

## EXAMINATION TWO

I \_\_\_\_\_ II \_\_\_\_\_ III \_\_\_\_\_ IV \_\_\_\_\_ V \_\_\_\_\_ VI \_\_\_\_\_ Total \_\_\_\_\_

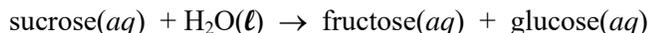
Glance over the entire exam, and then attempt the problems in the order of your choice. Rough point values are given for each problem. The total will be scaled to 100 points after the exams are marked. For questions with multiple parts, you do not necessarily need the answer to part A in order to work part B, etc. For calculations, give your answer to the correct number of **significant figures**, and be sure to include the **correct units** for your answer. **You must show your work to receive any credit for a calculated answer.** Additional information is provided in a separate information packet; you can use the back for scratch work. Good luck!

- I. (2 points) Circle the time corresponding to the recitation section you attend.

11 am	12 noon	1 pm	8 am	9 am	10 am	11 am	12 noon	1 pm
Mary Hertz , 219 HTL			Art Omran , 520 HTL			Elias Nakouzi, 520 HTL		

- II. (24 points) As we transitioned from chemical kinetics to chemical equilibrium, we considered the difficulty of trying to sweeten cold tea. Is the sugar less soluble (equilibrium) or slow to dissolve (kinetics)? Before leaving the topic, I dropped the personal observation that sweet tea seems to get sweeter over time.

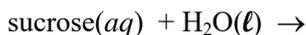
Sucrose is a disaccharide, composed of the two simple sugars fructose and glucose. Fructose is cheap, sweeter than the other sugars, and it makes us want more.\* It seems possible that when sucrose is dissolved in hot tea, it decomposes to form fructose and glucose, which together may be sweeter and more soluble. So let's run the numbers for the reaction



- A. The first-order rate constant for the above reaction is
- $3.92 \times 10^{-2} \text{ hr}^{-1}$
- at
- $27^\circ\text{C}$
- . If the tea is sweetened by adding one cup of sucrose to one gallon of tea, that would correspond to
- $204 \text{ g}/3785 \text{ mL} = 0.054 \text{ g/mL}$
- . What would be the concentration of sucrose after 24 hours at
- $27^\circ\text{C}$
- ?

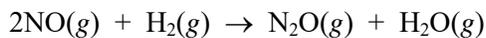
- B. If we use the rule of thumb that the reactant is gone after 10 half-lives, how long would it take for all of the sucrose to decompose?

- C. The rate determining step in the accepted mechanism for the decomposition of sucrose is the initial reaction between sucrose and water:



So why does this reaction follow first-order kinetics?

III. (28 points) We considered the equilibrium between  $\text{NO}_2(g)$  and  $\text{N}_2\text{O}_4(g)$  in class. The reaction shown below involves two different NO<sub>x</sub> compounds.



A. Use the data in the table to determine the rate law for the reaction.

exp	[NO] (M)	[H <sub>2</sub> ] (M)	$-\frac{\Delta[\text{H}_2]}{\Delta t}$ (M/min)
1	0.021	0.065	1.46
2	0.021	0.260	1.46
3	0.042	0.065	5.84

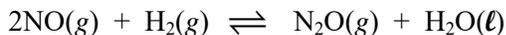
B. Determine the rate constant. Be sure to include the correct units in your answer.

C. What is the rate of the reaction when  $[\text{NO}] = 0.087 \text{ M}$  and  $[\text{H}_2] = 0.18 \text{ M}$ ?

D. Suggest two different mechanisms that are consistent with your rate law. Remember that the elementary reactions must add up to give the overall reaction:  $2\text{NO}(g) + \text{H}_2(g) \rightarrow \text{N}_2\text{O}(g) + \text{H}_2\text{O}(g)$ .

1. The first reaction is the rate determining step. (This one should be fairly easy.)
2. The first reaction is a rapid equilibrium, and the second reaction is the rate determining step. (This one might seem a little harder, but remember that the intermediate formed in the equilibrium does not have to be a known molecule. It is a reactive intermediate formed along the way.)

IV. (24 points) Now let's consider the overall reaction as an equilibrium process, carried out at a lower temperature such that H<sub>2</sub>O is obtained as a liquid.



A. Write the equilibrium expression for this reaction.

B. For each of the following, state whether the equilibrium distribution would shift to the left (more reactants), shift to the right (more products), or stay the same.

1. add N<sub>2</sub>(g) \_\_\_\_\_

2. remove H<sub>2</sub>(g) \_\_\_\_\_

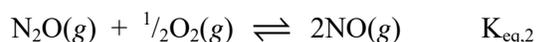
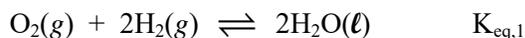
3. add N<sub>2</sub>O(g) \_\_\_\_\_

4. remove H<sub>2</sub>O(ℓ) \_\_\_\_\_

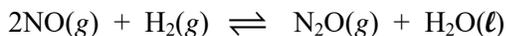
5. increase pressure by  
decreasing the volume \_\_\_\_\_

C. If we reduce the temperature even further, the equilibrium shifts to the right (more products, less reactants). Is this reaction endothermic or exothermic?

D. I don't actually know the equilibrium constant for this reaction. Later in the course we will be able to calculate it from thermodynamic parameters, but for now if we want this value, we need to get it some other way. We should be able to find the equilibrium constants for these reactions:

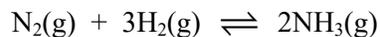


Show how you could use these equilibrium equations to determine the equilibrium constant for



Write the equilibrium constant in terms of  $K_{\text{eq},1}$  and  $K_{\text{eq},2}$ . Be sure to show your work so we can see how you manipulated the first two equilibrium equations to get the third one.

- V. (18 points) We briefly considered the Haber process as our “graduation exercise,” but not the mechanism.



At the surface of the catalyst,  $\text{N}_2$  and  $\text{H}_2$  are separated into atoms, and the atoms combine to form  $\text{NH}_3$ . Dissociation of  $\text{N}_2$  is generally accepted as the rate-determining step, followed by formation of  $\text{NH}$ . The activation energy for forming  $\text{NH}$  is 116.8 kJ/mol without a catalyst and 97.4 kJ/mol with a ruthenium cluster catalyst. The rate constant at 320 K is  $1.75 \times 10^{-4} \text{ s}^{-1}$  without the catalyst. (*J. Phys. Chem. Lett.* **2013**, *4*, 3779–3786)

- A. What is the rate constant at 320 K with the catalyst?

- B. Speculate on why dissociation of  $\text{N}_2$  is the rate determining step instead of dissociation of  $\text{H}_2$ .