Dr. Zellmer	Chemistry 1220	All Sections
Time: 7 PM Sun.	Spring Semester 2023	January 29, 2023
30 min	Quiz II	

Name KEY Rec. TA/time

1. (8 pts) At 63.5°C the vapor pressure of water is 175.0 torr and that of ethanol (C_2H_6O) is 400.0 torr. Assume that water and ethanol form an ideal solution. A solution is made by mixing 0.555 moles of H_2O and 0.217 moles of C_2H_6O. (Mol. Wts. H_2O = 18.02, C_2H_6O = 46.07)

a) What is the **<u>total</u> vapor pressure** above the solution?

Want total vapor pressure of a solution of two volatile substances - both will contribute to the vapor pressure above the solution. Assume that both follow Raoult's Law and the gas mixture follows Dalton's of Partial Pressures.

$$P_A = X_A P_A^{o} \qquad P_B = X_B P_B^{o} \qquad \text{Raoult's Law}$$

P_A = vapor pressure of A above solution P_B = vapor pressure of B above solution

X_A = mole fraction of A in **liquid phase** X_B = mole fraction of B in **liquid phase**

P_A^{o} = V.P. of pure A P_B^{o} = V.P. of pure B

$$P_T = P_A + P_B \qquad \text{Dalton's Law} \qquad P_T = \text{total vapor pressure above the solution}$$

$$P_T = X_A P_A^{o} + X_B P_B^{o} \qquad \text{for two volatile substances}$$

$$P_T = X_{H2O} P_{H2O}^{o} + X_{C2H6O} P_{C2H6O}^{o}$$

total moles of solution = 0.555 mol H_2O + 0.217 mol C_2H_6O = 0.772 mol soln

$$X_{H2O} = \frac{0.555 \text{ mol } H_2O}{0.772 \text{ mol}} = 0.71\underline{\mathbf{8}}9 \qquad X_{C2H6O} = \frac{0.217 \text{ mol } C_2H_6O}{0.772 \text{ mol}} = 0.28\underline{\mathbf{1}}0$$

$$P_T = (0.71\underline{\mathbf{8}}9)(175.0 \text{ torr}) + (0.28\underline{\mathbf{1}}0)(400.0 \text{ torr})$$

$$= 12\underline{\mathbf{5}}.809 \text{ torr} + 11\underline{\mathbf{2}}.435 \text{ torr} = 23\underline{\mathbf{8}}.244 \text{ torr} = 238 \text{ torr}$$

b) What is the **<u>mole</u>** **<u>fraction</u>** of ethanol (C_2H_6O) **in** the **<u>vapor</u>** above the solution? (Not asked on quiz.)

The partial pressure of gas A in a mixture is given by the following eqn (chapter 10):

$$P_A = X_{A,g} P_T$$

Where $X_{A,g}$ is the mole fraction of substance A in the gas phase (although you won't see the "g" as part of the subscript).

$$X_{C2H6O} = \frac{P_{C2H6O}}{P_T} = \frac{11\underline{\mathbf{2}}.435 \text{ torr}}{23\underline{\mathbf{8}}.244 \text{ torr}} = 0.47\underline{\mathbf{1}}9 = 0.472$$

2. (5 pts) You have a 0.0020 M aqueous $Fe(NO_3)_3$ solution? Assuming an "ideal" ionic solution (i.e. no ion-pairing), what would be the **<u>osmotic</u> <u>pressure</u>** at 30.0°C? **Show work or explain your answers.**

$$\Pi = i\,\mathrm{MRT} = (\mathrm{M}_{\text{particles}})\mathrm{RT} \qquad \mathrm{M}_{\text{particles}} = i\,\mathrm{M}_{\text{stated}}$$

for an "ideal" ionic solution, i = # ions from formula for the compound
(there is no ion-pairing between ions in the solution)

$$Fe(NO_3)_3\ (s) \xrightarrow{H_2O} Fe^{3+} + 3\ NO_3^-$$

i = 4 ions (NO_3^- stays together as a single particle in soln)

$$\Pi = 4\ (0.002\underline{0}\ \text{mol/L})\ (0.08206\ \text{L•atm/mol•K})(303.\underline{1}5\ \text{K}) = 0.1\underline{9}90\ \text{atm} = 0.20\ \text{atm}\quad (2\ \text{s.f.})$$

(1$\underline{5}$1 torr)

3. Which of the following statements is **<u>FALSE</u>**?

a) The vapor pressure of a solution with a nonvolatile solute is due just to the solvent.

b) A 0.10 ***m*** solution of $MgSO_4$ would be expected to exhibit more ion pairing than a 0.10 ***m*** solution of NaCl.

c) Hydrophilic colloid particles tend to stay dispersed in water.

d) The vapor pressure of a solution increases with increasing temperature.

e)* The vapor pressure of a solution of a nonvolatile solute is higher than that of the pure solvent.

a) T: Volatile substances in an ideal solution follow Raoult's Law:

$$P_A = X_A P_A^0 \qquad \text{Raoult's Law}$$

X_A = mole fraction of the volatile substance in the solution
P_A^0 = vapor pressure of pure substance
P_A = vapor pressure due to the substance in the solution.
$P_{\text{solution}} = P_{\text{solvent}}$ (for a nonvolatile solute which has no appreciable vapor pressure)

b) T: The charges on the ions in $MgSO_4$ (Mg^{2+} and SO_4^{2-}) are bigger than those for NaCl (Na^+ and Cl^-). This means the Mg^{2+} and SO_4^{2-} are more likely to form more ion pairs in solution and behave less ideally (stronger attraction due to the larger charges). See Table 13.5 in the text book.

c) T: Hydrophilic ("water loving") colloid particles have polar or charged groups that allow them to stay dispersed in water.

d) T: The VP_{soln} depends on temp, just like that of pure substances. As the temp inc the KE of the particles increases so there are more particles with enough KE able to escape into the vapor phase and thus giving a higher VP.

e) F: Vapor pressure lowering. The solute causes the VP to **decrease** compared to the pure solvent. Thus the $VP_{soln} < VP_{solvent}$.

4. (2 pts) Solution A is hypotonic with respect to solution B. What does this mean about the relative osmotic pressures of the two solutions and the relative concentrations of solute in the solutions? **Explain**.

$$\Pi = i\,\mathrm{MRT} = (\mathrm{M}_{\text{particles}})\mathrm{RT} \qquad \mathrm{M}_{\text{particles}} = i\,\mathrm{M}_{\text{stated}}$$

The greater the conc. of particles the greater the osmotic pressure. If soln. A is hypotonic w. respect to soln. B that means soln. A has a lower osmotic pressure than soln. B. This would mean the conc. of particles for soln A is smaller than the conc. of particles for soln. B. If the two solutions are separated by a membrane (such as a cell membrane) the solvent (water) would flow at a faster rate from soln. A to soln. B to try to dilute soln. B and make soln. A more conc. (tries to equalize the concentrations, although in practice they won't wind up with the same conc.).

5. The freezing point of p-dichlorobenzene is 53.1 °C. A solution of 1.26 g of a sulfa drug in 10.0 g of p-dichlorobenzene freezes at 47.9 °C. What is the **molecular** **weight** of the sulfa drug? ($K_f = 7.10$ °C/m)

Whenever you want MW think of g/mol: $\mathrm{MW} = \dfrac{\text{mass}}{\text{moles}}$

have mass of 1.26 g, need moles (get from molality)

$$\Delta T_f = (i\,m_{\text{solute}})\,K_f = m_{\text{particles}}\,K_f \qquad m_{\text{particles}} = i\,m_{\text{solute}}$$

i = # particles in solution (integer for ideal behavior)
= 1 for nonelectrolytes solutes (nondissociating or nonionizing)
= # particles resulting formula unit for ionizing/dissociating cmpds (ideal behavior)
m_{solute} = stated molality of solute
$i{*}m$ = molality of particles
K_f = freezing point depression constant (depends on solvent)

for an "ideal" ionic solution, i = # ions from formula for the compound (there is no ion-pairing between ions in the solution when it's behaving ideally)

For this form of the eqn; $\Delta T_f = T_{f,\text{solvent}} - T_{f,\text{soln}}$ and is a positive value

The newer editions (13th and 14th) of the book use:

$$\Delta T_f = -(i\,m_{\text{solute}})\,K_f = -\,m_{\text{particles}}\,K_f$$

where $\Delta T_f = T_{f,\text{soln}} - T_{f,\text{solvent}}$ and is a negative number but it corresponds to final - initial as most delta values do.

Normal f.p. of $C_6H_4Cl_2$ = 53.1 °C f.p. of soln = 47.9 °C K_f = 7.10 °C/m

$$m = \frac{\Delta T_f}{K_f} = \frac{53.1\,^\circ\mathrm{C} - 47.9\,^\circ\mathrm{C}}{7.10\ ^\circ\mathrm{C}/m} = 0.7\underline{3}239 \text{ molal}$$

$$\text{mol solute} = 0.010\underline{0} \text{ kg } C_6H_4Cl_2 \times \frac{0.7\underline{3}239 \text{ mol}}{1 \text{ kg } C_6H_4Cl_2} = 0.007\underline{3}239 \text{ mol solute}$$

$$\mathrm{MW} = \frac{1.26 \text{ g}}{0.007\underline{3}239 \text{ mol}} = 1\underline{7}2.03 \text{ g/mol} = 1\underline{7}2 \text{ g/mol} = 1.7 \times 10^2 \text{ g/mol} \text{ (technically only 2 s.f.)}$$

6. (3 pts) For the reaction below, the rate of disappearance of reactant A ($-\Delta[A]/\Delta t$) is 0.55 M/s. What is the rate of appearance of product C ($\Delta[C]/\Delta t$) in M/s? **Show work or explain your answer.**

$$5\,A + 3\,B \longrightarrow 2\,C + 3\,D$$

$$\text{THE rate of rxn} = \frac{1}{5}\left(\frac{-\Delta[A]}{\Delta t}\right) = \frac{1}{3}\left(\frac{-\Delta[B]}{\Delta t}\right) = \frac{1}{2}\left(\frac{\Delta[C]}{\Delta t}\right) = \frac{1}{3}\left(\frac{\Delta[D]}{\Delta t}\right)$$

Relate THE rate of reaction to the rates in terms of disappearance of reactants or formation of products by using the reciprocal of the coefficients in the balanced eqn as multiples of the various rates.

$$\left(\frac{\Delta[C]}{\Delta t}\right) = \frac{2}{5}\left(\frac{-\Delta[A]}{\Delta t}\right) = \frac{2}{5}(0.55\text{ M/s}) = 0.22\text{ M/s}$$

7. A reaction is **3/2 order** in **A**, **second order** in **B** and **1/2 order** in **C**. The initial rate of the reaction is 1.0×10^{-6} M/sec when the initial concentrations are, $[A]_o = 0.0100$ M, $[B]_o = 0.0200$ M and $[C]_o = 0.0100$ M. What is the **rate constant** (in $M^{-3}s^{-1}$)?

$$r = k\,[A]^{3/2}\,[B]^2\,[C]^{1/2}$$

3/2 order in A, 2nd order in B, 1/2 order in C, 4th order overall (1.5 + 2 + 0.5 = 4)

Treat this like any other math equation.

Given the initial rate of reaction, conc of A, B and C.

Want the rate constant, k. Solve the rate law above for k.

$$k = \left(\frac{r}{[A]^{3/2}[B]^2[C]^{1/2}}\right) = \left(\frac{1.0 \times 10^{-6}\text{ Ms}^{-1}}{(0.0100\text{M})^{3/2}(0.0200\text{M})^2(0.0100\text{M})^{1/2}}\right) = 25.0\text{ M}^{-3}\text{s}^{-1}$$

8. For the reaction and rate law given below, which of the statements is **CORRECT**?

$$A + 3B + C \rightarrow D + E \qquad \text{rate} = k\,[A]^3\,[C]$$

$$r = k\,[A]^3\,[C]$$

1) True: overall order = 3 + 1 = 4 (add the order with respect to each compd that appears in rate law)

2) False: if [A] triples, rate inc by factor of $3^3 = 27$

3) False: if [C] doubles, rate inc by factor of $2^1 = 2$

4) True: Using units of M and s (seconds) solve for k and you get $M^{-3} \bullet s^{-1}$

5) False: The rate and rate constant are directly proportional. When k triples the rate triples.

9. (12 pts) The following data were measure for the reaction

$$2\,A + 3\,B \longrightarrow C + 4\,D$$

Experiment	[A] (M)	[C] (M)	Initial rate (M/s)
1	0.200	0.200	0.2000
2	0.600	0.200	5.4000
3	0.600	0.400	1.3500
4	0.200	0.400	0.0500
5	0.400	0.600	0.1778

a) What is the **rate law** for the reaction?

$r = k\,[A]^x\,[C]^y$ general rate law - find x & y

$\frac{r_j}{r_i} = \frac{k\,[A]_j^x\,[C]_j^y}{k\,[A]_i^x\,[C]_i^y} = \left(\frac{[A]_j}{[A]_i}\right)^x \left(\frac{[C]_j}{[C]_i}\right)^y$ will always look similar to this

1) find order w/rsp to A (hold [C] constant) - use exp 1 & 2 (or 3 & 4 - [A] must chg)

$$\frac{r_2}{r_1} = \left(\frac{[A]_2}{[A]_1}\right)^x \left(\frac{[C]_2}{[C]_1}\right)^y \qquad \frac{5.4000\text{ M/s}}{0.2000\text{ M/s}} = \left(\frac{0.600\text{ M}}{0.200\text{ M}}\right)^x \left(\frac{0.200\text{ M}}{0.200\text{ M}}\right)^y$$

$27 = 3^x \Rightarrow x = 3 \qquad \log 27 = \log 3^x \Rightarrow \log 27 = x \log 3 \Rightarrow x = (\log 27)/(\log 3) = 3$

2) find order w/rsp to C (no need to hold [A] constant) - use exp 1 & 3 (any two - [C] must chg)

$$\frac{r_3}{r_1} = \left(\frac{[A]_3}{[A]_1}\right)^3 \left(\frac{[C]_3}{[C]_1}\right)^y \qquad \frac{1.3500\text{ M/s}}{0.2000\text{ M/s}} = \left(\frac{0.600\text{ M}}{0.200\text{ M}}\right)^3 \left(\frac{0.400\text{ M}}{0.200\text{ M}}\right)^y$$

$6.75 = (3)^3\,(2)^y \Rightarrow 6.75 = (27)\,2^y \Rightarrow 0.25 = 2^y \Rightarrow 1/4 = 2^y \Rightarrow y = -2$

$\log(0.25) = \log 2^y \Rightarrow \log(0.25) = y \log 2 \Rightarrow y = (\log 0.25)/(\log 2) = -2 \Rightarrow y = -2$

3) Rate Law

$$r = k\,[A]^3\,[C]^{-2}$$

NOTE: For step 2 above, when finding y (the order with respect to C) I did NOT have to hold [A] constant because I already knew it's power. I purposely used two exp. such that both substances changed conc. to show that once you know the exponent of a substance it no longer has to be held constant (last problem in the section of homework titled "Rate Laws", section 14.3). I did have to make sure I chose two exp. in which [C] changed.

NOTE: A product is in this rate law. That is fine. You can have reactants, products, catalysts and inhibitors in rates laws (we didn't see any examples of inhibitors in mechanisms but I have mentioned them - they slow down the reaction). Intermediates are different. When dealing with a mechanism you try to get rid of conc. of intermediates whenever possible.

**** Cont. on next page ****

9) (Cont.)

b) What is the reaction **order** with respect to each **compound** AND what is the **overall** reaction **order**?

order with respect to A = 3

order with respect to C = −2

overall order of the reaction = (3) + (−2) = **1** (first order overall)

c) What is the value of the **rate** **constant** (based on data from experiment 1)?

$$k = \frac{r_1}{[A]_1^{\ 3}\ [C]_1^{\ -2}} = \frac{0.2000\ \mathrm{M/s}}{(0.200\ \mathrm{M})^3\ (0.200\ \mathrm{M})^{-2}} = 1.00\ \mathrm{s}^{-1}$$