Final Exam
March 17, 2008

Law I $\Delta U = q + w$

$U = U(T,V)$

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

LawII: $dS = \frac{q_{rev}}{T}$

$S = S(T,V)$

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

Comb I,II: $dU = TdS - PdV$

$H = U + PV;\ A = U - TS$

$G = H - TS;\ dG = -SdT + VdP$

Thermodynamic Equation of State

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

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

$$\mu_A = \mu_A^o + RT\ln\frac{P_A}{P_o}$$

Dalton's Law

$P_A = y_A P_{Tot};\quad P_T = \sum_A P_A;\ G = \sum n_i\mu_i$

$$\Delta G_{mix} = RT\sum n_i \ln\left(\frac{P_i}{P_o}\right)$$

$P_A = x_A P_A^* = y_A P_{Tot}$ Raoult/Dalton Law

$n_\ell(Z-\chi) = n_v(y-Z)$ Lever Rule

Calculus Identities:

$$\Delta Z = \int_{x_i}^{x_f}\left(\frac{\partial Z}{\partial x}\right)_y dx$$

Cyclic rule: $\left(\frac{dx}{dy}\right)_z\left(\frac{dz}{dx}\right)_y\left(\frac{dy}{dz}\right)_x = -1$

$$\frac{d(yz)}{dx} = z\frac{d(y)}{dx} + y\frac{d(z)}{dx}$$

$$\frac{dx}{dz} = \frac{dy}{dz}\frac{dx}{dy};\ \left(\frac{\partial x}{\partial z}\right)_a = \left(\frac{\partial y}{\partial z}\right)_a\left(\frac{\partial x}{\partial y}\right)_a$$

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

vdW Gas EoS: $P = \frac{RT}{V_m - b} - \frac{a}{V_m^{\ 2}}$

$$\Delta H_{rxn}^o = \sum_i \nu_i \Delta H_f^o(i)$$

$$\Delta S_{rxn}^o = \sum_i \nu_i S_f^o(i)$$

$$dn_i = n_i - n_i^{Init} = \nu_i dX$$

$$\Delta C_{P,rxn} = \sum_i \nu_i C_{P,m}(i)$$

$$\Delta H^o = \Delta H_{rxn}^o dX$$

$$\Delta G_{rxn} = \Delta G_{rxn}^o + RT\ln Q_P = RT\ln\frac{Q_P}{K_P}$$

$\Delta E = \Delta E^o - \frac{RT}{\nu_e F}\ln Q_P$ Nernst Eqn.

$Q_P = \prod_{i=1}^N\left(\frac{P_i}{P_o}\right)^{\nu_i}$ @Eq $Q_P = K_P$

$$K_P = \left(\frac{P}{P_o}\right)^{\Delta\nu} K_x = \left(\frac{c_o RT}{P_o}\right)^{\Delta\nu} K_c$$

$\ln\left(\frac{K_P(T_2)}{K_P(T_1)}\right) = -\frac{\Delta H_{rxn}^o}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$ Van't Hoff Eqn :

$\ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta H^{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$ Clausius-Clapeyron

$\left(\frac{\partial P}{\partial T}\right)_{\Delta\mu} = \frac{\Delta S}{\Delta V}$ Clapeyron

Constants:

$R = 8.3 J / mol - K$

$R = 0.082 L - atm / mol - K$

$R \cdot 300 = 2.5\ kJ / mol$

$\frac{R\cdot 300}{F} = 25 mV$

$1 bar = 10^5 Pa$

$T(K) = T(C) + 273.15$

F=96,500Coulombs/mole-e

Show your work throughout; clearly show what equations you are using, and always show units for computed quantities.

More equations of state and Maxwell relations:

$$dU = TdS - PdV \qquad \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \qquad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \qquad \left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}$$

$$\frac{\Delta S_{\alpha,\beta}}{\Delta V_{\alpha,\beta}} = \frac{dP}{dT}$$

Useful equations for non-ideal gases:

$$z = \frac{PV}{RT} \qquad \ln\gamma = \int_0^P \frac{\{z-1\}}{P'}dP'$$

Useful equations for ionic solutions and electrochemistry:

$$\Delta G_{rxn} = -\nu_e F \mathrm{E}(V)$$

$$dq = Idt$$

$$dG = \Delta G_{rxn} dX$$

$$I = \tfrac{1}{2}\left(\nu_+ z_+^2 + \nu_- z_-^2\right)m$$

$$\ln\gamma_\pm = -1.173\left|z_+ z_-\right|\sqrt{I}$$

$$\ln\gamma_\pm = 2.3 \cdot \log_{10}\gamma_\pm$$

Appx Values $\log_{10} 5 = .7$ $\ln 2 = .7$ $\sqrt{\left(\frac{1}{2}\right)} = 0.7$ $\log_{10} 2 = .3$ $\exp\left(\frac{-1}{3}\right) = 0.7$

$$E = E^o - \frac{RT}{\nu_e F}\ln Q = -\frac{RT}{\nu_e F}\ln\frac{Q}{K} \qquad Q = \prod_{i=1}^{N}(a_i)^{\nu_i} = \prod_{i=1}^{N}\left(\gamma_i \frac{c_i}{c_o}\right)^{\nu_i}$$

$$\mu_A = \mu_A^o + RT\ln a_A$$

$$a_A = \gamma_A x_A$$

Cu half cell reduction potential: $Cu^{2+} + 2e^- \rightarrow Cu \qquad E^o = 0.34V$

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Q1) a) For any process (no constraints) what is the thermodynamic criterion of spontaneity?
Entropy (total) always increases: $\Delta S_{Total} \geq 0$

b) For any process carried out at constant pressure and temperature, what is the specific criterion of spontaneity?
The free energy (of the system) available must be negative (regadless of the environment, which is contained in the T and P): $\Delta G \leq w_{nonPdV} \leq 0$

c) In a chemical reaction (carried out at constant pressure and temperature) what is the criterion of equilibrium?
There are many choices (see d-f) ΔG is minimized at equilibrium

d) How can you use ΔG to define chemical equilibrium?
ΔG is minimzed

e) How can you use ΔG_{rxn} to define chemical equilibrium?
$\Delta G_{rxn} = 0$

f) How can you use ΔG^o_{rxn} to define chemical equilibrium?
At equilibrium: $\Delta G^o_{rxn} = -RT \ln Q$ or equivaneltly: $K = Q$

g) Fuel cells (and the hydrogen economy) will run on the chemical reaction
$2H_2 + O_2 \rightleftarrows 2H_2O$ for which $\Delta G^o_{rxn} = -475\ {kJ}/{mole}$. Analyze the following statement:
The fact that ΔG^o_{rxn} is far from zero implies that the system is far away from equilibrium.
The value of ΔG^o_{rxn} does not imply anything by itself about where the system is in respect to equilibrium, as you do not know how much of anything you have. A large negative number for this quantity implies that the equilibrium will lie near mostly products but the system, defined by Q, could be there already, or could be mostly reactants to start.

h) If I have a fuel cell set up so that all chemical species are at unit activity, and I run it long enough to consume 0.01 moles of Hydrogen gas, what is the maximum electrical work that can be obtained from the reaction?

$$w^{\max}_{elec} = \Delta G = \int_{x=0}^{x} \Delta G_{rxn} dX \approx \Delta G_{rxn} X \qquad dn_{H_2} = -2X = -0.01$$

$$\Delta G_{rxn} X = (-475)(0.005) kJ = -2.5 kJ$$

Q2) Consider a gas with the van der Waals; equation of state for which the constant $b = 0$.
a) Express the compressibility, z, for this van der Waals gas ($b = 0$)

$$z = \frac{PV_m}{RT} = 1 - \frac{a}{V_m}$$

b) Develop an exact expression for the fugacity (or activity) coefficient for this case.

$$\ln\gamma = \int_0^P \frac{\{z-1\}}{P'} dP' = -a\int_0^P \frac{dP'}{V_m P'}$$

c) From the complete expression, (part a) explain why the fugacity (or activity) coefficient for this gas is always positive but less than 1.
The integrand is always positive because both pressure and volume are each positive quantities and a is positive, so the $\ln\gamma < 0$, therefore $0 \le \gamma \le 1$ (you can't, in this class take the log of a negative number).

d) What is the physical interpretation of a fugacity (or activity) coefficient less than one?

A smaller coefficient implies that the fugacity (or the activity/chemical potential) is less than expected for an ideal gas, so the pressure is lower than anticipated for an ideal gas pressure. We knew that from the vdW EoS. Physically, the molecules are interacting or partially binding to each other and therefore show less "activity".

e) Assume that $nRT > a/V$, (using the result from part b) and derive an approximate expression for the fugacity coefficient.

$$\ln\gamma = -a\int_0^P \frac{dP'}{V_m P'} = -a\int_0^P \frac{dP'}{\left(nRT - a/V_m\right)} \approx -a\int_0^P \frac{dP'}{RT} = -a\frac{P}{RT}$$

Q3) The vapor pressure of a liquid can be written in an empirical form known as the Antoine equation, where the parameters A_1, A_2, and A_3 are constants determined from measurements:

$$\ln\left(\frac{P}{P_o}\right) = A_1 - \frac{A_2}{T - A_3}$$

[Hint: Use the Clausius-Clapeyron Equation as a guide. Consider T, A_2, and A_3 to be in units of Kelvin]
Starting with this equation derive an equation (in terms of the constants of the Antoine equation) giving $\Delta H_{vaporization}$ as a function of temperature.

From the C-C equation and the equation for ln(K) we know:

$$\ln\left(\frac{P_2}{P_0}\right) = -\frac{\Delta H^{vap}}{R}\left(\frac{1}{T} - \frac{1}{T_o}\right) \qquad \frac{\partial \ln\left(\frac{P_2}{P_0}\right)}{\partial\left(\frac{1}{T}\right)} = -\frac{\Delta H^{vap}}{R}\left(\frac{\partial\left(\frac{1}{T}\right)}{\partial\left(\frac{1}{T}\right)}\right) = -\frac{\Delta H^{vap}}{R}$$

We now apply this same derivative to the Antoine equation:

$$\frac{\partial \ln\left(\frac{P_2}{P_0}\right)}{\partial\left(\frac{1}{T}\right)} = \frac{\partial\left(A_1 - \frac{A_2}{T - A_3}\right)}{\partial\left(\frac{1}{T}\right)} = -A_2 \frac{\partial\left(\frac{1/T}{1 - A_3/T}\right)}{\partial\left(\frac{1}{T}\right)} = -A_2\left(\frac{1}{1 - A_3/T} + \frac{A_3/T}{\left(1 - A_3/T\right)^2}\right)$$

$$\frac{\Delta H^{vap}}{R} = A_2\left(\frac{1}{\left(1 - A_3/T\right)^2}\right)$$

If this derivative taking eludes you, you could argue that for small A3 the function forms are similar enough that

$$\frac{\Delta H^{vap}}{R} \approx A_2$$

And the more exact expression from the derivative shows the same result.

Q4) Benzene and Toluene form an ideal solution at 300K (i.e. the mixture obeys Rauolt's law). $P^*_{toluene} = 30.0Torr$ and $P^*_{Benzene} = 90.0Torr$. The liquid is composed of 2 moles of toluene and 3 moles of benzene. [You may want to sketch a pressure v. composition diagram.]

a) At what pressure does the first vapor form?

$$P_{Tot} = P_A + P_B = x_A P_A^* + x_B P_B^*$$
$$= \frac{2\cdot 30 + 3\cdot 90}{5} = \frac{30}{5}(2+9) = 6\cdot 11 = 66torr$$

b) What is the composition of the first trace of vapor formed?

$$P_A = y_A P_{Tot}$$
$$y_A = \frac{x_A P_A^*}{P_{Tot}} = \frac{2\cdot 30}{5\cdot 6\cdot 11} = \frac{2}{11} \qquad y_B = \frac{x_B P_B^*}{P_{Tot}} = \frac{3\cdot 90}{5\cdot 6\cdot 11} = \frac{9}{11}$$

It should be enriched in the benzene (B, the more volatile component) and it is..

c) If the pressure is reduced further, at what pressure does the last trace of liquid disappear?

The composition of the pure vapor after all liquid is gone must be the same as that of the liquid before any vapor was formed; and it must be in equilibrium with liquid (though trace amount).

$$\frac{1}{P_{Tot}} = \frac{y_A}{P_A^*} + \frac{y_B}{P_B^*} = \frac{2}{5\cdot 30} + \frac{3}{5\cdot 90} = \frac{(2+1)}{5\cdot 30} = \frac{1}{50}$$
$$P_{Tot} = 50torr$$

d) What is the composition of the last trace of liquid?
This is the liquid in equilibrium with the vapor of composition part c:

$$x_A = y_A \frac{P_{Tot}}{P_A^*} = \frac{2}{5}\frac{50}{30} = \frac{2}{3} \qquad x_B = y_B \frac{P_{Tot}}{P_B^*} = \frac{3}{5}\frac{50}{90} = \frac{1}{3}$$

Again the vapor is enriched in the benzene (more volatile) relative to liquid. Benzene mole fraction is 1/3 in the liquid and 3/5 in the vapor.

Q5) a) Solid silver sulfate can dissolve only sparingly in water as $Ag_2SO_4(s) \rightleftarrows 2Ag^{+1} + SO_4^{2-}$ because: $K_{sp}(Ag_2SO_4) = 4 \cdot 10^{-6}$. Compute the molar (or molal) solubility of this salt assuming that it behaves as an ideal salt.

$$K_{sp} = Q = (\nu_+ X)^{\nu_+} (\nu_- X)^{\nu_-}$$
$$4 \cdot 10^{-6} = 4 \cdot X^3$$
$$X = 1 \cdot 10^{-2}$$

b) Compute the ionic strength of this saturated solution of silver sulfate.

$$I = \tfrac{1}{2}\left(\nu_+ z_+^2 + \nu_- z_-^2\right) m$$
$$m = X$$
$$I = \tfrac{1}{2}\left(\nu_+ z_+^2 + \nu_- z_-^2\right) X = \tfrac{1}{2}\left(2 \cdot 1^2 + 1 \cdot 2^2\right) X = 3 \cdot 10^2$$

c) Estimate the activity coefficient for this solution using the Debye-Hückel limiting law.

$$\ln \gamma_\pm = -1.173 |z_+ z_-| \sqrt{I} = -1.173 |2| \sqrt{3 \cdot 10^{-2}} = -2.3 \cdot 0.17 = -\frac{1}{3}$$
$$\gamma_\pm = .7$$

d) Does the solubility increase or decrease when the activity coefficient is included in the calculation. Explain your reasoning with the appropriate equations.

$$K_{sp} = Q_A = \gamma_\pm^3 4X^3$$

The K is a fixed number: The original assumption was the activity coefficient is one. If the coefficient decreases (is less than one) then X or the solubility must increase. So coefficients less than one indicate that the ions stabilize the solution, and increase the amount of salt that will dissolve in them.

Q6) A van der Waals gas is allowed to expand adiabatically and reversibly so that the pressure decreases from its initial pressure and the volume increases.

a) What state functions do not change in this process, for any ideal or real gas?

$\Delta S = 0$, the entropy is the only state function that does not change. There is no heat transfer but that is not a state function. The temperature changes, so all of the energy state functions must change.

b) Assuming that the entropy is invariant over the process then it follows that $\int_A^B dS = 0$.

Use this constraint and the total derivative of the entropy in terms of T and V, to develop an expression that relates the temperature change to the volume change. (Leave the result in the integral form. Use the appropriate Maxwell relation to develop an expression that uses only heat capacity, P, V, and T).

$$0 = \int_A^B dS = \int_{T=T_o}^{T} \left(\frac{\partial S}{\partial T}\right)_{V=V_o} dT + \int_{V=V_o}^{V} \left(\frac{\partial S}{\partial V}\right)_{T=T} dV$$

$$\int_{T=T_o}^{T} \left(\frac{\partial S}{\partial T}\right)_{V=V_o} dT = -\int_{V=V_o}^{V} \left(\frac{\partial S}{\partial V}\right)_{T=T} dV$$

$$\int_{T=T_o}^{T} \left(\frac{C_V}{T}\right) dT_{V=V_o} = -\int_{V=V_o}^{V} \left(\frac{\partial P}{\partial T}\right)_V dV_{T=T}$$

c) Assume that the heat capacity $\left(C_V = \frac{4}{2} nR\right)$ is independent of temperature and find a relation between the temperature change and the volume change for this process.

$$P = \frac{nRT}{V-nb} - \frac{n^2 a}{V^2} \qquad \left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V-nb}$$

$$2\ln\left(\frac{T}{T_o}\right) = -\int_{V=V_o}^{V} \left(\frac{1}{V-nb}\right) dV = -\ln\left(\frac{V-nb}{V_o-nb}\right)$$

d) If the volume expands from $V_{I,m} = 6b$ to $V_{F,m} = 11b$ (here b is the van der Waals parameter) and $\frac{a}{V_{I,m}} = 0.1 Joules/mol$, for the vdW gas what is the temperature change as a ratio of the final to the initial temperature?

$$\left(\frac{T}{T_o}\right) = \left(\frac{V-nb}{V_o-nb}\right)^{\frac{-1}{2}} = \sqrt{\left(\frac{V_{m,o}-b}{V_m-b}\right)} = \sqrt{\left(\frac{6-1}{11-1}\right)} = \sqrt{\left(\frac{1}{2}\right)} = 0.7$$

Q7) Consider a battery described by: $Cu\left|Cu^{+2}\right|\left|Cu^{+2}\right|Cu$ Assume that the battery is composed of two solutions (in separate containers) of equal volume, one liter, with Cu plates in them. One solution is 0.1 M in $CuSO_4$ and the other is 0.01M in $CuSO_4$.
(Additionally there is a salt bridge between the two solutions and a wire with a volt meter connecting the two Cu plates.)
a) What is the standard EMF, E^o, of such a battery:

$$E^o = 0.0$$

b) Explain why there is any voltage to this batter at all.
The voltage comes from the concentration difference of the Cu ions in the two beakers; the two terminals are of the same material so the oxidation and reduction reactions are identical but of opposite direction.

c) Will oxidation or reduction occur in the solution with the 0.01M concentration? Explain.

The is the less concentrated solution, so the direction must be to increase the concentration of the ions so the reaction in this beaker is: $Cu \rightarrow 2e^- + Cu^{+2}$, and this is oxidation.

d) What is the voltage of this battery at $T = 300K$?

$$\Delta E = \Delta E^o - \frac{RT}{\nu_e F}\ln Q_P \qquad \nu_e = 2$$

$$\Delta E = 0 - \frac{25}{2}\ln\frac{0.01}{0.1} = 12 \cdot \ln 10 = 30mV$$

e) By what fraction would the voltage change if the temperature were increased by 10%.
The reaction is proportional to T, so 10% increase in T give a 10% voltage increase (note increase not decrease).

f) Determine the reaction entropy ΔS_{rxn} for this system:

$$\Delta G_{rxn} = \Delta H_{rxn} - T\Delta S_{rxn} \qquad \Delta S_{rxn} = -\frac{\partial \Delta G_{rxn}}{\partial T}$$

$$\Delta S_{rxn} = -R\ln Q = 8 \cdot \log(10) = 20 \, J/mol-K$$

Notice the entropy is positive, as it is spontaneous for the battery to run, and the battery is fully entropically driven. $\Delta E = \frac{T\Delta S_{rxn}}{F\nu_e}$

g) Determine the reaction enthalpy ΔH_{rxn} for this system:

$$\Delta H_{rxn} = \Delta G_{rxn} + T\Delta S_{rxn} = 0$$

h) When the battery is exhausted, what will the concentration of $CuSO_4$ be in the two solutions?

The two beakers must be at the same concentration at equilibrium. This happens by removing so many ions from A to B to bring them to equality:

$C_A^o - X = C_B^o + X \Rightarrow X = \frac{C_A^o - C_B^o}{2}$ The two beakers contain the same volume so the concentration will be the average of the two. You could arrive at this by simply pouring the contents of the one beaker into the contents of the other beaker. In fact you could use this to compute the temperature increase due to the mixing.

$$C_{equilib} = \frac{C_A + C_B}{2} = \frac{.11}{2} = .055M$$

i) What is the maximum amount of electrical work you can get from the battery assuming that it will perform at peak value for the entire running of the battery?

$$w_{elect}^{rev} = \Delta G = \int_0^{X_{eq}} \Delta G_{rxn} dX \approx RT \ln\left(Q_o\right) X_{eq} = -2.5 \ln\left(10\right) \cdot 0.05 = -0.28kJ$$

The electrical work is in kJ, not kJ/mole. This is the full work using so many moles, because each beaker contained a liter.

j) In some possible electrochemical cells, unlike the Cu-Cu battery, the change in cell potential with temperature is very small. What does this tell you about the thermodynamics of the cell reaction for these batteries?

Such batteries are enthalpically driven due to large inherent voltage differences in inherent redox processes. The entropy of mixing is not a large part of the cells.

k) Would such a battery have diminished power output at low temperatures? Why or why not?

It should not from a thermodynamic point of view; but of course, in real world systems, kinetic issues come up because the redox reaction has to happen and material must transfer. The lead battery in the car is about 30% entropy driven so there is a thermodynamic part to the temperature effect, as well as just kinetically sluggish at lower temperatures.

Q8) Differentials

a) Starting with the van der Waals equation of state, find an expression for the total differential dP in terms of dT and dV .

$$P = P(T,V) \Rightarrow \quad dP = \left(\frac{\partial P}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V-nb} \qquad \left(\frac{\partial P}{\partial V}\right)_T = -\frac{nRT}{(V-nb)^2} + 2\frac{n^2 a}{V^3}$$

b) By calculating the mixed partial derivatives $\left(\frac{\partial}{\partial T}\left(\frac{\partial P}{\partial V}\right)_T\right)_V$ and $\left(\frac{\partial}{\partial V}\left(\frac{\partial P}{\partial T}\right)_V\right)_T$, determine if dP is an exact differential.

$$\left(\frac{\partial}{\partial T}\left(\frac{\partial P}{\partial V}\right)_T\right)_V = \left(\frac{\partial}{\partial T}\left(-\frac{nRT}{(V-nb)^2} + 2\frac{n^2 a}{V^3}\right)\right)_V = -\frac{nR}{(V-nb)^2}$$

$$\left(\frac{\partial}{\partial V}\left(\frac{\partial P}{\partial T}\right)_V\right)_T = \left(\frac{\partial}{\partial V}\left(\frac{nR}{V-nb}\right)\right)_T = \left(\frac{-nR}{(V-nb)^2}\right)$$

Yes they are the same, and so dP is an exact differential, which it has to be as we started with a function of T and V.

c) Find $\left(\frac{\partial T}{\partial P}\right)_V$ for the van der Waals (vdW) gas. Express your answer in terms of the variables P,V and T, and the other constants of the vdW Gas. Do not express your answer in terms of β and κ . [Hint As a check: of P,V and T, the result should only depend on V.]

$$\left(\frac{\partial T}{\partial P}\right)_V^{-1} = \left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V-nb}$$

$$\left(\frac{\partial T}{\partial P}\right)_V = \frac{V-nb}{nR}$$