

General Chemistry II

7/14/2021

PLI #4 – Pre-exam review

1. The solubility of nitrogen gas in water is 821 $\mu\text{m/L}$ at 0°C when N_2 pressure above the water is 0.790 atm.
 - a. What is the Henry's Law constant for N_2 in units of $\text{mol/L}\cdot\text{atm}$?

$$S_g = k_H P_g$$

$$k_H = \frac{S_g}{P_g} = \frac{821 * 10^{-6} \text{mol}}{\text{L}} * \frac{1}{0.790 \text{ atm}} = 1.04 * 10^{-3} \frac{\text{mol}}{\text{L} * \text{atm}}$$

- b. What is the solubility of N_2 in water when the partial pressure of nitrogen above the water is 1.10 atm at 0°C ?

$$S_g = k_H P_g$$

$$S_g = \left(1.04 * 10^{-3} \frac{\text{mol}}{\text{L} * \text{atm}} \right) (1.10 \text{ atm}) = 1.14 * 10^{-3} \frac{\text{mol}}{\text{L}} = 1.14 * 10^{-3} \text{ M}$$

2. Hemoglobin is a large covalent molecule that carries oxygen in human blood. A water solution that contains 0.263 g of hemoglobin (Hb) in 10.0 mL of solution has an osmotic pressure of 7.51 Torr at 25°C. What is the molar mass of the hemoglobin?

Our goal is to find molar mass, which is a value in grams/mole. We are given grams of hemoglobin, so must find how many moles of hemoglobin are acting as solute. We can do this by first calculating the molarity of the solution in moles/liter. Since hemoglobin is covalent, it has a van't Hoff factor of 1. We will use the osmolarity equation.

$$\Pi = MRT$$

R is our gas constant and we can find T by converting the temperature given into Kelvin (25°C + 273.15 = 298.15 K). We also should convert Torr into atm so that we can use our atm-based gas constant.

$$\Pi = 7.51 \text{ Torr} * \frac{1 \text{ atm}}{760 \text{ Torr}} = 0.00988 \text{ atm}$$

$$M = \frac{\Pi}{RT} = \frac{0.00988 \text{ atm}}{(0.08206 \frac{\text{L} * \text{atm}}{\text{mol} * \text{K}})(298.15 \text{ K})} = 4.039 * 10^{-4} \frac{\text{mol}}{\text{L}} = 4.039 * 10^{-4} M$$

Next, use known volume to find how many moles are in the 10 mL given.

$$\frac{4.039 * 10^{-4} \text{ mol Hb}}{1 \text{ L}} * \frac{1 \text{ L}}{1000 \text{ mL}} * 10 \text{ mL} = 4.039 * 10^{-6} \text{ mol Hb}$$

Given the mass originally given in the problem, calculate grams per moles of Hb, which is the molar mass.

$$\frac{0.263 \text{ g Hb}}{4.039 * 10^{-6} \text{ mol Hb}} = 6.51 * 10^4 \frac{\text{g}}{\text{mol}}$$

Remember, proteins are big!

3. At 286 K, the osmotic pressure of a glucose solution is 9.97 atm. What is the freezing point depression? The density of the solution is 1.12 g/mL, and K_f for water is $1.86^\circ\text{C}/m$.

This is a problem that asks you to relate one colligative property to another. Use the osmotic pressure to determine the molar concentration first.

$$\Pi = MRT$$

$$M = \frac{\Pi}{RT}$$

$$M = \frac{9.97 \text{ atm}}{\left(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right) (286 \text{ K})} = 0.425 \frac{\text{mol glucose}}{\text{L}} = 0.425 \text{ M}$$

Now, since the freezing point depression calculation involves molality, the molarity must be converted to molality. Assume 1 L of solution to simplify the calculation.

$$1.12 \frac{\text{g}}{\text{mL}} * 1000 \text{ mL} = 1120 \text{ g solution}$$

We know that in 1 L of solution contains 0.425 moles of glucose, based on the molarity. Use the molar mass of glucose to find the mass of glucose present.

$$0.425 \text{ mol glucose} * \frac{180.16 \text{ g glucose}}{1 \text{ mol glucose}} = 76.53 \text{ g glucose}$$

$$\begin{aligned} \text{Mass solvent} &= \text{Mass solution} - \text{Mass solute} = 1120 \text{ g} - 76.53 \text{ g} = 1043.5 \text{ g H}_2\text{O} \\ &= 1.0435 \text{ kg H}_2\text{O} \end{aligned}$$

Thus, molality equals:

$$\text{molality} = \frac{0.425 \text{ moles glucose}}{1.0435 \text{ kg H}_2\text{O}} = 0.407 \text{ m}$$

Glucose is a covalent compound and thus has a van't Hoff factor of 1.

$$\Delta T_{fp} = K_{fp} * m * i = 1.86 \frac{^\circ\text{C}}{m} * 0.407 \text{ m} * 1 = 0.76^\circ\text{C}$$

Thus, the freezing point will be lowered by 0.76°C

4. The reaction $2 \text{NO (g)} + \text{O}_2 \text{(g)} \rightarrow 2\text{NO}_2 \text{(g)}$ is second order in NO and first order in O₂. When $[\text{NO}] = 0.040 \text{ M}$, and $[\text{O}_2] = 0.035 \text{ M}$, the observed rate of disappearance of NO is $9.3 \times 10^{-5} \text{ M/s}$

a. What is the rate of disappearance of O₂ at this moment?

Rate of disappearance is $\Delta\text{O}_2/\Delta t$. Remember that we can relate the relative rates of disappearance based on stoichiometric coefficients.

$$-\frac{1}{2} \frac{\Delta\text{NO}}{\Delta T} = -\frac{1}{1} \frac{\Delta\text{O}_2}{\Delta T}$$

$$-\frac{1}{2} \left(9.3 \times 10^{-5} \frac{\text{M}}{\text{s}} \right) = -\frac{\Delta\text{O}_2}{\Delta T} = 4.65 \times 10^{-5} \frac{\text{M}}{\text{s}}$$

b. What is the rate law?

$$\text{Rate} = k[\text{NO}]^2[\text{O}_2]^1$$

c. What is the rate constant, including units?

$$\text{Rate} = k[\text{NO}]^2[\text{O}_2]^1$$

The rate in this case is equal to one half of the given rate of disappearance of NO.

$$4.65 \times 10^{-5} \frac{\text{M}}{\text{s}} = k(0.040 \text{ M})^2(0.035 \text{ M})$$

$$k = 4.65 \times 10^{-5} \frac{\frac{\text{M}}{\text{s}}}{0.000056 \text{ M}^3} = 0.83 \text{ M}^{-2} \text{ s}^{-1}$$

d. What would happen if the concentration of NO was increased by a factor of 1.8?

If $[\text{NO}]$ increases by a factor of 1.8, we can think about the factor the rate increases by the following division:

$$\text{Rate} = \frac{k[1.8 \times \text{NO}]^2[\text{O}_2]^1}{k[\text{NO}]^2[\text{O}_2]^1} = 1.8^2 = 3.24$$

5. Cyclopentadiene (C_5H_6) reacts with itself to form dicyclopentadiene ($C_{10}H_{12}$). A 0.0400 M solution of C_5H_6 was monitored as a function of time as the reaction $2 C_5H_6 \rightarrow C_{10}H_{12}$ proceeded. The following data were collected:

Time (s)	$[C_5H_6]$ (M)	$\ln([C_5H_6])$	$1/[C_5H_6]$
0.0	0.0400 $\rightarrow 0.01$	-3.22 $\rightarrow 0.29$	25 $\rightarrow 8.33$
50.0	0.0300 $\rightarrow 0.006$	-3.51 $\rightarrow 0.22$	33.33 $\rightarrow 8.34$
100.0	0.0240 $\rightarrow 0.0039$	-3.73 $\rightarrow 0.18$	41.67 $\rightarrow 9.1$
150.0	0.0201 $\rightarrow 0.0027$	-3.91 $\rightarrow 0.14$	49.77 $\rightarrow 7.7$
200.0	0.0174	-4.05	57.47

- a. What is the order of the reaction?

The most linear relationship is found between time and $1/[C_5H_6]$; the reaction is second order.

- b. What is the rate constant?

The rate constant (k) is the slope of the graph between $1/[C_5H_6]$ and time. Slope is “rise over run” or change in $1/[C_5H_6]$ over change in time. We can choose any two points here, in this example we’ll use 0 seconds and 200.0 seconds.

$$k = \frac{\Delta \left(\frac{1}{[C_5H_6]} \right)}{\Delta t} = \frac{(57.47 M^{-1} - 25 M^{-1})}{200s - 0s} = 0.162 M^{-1}s^{-1}$$

6. The decomposition of ethanol (C_2H_5OH) on an alumina surface was studied at 600 K: $C_2H_5OH \rightarrow C_2H_4 + H_2O$. Concentration vs. time data were collected, and a plot of $[C_2H_5OH]$ vs. time resulted in a straight line slope of $-4.00 \times 10^{-5} M/s$.

- a. Determine the rate law, the integrated rate law, and the value of the rate constant for this reaction

This is a zero order reaction because the plot of $[C_2H_5OH]$ versus time is linear. The rate constant is equal to the negative slope of the graph. Thus, $k = 4.00 \times 10^{-5} M/s$.

Rate law:

$$\text{Rate} = k[C_2H_5OH]^0 = k = 4.00 \times 10^{-5} M/s$$

Integrated rate law:

$$[C_2H_5OH]_t = -4.00 \times 10^{-5} \times t + [C_2H_5OH]_0$$

- b. If the initial concentration of ethanol is $1.25 \times 10^{-2} \text{ M}$, calculate the half-life for the reaction

The solution will be at its half life when the concentration is one-half of the starting concentration. We can use our this relationship in and integrated rate law to find the time where this occurs.

$$[\text{C}_3\text{H}_5\text{OH}]_{t(1/2)} = \frac{1}{2} * [\text{C}_3\text{H}_5\text{OH}]_0$$

$$[\text{C}_3\text{H}_5\text{OH}]_{t(1/2)} = -4.00 * 10^{-5} * t + [\text{C}_3\text{H}_5\text{OH}]_0$$

$$[\text{C}_3\text{H}_5\text{OH}]_{t1/2} - [\text{C}_3\text{H}_5\text{OH}]_0 = -4.00 * 10^{-5} * t$$

$$\frac{1}{2} * [\text{C}_3\text{H}_5\text{OH}]_0 - [\text{C}_3\text{H}_5\text{OH}]_0 = -4.00 * 10^{-5} * t$$

$$-\frac{1}{2}[\text{C}_3\text{H}_5\text{OH}]_0 = -4.00 * 10^{-5} * t$$

$$\frac{-\frac{1}{2}[\text{C}_3\text{H}_5\text{OH}]_0}{-4.00 * 10^{-5}} = t$$

$$\frac{-6.25 * 10^{-3}}{-4.00 * 10^{-5}} = 156 \text{ seconds}$$

- c. How much time is required for all of the ethanol to decompose?

This questions is asking us to find t when $[\text{C}_3\text{H}_5\text{OH}]_t = 0$. Once again, we can use our integrated rate law.

$$0 = -4.00 * 10^{-5} * t + [\text{C}_3\text{H}_5\text{OH}]_0$$

$$0 = -4.00 * 10^{-5} * t + 1.5 * 10^{-2}$$

$$-1.25 * 10^{-2} = -4.00 * 10^{-5} * t$$

$$t = \frac{-1.25 * 10^{-2}}{-4.00 * 10^{-5}} = 313 \text{ seconds}$$

7. NOBr decomposes into NO and Br₂.

Time (s)	[NOBr] (M)	ln[NOBr]	1/[NOBr]
10.	0.50	-0.693	2.0 M ⁻¹
20.	0.33	-1.11	3.0 M ⁻¹
30.	0.25	-1.39	4.0 M ⁻¹
40.	0.20	-1.61	5.0 M ⁻¹

a. What is the order of the reaction?

The linear relationship is seen with time versus 1/[NOBr]. The difference between 1/[NOBr] for equivalent units of time is similar across multiple data points.

b. What is the rate constant?

Same as the problem from above, in a second order reaction $k = \text{change in } (1/[\text{NOBr}]) \text{ divided by change in time}$. We can calculate k using any two data points.

$$\begin{aligned}
 k &= (1/[\text{NOBr}]) - 1/[\text{NOBr}_0] / t \\
 &= (5.0 \text{ M}^{-1} - 4.0 \text{ M}^{-1}) / (40 \text{ s} - 30 \text{ s}) \\
 &= (1.0 \text{ M}^{-1}) / 10 \text{ s} \\
 &= 0.1 \text{ M}^{-1}\text{s}^{-1}
 \end{aligned}$$

8. Consider the following solutions (assume complete dissociation in water):

0.24 m K₃PO₄ 0.72 m CH₃OH 0.33 m CaI₂ 0.5 m C₂H₆O 0.45 m NaCl

a. Which has the highest boiling point?

0.33 m CaI₂ has the highest boiling point. Using the colligative properties of boiling point elevation, we know that the rise in boiling point is proportional to molality*van't Hoff. For each of the solutions above,

0.24 m K₃PO₄ *4 ions = 0.96

0.72 m CH₄ = 0.72 (covalent compound)

0.33 m CaI₂*3 ions = 0.99

0.5 m C₂H₆O = 0.5 (covalent compound)

0.45 m NaCl * 2 ions = 0.9

Since $\Delta T_b = k_b * m * i$, the largest boiling point change comes from CaI₂.

b. Rank in order of freezing point, lowest to highest.

0.33 m CaI₂ < 0.24 m K₃PO₄ < 0.45 m NaCl < 0.72 m CH₃OH < 0.5 M C₂H₆O

We can use the values calculated above with $\Delta T_f = k_f \cdot m \cdot i$ to see that freezing point depression is also proportional to molality * van't Hoff.

- a. What is the vapor pressure of the water in the solution of 0.72 m CH_3OH if $P^\circ_{\text{water}} = 525.8 \text{ mmHg}$ and the density of water is 1 g/mL?

We calculate this using Raoult's law, $P_{\text{solvent}} = X_{\text{solvent}} \cdot P^\circ_{\text{solvent}}$

$$\text{Mole fraction } X_{\text{solvent}} = \frac{\text{mols solvent}}{\text{mol solvent} + \text{moles solute}}$$

We can find our moles of solute by using the definition of molality and assuming we have a total of 1 kg of H_2O .

$$0.72 \text{ m } \text{CH}_3\text{OH soln} = \frac{0.72 \text{ mol } \text{CH}_3\text{OH}}{1 \text{ kg } \text{H}_2\text{O}}$$

Next, we need to find out how many moles of our solvent H_2O are in this kg of water we assumed above.

$$1 \text{ kg } \text{H}_2\text{O} \cdot \frac{1000 \text{ g } \text{H}_2\text{O}}{1 \text{ kg } \text{H}_2\text{O}} \cdot \frac{1 \text{ mol } \text{H}_2\text{O}}{18.02 \text{ g } \text{H}_2\text{O}} = 55.49 \text{ mol } \text{H}_2\text{O}$$

Now we can use our above X_{solvent} equation.

$$X_{\text{solvent}} = \frac{55.49 \text{ mol } \text{H}_2\text{O}}{55.49 \text{ mol } \text{H}_2\text{O} + 0.72 \text{ mol } \text{CH}_3\text{OH}} = 0.987$$

Put this value into Raoult's Law.

$$P_{\text{solvent}} = 0.987 \cdot 525.8 \text{ mm Hg} = 519 \text{ mm Hg}$$