V}{\Delta H} \\
\Delta T = \frac{240K \left( \frac{8m^3}{g} - \frac{7m^3}{g} \right) \times 10^{-8} \cdot 10^8 Pa}{10 J/g} = 24K \\
T_{melting} = 240 + 24 = 264 K
$$
10. (20 pts) A benzene-toluene solution is nearly ideal. Suppose that the mole fraction of benzene in the liquid mixture is 0.5 and the vapor pressures of pure benzene and pure toluene are 100 kPa and 40 kPa, respectively.

(a) Draw the $P$ vs. $x_{benzene}$ and $P$ vs. $y_{benzene}$ phase diagram and label the dew point and the bubble point curves.

(b) Calculate the vapor pressure of the mixture.

(c) Calculate the mole fraction of benzene in the vapor.

\[
P = x_B P^0_B + x_T P^0_T = \frac{1}{2} [100 + 40] = 70 \text{ kPa}
\]

\[
\gamma_B P = x_B P^0_B
\]

\[
\gamma_B = \frac{\left(\frac{1}{2}\right) \cdot 100}{70} = \frac{5}{7}
\]

11. (12 pts) Plot and label the following:

(a) $S(T)$ vs. $T$ in the neighborhood of a melting transition.

(b) $V(P)$ vs. $P$ along the critical isotherm.
12. (24 pts) Provide numerical answers appropriate to the processes conducted on one mole of liquid water at 300K. $C_p = 9R$, $\kappa_T = 5 \times 10^{-5}$ bar$^{-1}$, $\alpha_P = 6 \times 10^{-4} K^{-1}$, 1 bar $= 10^5$ Pa. Circle your answers.

(a) Calculate the fractional change in volume $\Delta V/V$ when the temperature is increased by 20 K at a fixed pressure of 1 bar.

(b) If the temperature changes by 10 K, what is $\Delta H$ at 1 bar?

(c) What is the fractional change in volume when the pressure increases by 1 kbar?

(d) What is the change in the Gibbs energy if the pressure increases by 1 kbar?

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

\[= \left(6 \times 10^{-4} \frac{1}{K}\right)(20K) = 1.2 \times 10^{-2}\]

\[\Delta H = C_p \Delta T = 9 \cdot R \cdot 10K = 9 \cdot 8 \cdot 10^3 J/mole = 720 J/mole\]

\[R = 8 J/K \cdot mole\]

\[\kappa_T = -\frac{1}{V} \frac{\partial V}{\partial P} \Rightarrow \frac{\Delta V}{V} = -\kappa_T \cdot \Delta P = -5 \times 10^{-5} \text{ bar}^{-1} \times 10^3 \text{ bar}^{-1}\]

\[= -5 \times 10^{-2}\]

\[\Delta G = \nu dP = \left(18 \text{ cm}^3\right) \times \left(\frac{1 \text{ m}}{100 \text{ cm}}\right)^3 \times 10^3 \text{ bar}^{-1} \times 10^5 \text{ Pa}^{-1} \text{ bar}\]

\[\Delta G = 1.8 \times 10^2 \text{ m}^3 \cdot \text{Pa} = 1.8 \times 10^3 \text{ J}\]
13. (20 pts) A fictional phase diagram representing gas-liquid, liquid-liquid and liquid-solid phase equilibria is shown for a two component system. Label the points a-d:

- (a) azeotrope
- (b) liq-liq critical point
- (c) melting point of pure a
- (d) eutectic point

For the following, provide the identity of the phases,

- (e) mixture of solid B and solid AB₂
- (f) A(S) + A(L), B(L)
- (g) [A(L),B(L)] phase 1 and [A(L),B(L)] phase 2
- (h) coexisting gaseous A+B phases?
- (i) gaseous A and B

What's wrong with the part of the diagram encircling point h? Can't have phase sep. in a gas.