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Section Number: 10

CHEMISTRY 443, Fall, 2015(15F)
Midterm Examination #2, November 6, 2015

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.

1. (10 points) Calculate the ideal entropy of mixing of air on a molar basis at 298.15 K. Assume that air consists only of oxygen and nitrogen, with the mole fractions being exactly 0.21 and 0.79, respectively.

$$\Delta_{mix}S_m = -R(X_A \ln X_A + X_B \ln X_B) = -(8.314473 \text{ J K}^{-1} \text{ mol}^{-1})(0.21 \ln(0.21) + 0.79 \ln(0.79))$$

Doing the mathematics gives

$$\Delta_{mix}S_m = 4.27326 \text{ J K}^{-1} \text{ mol}^{-1}$$

DO NOT WRITE
IN THIS SPACE

1,2 _____/25

3,4 _____/25

5 _____/20

6,7 _____/20

8 _____/10

9 _____/5
(Extra credit)

TOTAL PTS

2. (15 points) For a gas obeying the equation of state (R and b are constants; all other symbols have their usual meanings)

$$P(V_m - b) = RT,$$

determine the following derivatives. Put the derivatives in the simplest forms possible.

$$\left(\frac{\partial P}{\partial T}\right)_{V_m} = \frac{R}{V_m - b}$$

$$\left(\frac{\partial V_m}{\partial P}\right)_T = -\frac{RT}{P^2} = -\frac{(V_m - b)^2}{RT}$$

$$\left(\frac{\partial S_m}{\partial P}\right)_T = -\left(\frac{\partial V_m}{\partial T}\right)_P = -\frac{R}{P} = -\frac{V_m - b}{T}$$

3. (15 points) Calculate the standard molar Gibbs energy of vaporization of methanol at 298.15 K.

From Table 5.8, one may find the Gibbs energies of formation of the liquid and the gas. They are

$$\Delta_f G_m^\theta(\text{liquid}) = -166.6 \text{ kJ}$$

$$\Delta_f G_m^\theta(\text{gas}) = -162.3 \text{ kJ}$$

The vaporization reaction is $\text{CH}_3\text{OH}(\text{liquid}) \rightarrow \text{CH}_3\text{OH}(\text{gas})$. By Hess's law, we may use the formation free energies to determine the free-energy change in this reaction:

$$\Delta G_m^\theta = \Delta_f G_m^\theta(\text{gas}) - \Delta_f G_m^\theta(\text{liquid}) = -162.3 \text{ kJ} - (-166.6 \text{ kJ}) = 4.3 \text{ kJ}$$

4. (10 points) Monoclinic sulfur is reported to melt at 115.21°C, and it has a standard enthalpy of fusion of 1.727 kJ/mol. What is the standard molar entropy of fusion of monoclinic sulfur at its melting point?

For this calculation, we recall that for a phase transition

$$\Delta S_m^\theta = \frac{\Delta H_m^\theta}{T_f} = \frac{1727 \text{ J mol}^{-1}}{388.36 \text{ K}} = 4.447 \frac{\text{J}}{\text{K (mol)}}$$

(It is necessary to use the absolute temperature, not the temperature on the Celsius scale.)

5. (20 points) In the table below, indicate the best definition of each word or phrase in **column A** by inserting the letter of the word or phrase in column B. (Graded right minus 0.5 wrong; do not guess.)

Column A	Column B
__H__ Carnot cycle	(A) Alternate statement of the second law of thermodynamics
__E__ Chemical potential	(B) Efficiency
__A__ Clausius inequality	(C) Entropy decrease in an open system
__J__ Efficiency of an ideal Carnot heat pump	(D) Melting
__K__ Efficiency of an ideal Carnot refrigerator	(E) Molar free energy at constant T and P
__L__ Efficiency of an ideal Otto cycle	(F) Joule-Thomson coefficient
__D__ Fusion	(G) The entropy of a pure crystalline solid at 0 K is defined to be zero.
__B__ Numerical statement of quality of a process	(H) Theory of the steam engine
__I__ Otto cycle	(I) Widely used cycle for automobile engines
__G__ Third law of thermodynamics	(J) $\epsilon = \frac{T_{hot}}{T_{hot} - T_{cold}}$
	(K) $\epsilon = \frac{T_{cold}}{T_{hot} - T_{cold}}$
	(L) $\epsilon = \frac{T_d - T_c}{T_d}$

6. (10 points) SiO₂ exists in three different crystalline forms, cristobalite, quartz, and tridymite. Using thermodynamic arguments based on information in your Handbook, explain which of these is the most stable at 298.15 K and why. [HINT: Showing some calculations will help you with the explanation.]

From information in Table 5.8, one may predict the Gibbs energy of transformation of the forms:

$$\Delta G_m^\theta(\text{crys.} \rightarrow \text{qtz.}) = -856.3 \text{ kJ} - (-855.43 \text{ kJ}) = -0.87 \text{ kJ}$$

And

$$\Delta G_m^\theta(\text{qtz.} \rightarrow \text{tri}) = -855.26 \text{ kJ} - (-856.3 \text{ kJ}) = +1.04 \text{ kJ}$$

Finally one may calculate

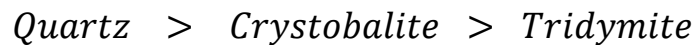
$$\Delta G_m^\theta(\text{crys.} \rightarrow \text{tri}) = -855.26 \text{ kJ} - (-855.43 \text{ kJ}) = +0.17 \text{ kJ}$$

By the first equation, one sees that quartz is more stable than cristobalite because the Gibbs energy of transition to go from cristobalite to quartz is negative.

By the second equation, one sees that to transform quartz into tridymite one must increase the Gibbs energy, so quartz is more stable than tridymite.

Finally, by the third equation, one sees that cristobalite is slightly more stable than tridymite.

So, at 298.15 K, one may write the relative stabilities of these three forms as:



The most stable form at 298.15 K is QUARTZ.

7. (10 points) (a) At 298.15 K, what is the activity of an ideal gas which is at a pressure of 6.302 bar?

The activity of an ideal gas is simply the ratio of its pressure to the standard pressure:

$$a_{\text{ideal}} = \frac{P}{P^\theta} = \frac{6.302 \text{ bar}}{1 \text{ bar}} = 6.302$$

(b) Under the same conditions, the activity of a real gas is measured to be 4.003. What is the activity coefficient for the real gas under these conditions?

For a real gas, the activity is related to that of an ideal gas by the equation:

$$a_{\text{real}} = \gamma a_{\text{ideal}} = \gamma \left(\frac{P}{P^\theta} \right)$$

Hence, the activity coefficient is given by

$$\gamma = \frac{a_{\text{real}}}{a_{\text{ideal}}} = \frac{4.003}{6.302} = 0.6352$$

8. (10 points) For a solid one may write an approximate equation of state:

$$V_m = V_0(1 - \kappa_T(P - P_0))$$

where V_m is the volume, P is the pressure, κ_T is the isothermal compressibility (assumed independent of pressure), and V_0 and P_0 are reference constants that do not depend on the pressure. For a solid that obeys this equation, derive an equation for the change in the molar Gibbs energy when the pressure over the solid is changed from P_1 to P_2 . (Show all work clearly.)

To determine the change in molar Gibbs energy when the pressure is being changed, one needs to use

$$\Delta G_m = \int_{P_1}^{P_2} \left(\frac{\partial G_m}{\partial P} \right)_T dP$$

So, one must identify this derivative. That can be done from the equation

$$dG_m = -S_m dT + V_m dP$$

Thus,

$$\left(\frac{\partial G_m}{\partial P} \right)_T = V_m$$

Substitution gives

$$\begin{aligned} \Delta G_m &= \int_{P_1}^{P_2} V_m dP = V_0 \int_{P_1}^{P_2} (1 - \kappa_T(P - P_0)) dP \\ &= V_0(P_2 - P_1) - \frac{\kappa_T V_0}{2} [(P_2 - P_0)^2 - (P_1 - P_0)^2] \end{aligned}$$

9. (5 points, extra credit) Suppose one were to use a sprayer to produce small droplets of water. In particular, suppose one takes a volume of exactly 1 cm^3 of water at 298.15 K and produces a spray of droplets, each of which has a diameter of 1 micron . How much would the free energy of the water change in this process?

This is a calculation of the free energy change due to changing the surface area. The volume of the droplet is

$$V_{\text{droplet}} = \frac{4}{3}\pi r^3$$

And the surface area of the droplet is

$$A_{\text{droplet}} = 4\pi r^2$$

The number of droplets formed is

$$N = \frac{V_{\text{total}}}{V_{\text{droplet}}} = \frac{3V_{\text{total}}}{4\pi r^3}$$

The total area at the end is

$$A_{\text{total}} = N A_{\text{droplet}} = \frac{V_{\text{total}} A_{\text{droplet}}}{V_{\text{droplet}}} = \frac{3V_{\text{total}}}{4\pi r^3} (4\pi r^2) = \frac{3V_{\text{total}}}{r}$$

The change in area is then this minus the original surface area:

$$\Delta A = \frac{3V_{\text{total}}}{r} - A_{\text{initial}}$$

The initial area depends on the exact shape of the initial volume (for example, whether it is a cube or sphere), but in the end that will not matter because it is much smaller than the final area. So, the change in area is approximately (to a good approximation) the final total area.

The free energy change is then approximately (again to a good approximation)

$$\Delta G = \gamma \Delta A \cong \gamma A_{\text{total}} = \frac{3\gamma V_{\text{total}}}{r}$$

Substitution gives

$$\Delta G = \frac{3\gamma V_{\text{total}}}{r} = \frac{3(71.99 \text{ mN m}^{-1})(10^{-6} \text{ m}^3)}{0.5 \times 10^{-6} \text{ m}} = 431.9 \times 10^{-3} \text{ N m} = 0.4319 \text{ J}$$

Let's demonstrate the insignificance of the initial surface area. Suppose it was a cubic volume. It would have a surface area of 6 cm^2 . However the final surface area is $A_{\text{total}} = \frac{3(1 \text{ cm}^3)}{0.5 \times 10^{-4} \text{ cm}} = 6 \times 10^4 \text{ cm}^2$, which is 10,000 times larger than the original surface area. So, the starting surface area is, indeed, negligible.