Class Worksheet 11

1. (a) What is meant by the term reaction rate?
   (b) Name three factors that can affect the rate of a chemical reaction?
   (c) What information is necessary to relate the rate of disappearance of reactants to the rate of appearance of products?

2. Consider the hypothetical aqueous reaction A(aq) → B(aq). A flask is charged with 0.065 mol of A in a total volume of 100.0 mL. The following data are collected:

Time (min)	0	10	20	30	40
Moles of A	0.065	0.051	0.042	0.036	0.031

(a) Calculate the number of moles of B at each time in the table. Assume there are no molecules of B at time zero.
(b) Calculate the average rate of disappearance of A for each 10-minute interval, in units of mol/s.
(c) Between t = 10 min and t = 30 min, what is the average rate of disappearance of B in units of M/s? Assume that the volume of the solution is constant.

3. The isomerization of methyl isonitrile, CH_3NC, to acetonitrile, CH_3CN, was studied in the gas phase at 215°C, and the following data were obtained:

Time (s)	**[CH_3NC] (M)**
0	0.0165
2000	0.0110
5000	0.00591
8000	0.00314
12000	0.00137
15000	0.00074

Calculate the average rate of reaction between, in M/s, for the time interval between each measurement.

4. Using the data provided in question 3, make a graph of [CH_3NC] versus time. (a) Draw tangents to the curve at t = 4000 and t = 10000s. (b) Use the lines in part (a) to determine the instantaneous rates in M/s at t = 4000 and t = 10000s.

5. For each of the following gas-phase reactions, indicate how the rate of disappearance of each reactant is related to the rate of appearance of each product:
   (a) $H_2O_2(g) \rightarrow H_2(g) + O_2(g)$
   (b) $2N_2O(g) \rightarrow 2N_2(g) + O_2(g)$
   (c) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

6. (a) Consider the combustion of $H_2(g)$: $2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$. If hydrogen is burning at the rate of 4.6 mol/s, what is the rate of consumption of oxygen? What is the rate of formation of water vapor?
   (b) The reaction $2NO(g) + Cl_2(g) \rightarrow 2NOCl(g)$ is carried out in a closed vessel. If the partial pressure of NO is decreasing at the rate of 30 torr/min, what is the rate of change of the total pressure of the vessel?

7. A reaction obeys the following rate law: Rate = $k[A][B]^2$. (a) If [A] changes, will the rate change? Will the rate constant change? Explain. (b) What are the reaction orders for A and B? What is the overall reaction order? (c) what are the units of the rate constant?

8. Consider the following reaction: $CH_3Br(aq) + OH\text{-}(aq) \rightarrow CH_3OH(aq) + Br\text{-}(aq)$
   The rate law for this reaction is first order in CH_3Br and first order in OH^-. When [CH_3Br] is 5.0×10^{-3}M and [OH^-] is 0.050M, the reaction rate at 298K is 0.0432M/s. (a) What is the value of the rate constant? (b) What are the units of the rate constant? (c) What would happen to the rate if the concentration of OH^- were tripled?

9. The following data were collected for the rate of disappearance of NO in the reaction
   $2NO(g) + O_2(g) \rightarrow 2NO(g)$:

Experiment	[NO] (M)	[O_2] (M)	Initial Rate (M/s)
1	0.0126	0.0125	1.41×10^{-2}
2	0.0252	0.0250	1.13×10^{-1}
3	0.0252	0.0125	5.64×10^{-2}

(a) What is the rate law for the reaction? (b) What are the units of the rate constant? (c) What is the average value of the rate constant calculated from three data sets?

10. Consider the gas phase reaction between nitric oxide and bromine at 273°C:
$2NO(g) + Br_2(g) \rightarrow 2NOBr(g)$. The following data for the initial rate of appearance of NOBr were obtained:

Experiment	[NO] (M)	[Br_2] (M)	Initial Rate (M/s)
1	0.1	0.2	24
2	0.25	0.20	150
3	0.10	0.50	60
4	0.35	0.50	735

(a) Determine the rate law. (b) Calculate the average value of the rate constant for the appearance of NOBr from the four data sets. (c) How is the rate of appearance of NOBr related to the rate of disappearance of Br_2? (d) What is the rate of disappearance of Br_2 when [NO] = 0.075M and [Br_2] = 0.185M?

11. (a) what is a first order reaction? (b) What quantity, when graphed against time, will yield a straight line for a first-order reaction? (c) Does the half-life of a first-order reaction depend on the initial concentration?

12. The thermal decomposition of $N_2O_4(g)$, $N_2O_5(g) \rightarrow 2NO_2(g) + \frac{1}{2}O_2(g)$, is a first order reaction. The rate constant for the reaction is $5.1 \times 10^{-4}\ s^{-1}$ at 318K. What is the half-life of this process?

13. The reaction $SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$ is first order in SO_2Cl_2. Use the following kinetic data to determine the magnitude of the first order rate constant:

Time (s)	Pressure SO_2Cl_2 (atm)
0	1.000
2500	0.947
5000	0.895
7500	0.848
10000	0.803

14. The gas-phase decomposition of NO_2, $NO_2(g) \rightarrow NO(g) + \frac{1}{2}O_2(g)$, is studied at 383°C, giving the following data. (a) Is the reaction first order or second order with respect to the concentration of NO_2? (b) What is the value of the rate contant?

Time (s)	Pressure SO_2Cl_2 (atm)
0.0	0.100
5.0	0.017
10.0	0.0090
15.0	0.0062
20.0	0.0047

15. Calculate the fraction of atoms in a sample of argon gas at 400K that have an energy of 12.5 kJ or greater.

16. A certain first-order reaction has a rate constant of 1.75 x 10-1 s^{-1} at 20°C. What is the value of k at 60°C if (a) E_a = 55.5 kJ/mol; (b) E_a = 121 kJ/mol.

17. The rate of reaction $CH_3COOC_2H(aq) + OH^-(aq) \rightarrow CH_3COO^-(aq) + C_2H_5OH(aq)$ was measured at several temperatures, and the following data were collected. Use a graph to determine the value of E_a.

Temperature (°C)	K ($M^{-1}s^{-1}$)
15	0.0521
25	0.101
35	0.184
45	0.332

18. The activation energy of a certain reaction is 76.7 kJ/mol. How many times faster will the reaction occur at 50.0°C than at 0.00°C?

19. (a) What is meant by the term "elementary step?" (b) What is the difference between a unimolecular and a bimolecular elementary step? (c) What is a reaction mechanism?

20. What is the molecularity of each of the following elementary steps? Write the rate law for each.
    (a) $N_2O(g) + Cl(g) \rightarrow N_2(g) + ClO(g)$
    (b) $Cl_2(g) \rightarrow 2Cl(g)$
    (c) $NO(g) + Cl_2(g) \rightarrow NOCl_2(g)$
    (d) $SO_3(g) \rightarrow SO_2(g) + O(g)$

21. The following mechanism has been proposed for the reaction of NO with H_2 to form N_2O and H_2O:

$$NO(g) + NO(g) \rightarrow N_2O_2(g)$$
$$N_2O_2(g) + H_2(g) \rightarrow N_2O(g) + H_2O(g)$$

    (a) Show that the elementary steps of the proposed mechanism add to provide a balanced equation for the reaction.
    (b) Write a rate law for each elementary step in the mechanism.
    (c) Identify any intermediates.
    (d) The observed rate law is: rate = $k[NO]^2[H_2]$. If the proposed mechanism is correct, what can we conclude about the relative speeds of the first and second steps? Explain your answer.

22. (a) What part of the energy profile of a reaction is affected by a catalyst?
    (b) What is the difference between a homogeneous and a heterogeneous catalyst?

23. The oxidation of SO_2 to SO_3 is catalyzed by NO_2. The reaction proceeds as follows:

$$NO_2(g) + SO_2(g) \rightarrow NO(g) + SO_3(g)$$
$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

    (a) Show that the two reactions can be summed to give the overall oxidation of SO_2 by O_2 to give SO_3.
    (b) Why do we consider NO_2 a catalyst and not an intermediate?
    (c) Is this an example of homogeneous catalysis or heterogeneous catalysis?

24. The activation energy of an uncatalyzed reaction is 85kJ/mol. The addition of a catalyst lowers the activation energy to 55kJ/mol. Assuming that the collision factor remains the same, by what factor will the catalyst increase the rate of reaction at (a) 25°C; (b) 125°C?