NAME: KEY

Section Number: 10 80

CHEMISTRY 443, Fall, 2007(07F)

Midterm Examination #2, November 3, 2007

*Answer each question in the space provided; use back of page if extra space is needed. Answer questions so the grader can READILY understand your work; only work on the exam sheet will be considered. Write answers, where appropriate, with reasonable numbers of significant figures. You may use **only** the "Student Handbook," a calculator, and a straight edge.*

DO NOT WRITE IN THIS SPACE	
p. 1	/15
p. 2	/10
p. 3	/10
p. 4	/15
p. 5	/10
p. 6	/10
p. 7	/15
p. 8	/15
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p. 9 (Extra credit)	/5
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TOTAL PTS	/100

1. (15 points) Calculate the standard entropy of **liquid** water at its normal boiling point of 373.15 K as accurately as you can.

The calculation is straightforward. Since the standard entropy of water at 298.15 K is known, one may add to that the change in entropy in going from 298.15 K to 373.15 K.

$$
\begin{aligned}
S^\theta(373.15K) &= S^\theta(298.15K) + \int_{298.15K}^{373.15K} \frac{C_P^\theta}{T}\,dT \\
&= S^\theta(298.15K) + \int_{298.15K}^{373.15K} \frac{c_1 + c_2 T + c_3 T^2 + c_4 T^3 + c_5/T^2}{T}\,dT \\
&= S^\theta(298.15K) + \int_{298.15K}^{373.15K} \frac{c_1}{T} + c_2 + c_3 T + c_4 T^2 + \frac{c_5}{T^3}\,dT \\
&= S^\theta(298.15K) + c_1 \ln\left(\frac{373.15}{298.15}\right) + c_2\left(373.15K - 298.15K\right) \\
&\quad + \frac{c_3}{2}\left((373.15K)^2 - (298.15K)^2\right) + \frac{c_4}{3}\left((373.15K)^3 - (298.15K)^3\right) \\
&\quad - \frac{c_5}{2}\left(\left(\frac{1}{373.15K}\right)^2 - \left(\frac{1}{298.15K}\right)^2\right)
\end{aligned}
$$

The value of the entropy at 298.15 K is found from Table 5.8 to be 70.0 J K^{-1} mol^{-1}. The coefficients of the Shomate equation are given in Table 5.6. Substitution gives, in units of J K^{-1} mol^{-1}

$$
\begin{aligned}
S^\theta(373.15K) &= 70.0 - 203.6060 \ln\left(\frac{373.15}{298.15}\right) + 1.523290\left(373.15K - 298.15K\right) \\
&\quad - \frac{3196.413\times10^{-6}}{2}\left((373.15K)^2 - (298.15K)^2\right) + \frac{2474.455\times10^{-9}}{3}\left((373.15K)^3 - (298.15K)^3\right) \\
&\quad - \frac{3.855326\times10^{6}}{2}\left(\left(\frac{1}{373.15K}\right)^2 - \left(\frac{1}{298.15K}\right)^2\right) \\
&= (70.0 - 45.69 + 114.25 - 80.47 + 21.00 + 5.83)\ J\ K^{-1}\ mol^{-1} \\
&= 84.92\ J\ K^{-1}\ mol^{-1}
\end{aligned}
$$

2. (10 points) Match the best ending of the phrase from the right column with the beginning of the phrase from the left column:

1) An apparatus to measure ΔU at constant volume is called __J__ 2) A process characterized by an overall negative free energy change is __A__ 3) One of the reversible cycles used to describe heat engines is _C__ 4) The formula $dS > \frac{dq}{T}$ represents__M__ 5) $\left(\frac{\partial A}{\partial n}\right)_{V,T}$ is a definition of __E__	A) Spontaneous B) First law of thermodynamics C) Carnot cycle D) Forbidden E) Chemical potential F) Internal energy measurer G) Third law of thermodynamics H) Spectrophotometer I) Dybowski cycle J) Bomb calorimeter K) Nonsense L) Ertl cycle M) Clausius inequality N) Partial molar Gibbs free energy O) Partial molar entropy

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Score for Page

3. (10 points) Starting with any differential equation presented in Table 5.3, prove the following Maxwell relation:

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

Start with $dA = -SdT - PdV$

The corresponding slope formula is: $dA = \left(\frac{\partial A}{\partial T}\right)_V dT - \left(\frac{\partial A}{\partial V}\right)_T dV$

$$\text{Thus: } -S = \left(\frac{\partial A}{\partial T}\right)_V \; and \; -P = \left(\frac{\partial A}{\partial V}\right)_T$$

Differentiate the first equality over V, holding T constant; differentiate the second equality over T, holding V constant:

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

For a smooth and continuous function of two variables, the order of differentiation can be exchanged and

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

or

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

and

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

Score for Page

4. (15 points) In a diving expedition, a repair has to be made by welding two aluminum wires at a depth where the pressure is 5 atmospheres. Assuming that the latent heat is not affected significantly by this pressure change, estimate the melting point of aluminum at that depth? [The molar volume of solid aluminum is 10 cm^3. For molten aluminum, Assael et al. (*J. Phys. Chem. Ref. Data* **2006**, *35(1)*, 285), report the density to be approximately 2370 kg/m^3.]

From Table 7.1, $\Delta_f H_m^{\ominus} = 10.789 \frac{kJ}{mol}$

The density of 2370 kg/m^3 yields $V_m = \dfrac{1}{2370\frac{kg}{m^3} \times \frac{1000g}{kg} \times \frac{1}{26.98 \, g/mol}} = 1.138 \times 10^{-5} \frac{m}{mol}$, while 10 cm^3 = 10^{-5} m^3

Use Clapeyron's equation:

$$\frac{dP}{dT} = \frac{\Delta_\phi H}{T\Delta_\phi V} \text{ or } \frac{dT}{T} = \frac{\Delta_\phi V}{\Delta_\phi H} dP$$

Then $\ln\dfrac{T(5atm)}{T(1atm)} = \dfrac{\Delta_\phi V}{\Delta_\phi H}(\Delta P) = \dfrac{(1.138-1)\times 10^{-5} \frac{m^3}{mol}}{10789 \frac{J}{mol}} \times 4 \; atm \times \dfrac{101325 \; Pa}{1 \; atm} = 5.184 \times 10^{-5}$

$$T(5atm) = T(1atm) \times 1.0000518 = (660.32 + 273.15)K \times 1.0000518 = 933.518K$$

The change is only 0.05 K. No need to worry about the pressure effect in this case.

Score for Page

5. (10 points). Derive the expression for fugacity of a gas obeying the abbreviated virial equation:

$$PV_m = RT + \beta P + \gamma P^2 ,$$

where β and γ depend only on temperature

By definition, the fugacity is

$$f = \phi P \ .$$

The fugacity coefficient is found from the following equation:

$$\ln\phi \quad = \quad \int_0^P \frac{z(P')-1}{P'} dP' \quad = \quad \int_0^P \frac{\left(\frac{P'V_m}{RT}\right)-1}{P'} dP' \quad = \quad \int_0^P \left(\frac{V_m}{RT}\right) - \frac{1}{P'} dP'$$

Substitution into this equation from the equation of state gives

$$\ln\phi \quad = \quad \frac{1}{RT}\int_0^P \left(V_m - \frac{RT}{P'}\right) dP' \quad = \quad \frac{1}{RT}\int_0^P \left(\frac{RT}{P'} + \beta + \gamma P' - \frac{RT}{P'}\right) dP' \quad = \quad \frac{1}{RT}\int_0^P (\beta + \gamma P') dP' \quad = \quad \frac{\beta P}{RT} + \frac{\gamma P^2}{2RT}$$

Inversion of this equation gives the dependence of the fugacity coefficient on pressure and temperature.

$$\phi = \exp\left(\frac{\beta P}{RT} + \frac{\gamma P^2}{2RT}\right)$$

Therefore, the fugacity is

$$\boxed{f \quad = \quad \phi P \quad = \quad P\exp\left(\frac{\beta P}{RT} + \frac{\gamma P^2}{2RT}\right)}.$$

Score for Page

6. (10 points) For each expression given in the left column, chose the appropriate description from the right column.

1) $d\mu_\alpha = d\mu_\beta$ __F__	A) Condition of phase separation B) Trouton's rule (never use it unless you have to) C) Trofimenko's rule D) ΔS_{mixing} for solids upon diffusion E) Murphy's law F) Condition of phase equilibrium G) An example of Maxwell relation H) Entropy change for a cycle in Otto engine I) The definition of chemical potential J) An example of sublimation process K) The Gibbs-Helmholtz equation L) The definition of extent of reaction M) An example of standard boiling temperature N) The P-S diagram equation O) The reaction quotient of pressures P) The probability of the low energy transition Q) ΔS_{mixing} for ideal gases R) The definition of thermodynamic equilibrium constant S) Condition of the spontaneity of a process
2) $-nR\sum_i x_i \ln x_i$ __Q__	
3) $\left(\frac{\partial\left(\frac{G}{T}\right)}{\partial T}\right)_P = -\frac{H}{T^2}$ __K__	
4) $\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$ __G__	
5) $\Delta S_m^{vaporization} \approx 90\ J/K-mol$ __ B_	

Score for Page

7. (15 points) Estimate the activity of pure solid gold at 100 MPa and 300 K [Note: the molar volume of gold at room temperature is 10.2 cm^3]. Comment on the number that you obtained, as compared to the activity of gold at room temperature and 1 atmosphere.

The chemical potential at a particular pressure can be determined by the following equation:

$$\mu \quad = \quad \mu^{\Theta} + \int_{P^{\Theta}}^{P} V_m dP \quad = \quad \mu^{\Theta} + RT \ln \Gamma$$

which gives a means to calculate the activity coefficient, Γ, under conditions of pressure different from the standard state.

$$\ln \Gamma \quad = \quad \frac{\mu - \mu^{\Theta}}{RT} \quad \approx \quad \frac{V_m \left(P - P^{\Theta}\right)}{RT},$$

where the second approximate equality arises by assuming that gold is incompressible.

From the values given above, we find the activity of the gold at this high pressure under this assumption.

$$\Gamma \quad \approx \quad \exp\left(\frac{V_m \left(P - P^{\Theta}\right)}{RT}\right) \quad = \quad \exp\left(\frac{10.2 \frac{cm^3}{mol} \times 10^{-6} \frac{m^3}{cm^3} \times (100000000\ Pa - 100000\ Pa)}{8.3144 \frac{J}{mol \times K} 300K}\right) \quad = \quad 1.5$$

where 1 Pa = 1 N m^{-2} = 1 J m^{-3}. At such an extreme pressure, the activity of a solid is substantially different from 1. Of course, since the molar volume at such an extreme pressure will be different from its value at standard pressure (i.e. gold is not really totally incompressible), the actual activity will be slightly smaller than 1.5. For example, a reduction of the molar volume by 10% would make the activity about 1.44, which is still closer to 1.5 than it is to 1.

Room conditions are 298.15 K and 1 atm = 101325 Pa:

$$\Gamma \quad \approx \quad \exp\left(\frac{V_m \left(P - P^{\Theta}\right)}{RT}\right) \quad = \quad \exp\left(\frac{10.2 \frac{cm^3}{mol} \times 10^{-6} \frac{m^3}{cm^3} \times (101325\ Pa - 100000\ Pa)}{8.3144349 \frac{J}{mol \times K} 298.15K}\right) \quad = \quad 1.000055$$

The activity coefficient at conditions near the standard condition is expected to be almost 1. The calculation at room temperature shows that to be the case. However, at more extreme conditions (e.g. high pressure) one would expect the activity to be much different from that at the standard state, and that is also reflected in the first calculated value.

Score for Page

8. (15 points) Uranium hexafluoride (UF_6) is used for isotopic enrichment of uranium. In uranium mining, after uranium ore is obtained, it is refined into uranium oxide often called “yellow cake”. Since the industry has to go to all the trouble of converting uranium ore into “yellow cake” and then into uranium hexafluoride, the storage of UF_6 may potentially become a problem. If 1 kg of solid UF_6 before isotopic enrichment is placed into an evacuated standard 100 L cylinder at room temperature and chemical equilibrium is established between gaseous and solid UF_6, what is the percentage of UF_6 lost to the gas phase if there is no chemical decomposition?

$$UF_6(s) \rightarrow UF_6(g)$$

Materials	UF_6 (s)	UF_6 (g)
Initial Pressure	0	0
Initial Moles	1000g/(352.0193 g/mol)	0
Final Moles	2.8408-X	X
Final Pressure	0	$P = \frac{XRT}{100L}$, Here we disregard the volume of solid

$$\Delta G^{\Theta}_{rxn} = \Delta G^{\Theta}_{f,UF_6(g)} - \Delta G^{\Theta}_{f,UF_6(s)} = -2063.7\frac{kJ}{mol} - \left(-2068.5\frac{kJ}{mol}\right) = 4.8\frac{kJ}{mol}$$

$$\Delta G^{\Theta}_{rxn} = -RT\ln(K_a);\; K_a = \exp\left(-\frac{4800\frac{J}{mol}}{8.3144\frac{J}{mol\times K}\pm\times 298.15K}\right) = 0.144$$

$$K_a = 0.144 = \frac{a_{UF_6(g)}}{a_{UF_6(s)}} \approx \frac{\dfrac{XRT}{100L\times 0.001\frac{m^3}{L}\times P^{\Theta}}}{1} = \frac{XRT}{0.1m^3\times 1bar}$$

$$X = \frac{0.144\times 0.1m^3\times 100000Pa}{8.3144\frac{J}{mol\times K}\times 298.15K} = 0.5809\ mol$$

Thus, the percentage of UF_6(s) lost to the gas phase is:

$$\% = \frac{0.5809\ mol}{2.8048\ mol}\times 100\% = 20.7\%$$

This is very significant. Better fill up the cylinders completely to store UF_6(s).

Score for Page

9. (5 points, extra credit) I heat my house with a heat pump on mild winter days. I found out that the major use of energy by the heat pump is actually for turning the fan, which consumes 90% of the electrical energy. By a mild winter day, I mean 41°F (5°C). I like to have the interior of the house at 68°F (20°C). My neighbor uses electrical resistance heaters to warm her all-electric house, which is otherwise identical to my house. Presuming the neighbor heats her house to the same interior temperature, ideally what fraction of her electricity usage (for heating) do I use per hour?

This is actually a very simple question. One must calculate the coefficient of performance of the heat pump, which is the ratio of the heat pumped out to the amount of work done. The maximum coefficient of performance depends only on the two temperatures:

$$\eta = \frac{T_{inside}}{T_{inside} - T_{outside}} = \frac{293.15K}{293.15K - 278.15K} = 19.5$$

But, the pump uses only 10% of the energy input into the unit because 90% goes to operate the fan. Hence, the actual ratio is down by a factor of 10, when considering the total energy into the unit:

$$\eta_{actual} = 19.5 \times 0.1 = 1.95$$

Assuming that all of the electrical energy (i.e. work) my neighbor receives goes into resistive heating (i.e. the electrical heating is perfect in her house), I would use $\frac{1}{1.95} = 0.51$ times the energy she does to do the same heating of identical spaces. So, the heat pump is quite efficient under these conditions.

Score for Page