

## CHEM 361

## Exam 3

November 10, 2016, 7:55-8:55 AM

Name KEY

4 x 6 note card

Last,

First

100 points in 8 questions on 5 pages including part of Table A.5

For full credit show all work and put correct units on final answers.

Read, please: If you get a quantitative answer that is many powers of 10 from what you think it should be and cannot find the error, you will be rewarded for pointing out approximately what you expected and why. 25% will be deducted on a problem for sign and unit errors that lead to unreasonable results if you do not say why it is unreasonable.

(16 pts) 1. (a) From the modified Table A.5, calculate the Henry's Law constant for  $N_2$  (gas) evaporating from water at 298 K? The units must be correct for full credit.

$$K_{eq} = K_{Henry} = e^{-\frac{\Delta G^\circ}{RT}} \text{ for } N_2(g) \rightarrow N_2(l) \quad \Delta G^\circ = 0 - 18.16 \frac{kJ}{mol} = -18160 \frac{J}{mol}$$

$$K = e^{-\frac{-18160}{8.3145 \cdot 298}} = \boxed{1524 \frac{bar}{M}}$$

standard state for solute in Table A.5 = 1M

(b) From the modified Table A.5, calculate the Henry's Law constant for dissolving of  $N_2$  (gas) in water at 373 K.

for evaporation  $\Delta H^\circ = 0 - (-10300) = 10300 \text{ J/mol}$

$$\ln \frac{K_{373}}{K_{298}} = -\frac{\Delta H^\circ}{R} \left( \frac{1}{T_{373}} - \frac{1}{T_{298}} \right) = -\frac{10300}{8.3145} \left( \frac{1}{373} - \frac{1}{298} \right) = 0.833$$

$$K_{373(evap)} = K_{298 evap} \cdot e^{0.833} = 1524 \cdot 2.30 = 3504 \text{ b/m}$$

FOR DISSOLVING:  $K_{373 dissolving} = \frac{1}{K_{373 evap}} = \boxed{2.85 \times 10^{-4} \frac{M}{bar}}$

(12 pts) 2. If the osmotic pressure of an aqueous solution = 100 bar at 373 K, what will be the boiling point when the applied pressure = 1 bar? (the volume of 1 mol of pure water is 18 mL.)

$$a = e^{-\frac{\pi V_{H_2O}}{RT}} = e^{-\frac{100 \text{ bar} \cdot 0.018 \text{ L mol}^{-1}}{0.083145 \text{ L bar mol}^{-1} \text{ K}^{-1} \cdot 373 \text{ K}}} = 0.944$$

$$H_2O(l, a) \rightarrow H_2O(g, P_{H_2O}=1 \text{ bar}) \rightarrow Q = \frac{P_{H_2O(g)}}{a}, \quad K = \left( \frac{P_{H_2O(g)}}{a} \right)_{eq}$$

$$\ln \frac{K_2}{K_1} = -\frac{\Delta H^\circ}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \quad -\frac{R}{\Delta H^\circ} \ln \frac{K_2}{K_1} + \frac{1}{T_1} = \frac{1}{T_2}$$

$$-\frac{8.3145}{44010} \ln \frac{1}{0.944} + \frac{1}{373} = \frac{1}{T_b}$$

$$\Delta H^\circ = -241.82 - (-285.83) = 44010 \text{ J mol}^{-1}$$

$$\boxed{T_b = 374.5 \text{ K}} \quad \boxed{\Delta T_b = +1.5 \text{ K}}$$

OK

(12 pts) 3. (a) Calculate the equilibrium  $\text{Ca}^{2+}$  concentration on the inside of the vesicle below if the concentration on the outside is  $1 \times 10^{-9} \text{ M}$  at 298K and electric potential inside the vesicle is more negative than the outside by 59 mV.

Diagram of a vesicle: Inside,  $\text{Ca}^{2+} = ? \text{ M}$ ,  $\Phi(\text{in}) = -59 \text{ mV}$ . Outside,  $1 \times 10^{-9} \text{ M}$ ,  $\Phi(\text{out}) = 0 \text{ mV}$ .

$$\Delta \mu = \Delta \mu^0 + RT \ln \frac{[\text{Ca}^{2+}]_{\text{in}}}{[\text{Ca}^{2+}]_{\text{out}}} + zF(\Phi_{\text{in}} - \Phi_{\text{out}}) = 0$$

$$RT \ln \left( \frac{[\text{Ca}^{2+}]_{\text{in}}}{1 \times 10^{-9}} \right) = -2.96500 (-0.059 - 0)$$

$$[\text{Ca}^{2+}]_{\text{eq}} = (1 \times 10^{-9}) \cdot e^{\frac{2.96500(0.059)}{8.3145 \cdot 298}}$$

$$= 1 \times 10^{-7} \text{ M}$$

$\Delta \mu = 0$

(b) What is  $\Delta G$  for moving 3 moles of  $\text{Ca}^{2+}$  from the inside to the outside of the cell after equilibrium is reached?

$$\Delta G = n \Delta \mu = 3 \cdot 0 = 0 \quad \text{equilibrium}$$

(12 pts) 4. What can be said about the mutated form of a protein if the diffusion coefficient and sedimentation coefficients are unaffected by the mutation but the electrophoretic mobility is increased by a factor of two?

$$D = \frac{k_B T}{f} \quad \mu = \frac{ze}{f} \quad S = \frac{m}{f}$$

$f$  is same.  $S$  is same

Therefore  $z$  (charge) is increased by 2 times

OK

- 12 pts) 5. (a) From Table A.5, what is the equilibrium constant for evaporating water from the pure liquid at 298 K, i.e., for the process  $\text{H}_2\text{O}(\text{liquid}, a) \rightarrow \text{H}_2\text{O}(\text{g}, p_{\text{H}_2\text{O}})$ , where  $a$  = activity of the liquid water.

$$K = e^{\frac{-\Delta G^\circ}{RT}}$$

$$\Delta G^\circ = -228.73 - (-237.13) = +8.4 \text{ kJ/mol}$$

$$K = \left( \frac{p_{\text{H}_2\text{O}}}{a} \right)_{\text{eq}} = \text{vapor pressure} = e^{\frac{-8400}{8.3145 \cdot 298}} = \boxed{0.0337} \text{ bar}$$

- (b) Calculate the boiling point of water near the summit of Granite Peak, where the atmospheric pressure is 0.6 bar. Again, use data in Table A.5

$$\Delta H^\circ = 10.3 \text{ kJ/mol}$$

$$\ln \frac{K_2}{K_1} = -\frac{\Delta H^\circ}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$-\frac{8.3145}{44010 \text{ J/mol}} \ln \frac{0.6}{(0.033)} + \frac{1}{298} = \frac{1}{T_b} = 0.00281$$

$$T_b = \boxed{355.6 \text{ K}}$$

Much lower  
than  
373

from prob #2

- (c) Briefly explain in words why the boiling point is lower at high elevations.

boiling will happen when  $(p_{\text{H}_2\text{O}})_{\text{eq}} = p_{\text{atmosphere}} = 0.6 \text{ bar}$ .

this will happen at much lower  $T$  than 373 K

because  $\Delta H_{\text{vap}}^\circ = +$  (endothermic), and therefore the vapor pressure\* increases as  $T$  increases

\* Vapor pressure is  $K_{\text{eq}}$  for  $\text{H}_2\text{O}(\text{l}, a) \rightleftharpoons \text{H}_2\text{O}(\text{g}, p_{\text{H}_2\text{O}})$

- OK
- (12 pts) 6. (a) Calculate the root mean square speed of an  $H_2$  molecule at 6000 K. (temperature of sun).

$$u_{rms} = \sqrt{\frac{3RT}{M}} = \left( \frac{3 \cdot 8.3145 \cdot 6000}{0.002} \right)^{1/2} = \boxed{8650 \text{ m s}^{-1}}$$

- (b) **Estimate** the collisions  $s^{-1}$  and the mean free path for an  $H_2$  molecule, molecule at 6000 K on the Sun's surface where the pressure = is about 0.001 bar, and assuming the collision area ( $\sigma$ ) is  $1 \times 10^{-17} \text{ m}^2$ . (notice that an adjustment for both temperature and pressure is required)

$1 \times 10^{-19} \text{ m}^2$

$$Z = (u_{rms} \times \frac{P}{k_B T} \times \sigma) = 8650 \times \frac{0.001 \times 10^5}{(1.38 \times 10^{-23} \cdot 6000)} \times 1 \times 10^{-17}$$

$$= \boxed{1.2 \times 10^8} \text{ or } (10^{10} \times 0.001) \times \sqrt{\frac{6000 \cdot 0.028}{300 \cdot 0.002}} \approx \boxed{1.7 \times 10^8 \text{ col s}^{-1}}$$

$PV = Nk_B T$   
 $\frac{N}{V} = \frac{P}{k_B T}$

mean free path =  $\lambda = \frac{u_{rms} (\text{m s}^{-1})}{Z (\text{col s}^{-1})} = \frac{8650 \text{ m s}^{-1}}{1.7 \times 10^8 \text{ col s}^{-1}} = \boxed{5 \times 10^{-5} \text{ m col}^{-1}}$

Also accepted:  $u_{rms} \approx 10^{10} \times 0.001 = 10^7 \text{ col s}^{-1}$

$$\lambda \approx \frac{8650 \text{ m s}^{-1}}{10^7 \text{ col s}^{-1}} = 8.65 \times 10^{-4} \text{ m col}^{-1}$$

100 kg

- (12 pts) 7. What is the diffusion coefficient of a protein with a molecular weight equal to 100,000 g/mol if its sedimentation coefficient in Svedbergs is 200 S and its partial specific volume is  $0.5 \text{ cm}^3/\text{g}$  in water at 293 K? The density of water at this temperature =  $1 \text{ g cm}^{-3}$ .

$$S = \frac{m_{eff}}{f} \approx \frac{m(1-\rho v)}{k_B T} D = \frac{M(1-\rho v)}{RT} D$$

$$D = \frac{S R T}{M (1-\rho v)} = \frac{(200 \times 10^{-13}) (8.3145) (293)}{100 \text{ kg} (1-0.5)}$$

$$= \boxed{9.74 \times 10^{-10} \text{ m}^2/\text{s}}$$

OK

(12 pts) 8. (a) For a peptide with 1 lysine, 1 tyrosine, and 1 histidine with no charged terminal groups, indicate the fraction protonated and the average charge of each residue at pH 8, accurate to within 0.01 charge unit. What will be the total charge on the peptide at pH 8? ~~Parts b) and c) are on the next page.~~

Amino acid	pKa	Charge when protonated	Fraction Protonated	Ave. Charge
Lysine	10	+1	0.99	0.99
Tyrosine	8	0	0.5	-0.5
Histidine	6	+1	0.01	0.01

Total charge =  $1 - 0.5 = 0.5$

(b) In a pH gradient gel with low pH at the positive electrode, is this peptide at a higher or lower pH than its isoelectric point? Explain very briefly.

lower pH will move to higher pH  $\rightarrow$  neg. electrode.

TABLE A.5 Inorganic Compounds\* (cont.)

	$\Delta_f H^\circ$ (kJ mol <sup>-1</sup> )	$S^\circ$ (J K <sup>-1</sup> mol <sup>-1</sup> )	$\Delta_f G^\circ$ (kJ mol <sup>-1</sup> )
HCO <sub>3</sub> <sup>-</sup> (aq)	-691.99	91.2	-586.77
CO <sub>3</sub> <sup>2-</sup> (aq)	-677.14	-56.9	-527.81
Fe(s)	0	27.28	0
Fe <sub>2</sub> O <sub>3</sub> (s)	-824.2	87.40	-742.2
H <sub>2</sub> (g)	0	130.79	0
H <sub>2</sub> O(g)	-241.82	188.93	-228.73
H <sub>2</sub> O(l)	-285.83	69.91	-237.13
H <sup>+</sup> (aq)	0	0	0
OH <sup>-</sup> (aq)	-229.99	-10.75	-157.244
H <sub>2</sub> O <sub>2</sub> (aq)	-191.17	143.9	-134.03
H <sub>2</sub> S(g)	-20.63	205.90	-33.56
H <sub>2</sub> SO <sub>4</sub> (g)	-735.13	298.8	-653.37
N <sub>2</sub> (g)	0	191.72	0
N <sub>2</sub> (aq)	-10.30	—	18.16

\* Standard thermodynamic values at 25°C (298.15 K) and 1 bar pressure. Values for ions refer to an aqueous solution at unit activity on the molality scale. Standard enthalpy of formation,  $\Delta_f H^\circ$ , third-law entropies,  $S^\circ$ , and standard Gibbs free energy of formation,  $\Delta_f G^\circ$ , are given.

† The standard state for all ions and for species labeled (aq) is that of a solute on the molality scale.

(Data from The NBS Tables of Thermodynamic Properties, D. D. Wagman et al., eds., J. Phys. Chem. Ref. Data, 11, Suppl. 2 (1982), corrected to 1 bar pressure.)