

## Answers to Unit 4 Review: Reaction Rates

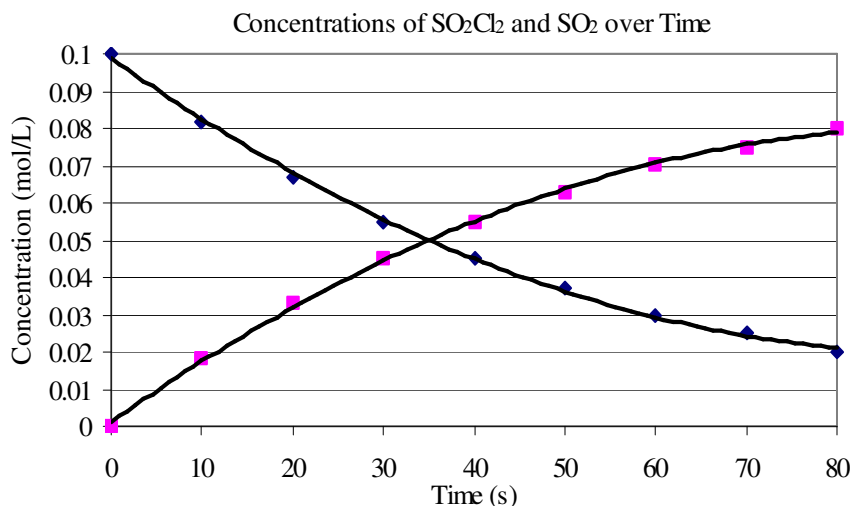
### Answers to Multiple Choice

1. c	13. a	25. a	37. c	49. d
2. d	14. a	26. c	38. c	50. d
3. c	15. d	27. c	39. c	51. b
4. d	16. a	28. b	40. c	52. c
5. c	17. b	29. c	41. a	53. b
6. d	18. c	30. c	42. a	54. c
7. d	19. d	31. c	43. a	55. d
8. b	20. b	32. a	44. c	56. b
9. b	21. d	33. c	45. c	57. c
10. d	22. c	34. d	46. d	58. c
11. d	23. a	35. d	47. a	59. c
12. c	24. d	36. d	48. a	60. b

### Answers to Review, long answer questions:

1. The following data were collected for the reaction  $\text{SO}_2\text{Cl}_2 \rightarrow \text{SO}_2 + \text{Cl}_2$  at a constant temperature:

Time (s)	$[\text{SO}_2\text{Cl}_2]$ (mol/L)	$[\text{SO}_2]$ (mol/L)
0	0.100	0.000
10	0.082	0.018
20	0.067	0.033
30	0.055	0.045
40	0.045	0.055
50	0.037	0.063
60	0.030	0.070
70	0.025	0.075
80	0.020	0.080



\* When you are graphing, draw a circle around each data point to indicate that there is some experimental error involved in each measurement.

- Following all graphing conventions, graph concentration of  $\text{SO}_2\text{Cl}_2$  and  $\text{SO}_2$  versus time.
- For  $\text{SO}_2\text{Cl}_2$ , determine the **instantaneous** rates of the reaction at  $t=20$  seconds and  $t=60$  seconds.
- Determine the **average** rate of reaction during the first 30 seconds of the reaction.

$$\text{Average rate} = \frac{\Delta \text{concentration}}{\Delta t}$$

over the first 30 s, the average rate is 0.0015 mol/L/s for either the appearance of  $\text{SO}_2$  or the disappearance of  $\text{SO}_2\text{Cl}_2$

d) What happens to the rate of the reaction as the reaction proceeds? Explain why.

As the reaction proceeds, the rate of the reaction slows down (the slope of the tangent to the line decreases). This is because there are fewer reactant molecules left in the container, so there are fewer collisions between the reactant molecules so less product forms over time.

e) How many elementary steps will there most likely be in the reaction mechanism for this reaction?

Because this reaction involves a single molecule breaking down to form two products, the reaction is very likely unimolecular. It will very likely have only one elementary step in the reaction mechanism.

2. The rate law for the reaction  $2 \text{NO} + \text{O}_2 \rightarrow 2 \text{NO}_2$  is  $\text{rate} = k[\text{NO}]^2[\text{O}_2]$ .  
At  $25^\circ\text{C}$ ,  $k = 7.1 \times 10^9 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$ .

a) What is the overall order for this reaction?

The exponents for the rate law are 2 and 1. This means that the reaction is second order with regard to NO (ie. two NO molecules collide in the RDS) and first order with regard to  $\text{O}_2$  (ie. one molecule of  $\text{O}_2$  collides with the two NO molecules) so this reaction is third order overall (involves the collision of three particles in the RDS).

b) Is the activation energy for this reaction high or low?

The rate constant for this reaction is extremely large ( $k = 7.1 \times 10^9$ ) which indicates that the reaction occurs very quickly, which in turn means that the activation energy for the reaction must be very low.

c) If the temperature is increased, what will happen to the value of k?

In general, as the temperature of a system is increased, the reaction rate increases so this will cause the value of k to increase.

d) If the concentration of NO is doubled, what will happen to the reaction rate?

If the concentration of NO is doubled, the rate of the reaction will quadruple because the reaction is second order with respect to NO.

- as a double check, substitute numbers in for the rate law and see what happens.
- for example, when  $[\text{NO}]$  is 1.0 M, the reaction rate will be  $7.1 \times 10^9 \times 1^2 \times [\text{O}_2] = 7.1 \times 10^9 [\text{O}_2]$   
when  $[\text{NO}]$  is 2.0 M, the reaction rate will be  $7.1 \times 10^9 \times 2^2 \times [\text{O}_2] = 2.84 \times 10^{10} [\text{O}_2]$

so when  $[\text{NO}]$  doubles, the rate increases by 4x

e) If the concentrations of both NO and  $\text{O}_2$  are doubled, how will the reaction rate change?

If the concentration of both NO and  $\text{O}_2$  are doubled, the rate will increase by  $(2^2) \times (2^1)$  for a total of  $(2^3)$  or 8x

f) Which will cause the rate to increase more: doubling  $[\text{NO}]$  or tripling  $[\text{O}_2]$ ?

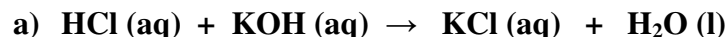
- if the concentration of NO is doubled, the reaction rate will increase by  $(2^2)$  or 4x
- if the concentration of  $\text{O}_2$  is tripled, the reaction rate will increase by  $(3^1)$  or 3x
- therefore, doubling the  $[\text{NO}]$  will cause a greater increase in reaction rate

g) What is the rate of reaction when  $[\text{NO}] = 0.0010 \text{ mol/L}$  and  $[\text{O}_2] = 0.034 \text{ mol/L}$ ?

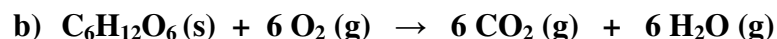
- substitute these values into the rate law and solve:

$$\begin{aligned}\text{rate} &= 7.1 \times 10^9 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1} [\text{NO}]^2 [\text{O}_2] \\ &= 7.1 \times 10^9 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1} [0.0010 \text{ mol/L}]^2 [0.034 \text{ mol/L}] \\ &= 241 \text{ mol/L}\cdot\text{s} \\ &= 2.4 \times 10^2 \text{ mol/L}\cdot\text{s}\end{aligned}$$

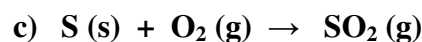
3. For the following reactions, suggest a variable that could be used to measure reaction rate:



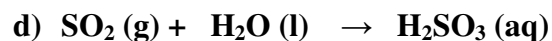
- reaction rate could be measured using a change in pH or decrease in conductivity of the solution (because both reactants conduct, but only one of the products conduct)



- reaction rate could be measured using a change in mass if the reaction is carried out in an **open** container on a balance or an increase in pressure if the reaction is carried out in a **closed** system (because only one reactant is a gas but both products are gases so pressure will increase)



- reaction rate could be measured using a change in mass if the reaction is carried out in an **open** container on a balance or by decrease in colour (sulfur is yellow while  $\text{SO}_2$  is colourless).
- change in pressure in a closed system can **NOT** be used because there are the same number of gas particles in the products as there are in the reactants



- reaction rate could be measured using a change in pH or increase in conductivity of the solution (because neither of the reactants conducts but the product does conduct)
- reaction rate could also be measured by a decrease in pressure in a **closed** system because the only gas in the reaction is a reactant



- reaction rate could be measured by a change in colour ( $\text{KMnO}_4$  is purple, but when it reacts with propene gas it turns to a green/brown colour)
- reaction rate could also be measured by a decrease in pressure in a **closed** system because the only gas in the reaction is a reactant

4. Consider the reaction:  $\text{BrO}_3^-(\text{aq}) + 5 \text{Br}^-(\text{aq}) + 8 \text{H}^+(\text{aq}) \rightarrow 3 \text{Br}_2(\text{l}) + \text{H}_2\text{O}(\text{l})$

The initial rate of the reaction has been measured at the reactant concentrations shown:

Trial	$[\text{BrO}_3^-]$ (mol/L)	$[\text{Br}^-]$ (mol/L)	$[\text{H}^+]$ (mol/L)	Initial rate (mol/L·s)
1	0.10	0.10	0.10	8.0
2	0.20	0.10	0.10	16
3	0.10	0.20	0.10	16
4	0.10	0.10	0.20	32

a) Determine “k” and the rate law for this reaction.

**Trials 1 and 2:**  $[\text{Br}^-]$  and  $[\text{H}^+]$  are held constant

- when  $[\text{BrO}_3^-]$  doubles, the reaction rate also doubles
- the reaction is first order with respect to  $[\text{BrO}_3^-]$

**Trials 1 and 4:**  $[\text{Br}^-]$  and  $[\text{BrO}_3^-]$  are held constant

- when  $[\text{H}^+]$  doubles, the reaction rate quadruples
- the reaction is second order with respect to  $[\text{H}^+]$

**Trials 1 and 3:**  $[\text{BrO}_3^-]$  and  $[\text{H}^+]$  are held constant

- when  $[\text{Br}^-]$  doubles, the reaction rate doubles
- the reaction is first order with respect to  $[\text{Br}^-]$

**The Rate Law is:**  $\text{rate} = k[\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2$

**Determine k:** use the values from any ONE trial and substitute them into the rate law, then solve for k

- $k = \frac{\text{rate}}{[\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2}$   
 $= \frac{8.0 \text{ mol/L}\cdot\text{s}}{(0.10 \text{ mol/L})(0.10 \text{ mol/L})(0.10 \text{ mol/L})^2}$   
 $= 8.0 \times 10^4 \text{ L}^3\cdot\text{mol}^{-3}\cdot\text{s}^{-1}$  (these are the rate units for a fourth order reaction)

**The complete Rate Law is:**  $\text{rate} = 8.0 \times 10^4 \text{ L}^3\cdot\text{mol}^{-3}\cdot\text{s}^{-1} [\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2$

b) Is the activation energy for this reaction high or low?

- the value for k for this reaction is very large, which means that reaction rate is very high so activation energy must be very low

c) What is the order of the reaction with regard to reactant  $\text{BrO}_3^-$ ? **first**

d) What is the order of the reaction with regard to reactant  $\text{Br}^-$ ? **first**

e) What is the order of the reaction with regard to reactant  $\text{H}^+$ ? **second**

f) What is the overall order of this reaction? **fourth order overall**

g) What would be the initial rate (in mol/L·s) if the concentrations of all three reactants is 0.20 mol/L?

$$\begin{aligned} \text{rate} &= 8.0 \times 10^4 \text{ L}^3\cdot\text{mol}^{-3}\cdot\text{s}^{-1} [\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2 \\ &= 8.0 \times 10^4 \text{ L}^3\cdot\text{mol}^{-3}\cdot\text{s}^{-1} [0.20 \text{ mol/L}] [0.20 \text{ mol/L}] [0.20 \text{ mol/L}]^2 \\ &= 128 \text{ mol/L}\cdot\text{s} \quad \text{or} \quad 1.3 \times 10^2 \text{ mol/L}\cdot\text{s} \end{aligned}$$

5. Suggest an explanation for each of the following observations.

a) **The reaction  $\text{Ag (s)} + \frac{1}{2} \text{I}_2 \text{(s)} \rightarrow \text{AgI (s)}$  is very slow.**

- the reaction is very slow because both reactants are solids. They can only react where the surfaces are in contact (where they can collide) so they will not react much at all

b) **The rate of reaction for  $\text{Ag}^+(\text{aq}) + \text{I}^-(\text{aq}) \rightarrow \text{AgI (s)}$  is very high.**

- the reaction occurs very quickly for several reasons: the reactants are dissolved in water so they are free to move and react, the reactants are charged ions so they will attract one another in solution which will increase the reaction rate, also the ions are very small, simple charged particles so they will probably collide in the correct orientation every time, so each collision will be effective

c) **The rate of reaction for  $\text{Ag}^+(\text{aq}) + \frac{1}{2} \text{I}_2 \text{(s)} \rightarrow \text{AgI (s)}$  is low.**

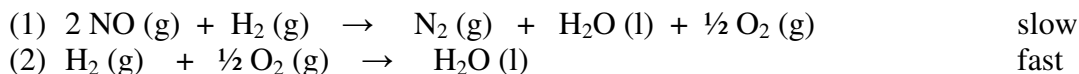
- the reaction is slow because one of the reactants is a solid. Reaction can only occur where the solution is in contact with the surface of the solid (where they can collide) so the amount of surface area will limit the reaction. Also, the solid  $\text{I}_2$  is uncharged, so it will have little attraction for the silver ions

d) **The rate of reaction of liquid octene with bromine is very low.**

- octene and bromine are both uncharged and non-polar molecules so there are no charged regions to help line the molecules up in the correct orientation for a successful collision. Also, the octene molecule is large and “bulky” so it will not be able to move around and collide easily with the bromine. For these reasons, the reaction rate is relatively slow.

6. For the reaction:  $2 \text{NO (g)} + 2 \text{H}_2 \text{(g)} \rightarrow \text{N}_2 \text{(g)} + 2 \text{H}_2\text{O (l)}$ , the rate law is  $\text{rate} = k[\text{NO}]^2[\text{H}_2]$

Does the following proposed mechanism (below) agree with this rate law? Explain.



- the rate law indicates that two molecules of NO collide with one molecule of  $\text{H}_2$  in the rate-determining step
- the slow step in the reaction mechanism (the RDS) shows that that two molecules of NO collide with one molecule of  $\text{H}_2$
- because the exponents of the rate law equation agree with the molar coefficients of the RDS, the rate law and proposed mechanism seem to agree

7. A reacts with 2 B in a one-step reaction to give  $\text{AB}_2$ .

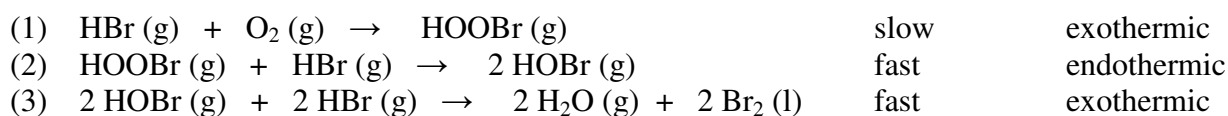
a) Write a rate law for this reaction.

b) If the initial rate of formation of  $\text{AB}_2$  is  $2.0 \times 10^{-5} \text{ M/s}$  and the initial concentrations of A and B are 0.30 M, what is the value of the rate constant “k” at this temperature?

- $\text{rate} = k [\text{A}] [\text{B}]^2$  (it is a one-step reaction, so this is the RDS. The molar coefficients in the RDS indicate the exponents in the rate law.)
- $k = \frac{\text{rate}}{[\text{A}][\text{B}]^2}$   
 $= \frac{2.0 \times 10^{-5} \text{ mol/L}\cdot\text{s}}{[0.30 \text{ mol/L}][0.30 \text{ mol/L}]^2}$   
 $= 7.4 \times 10^{-4} \text{ L}^2\cdot\text{mol}^{-2}\cdot\text{s}^{-1}$  (these are the rate units for a third order reaction)

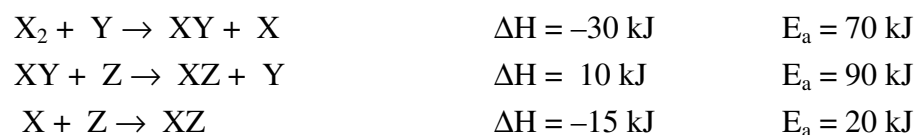
8. A mixture of natural gas and air does not react appreciably at room temperature. When a piece of platinum metal is inserted into the mixture, it explodes. Why?
- natural gas and air do not react at room temperature unless a spark (or other energy) is added to provide the activation energy for the reaction. Once the reaction is going, the heat released when the methane burns provides the activation energy to keep the reaction going
  - alternatively, if a piece of platinum is present, platinum acts as a catalyst for the reaction. It provides an alternative pathway for the reaction which has a lower activation energy. The methane and oxygen have sufficient energy at room temperature to react by this alternative pathway, so the mixture explodes when platinum is present
9. If you wish to dissolve a lump of sugar in water, what are three ways you could increase the rate at which the sugar dissolves? Explain why each procedure is effective.
- if the temperature of the water is increased, the water molecules will have more kinetic energy so they will move faster and surround the sugar molecules more quickly, which will increase the rate at which the sugar dissolves
  - if the sugar is ground up into a fine powder, it will dissolve more quickly because there will be a larger surface area. This allows more of the sugar to interact with the water molecules, which will increase the rate at which the sugar dissolves
  - if the sugar and water mixture is stirred, this will increase dissolving because it will spread the water and sugar out more evenly allowing increased interaction between the molecules
  - if the amount of water is increased, this will increase the concentration of water and spread out the sugar more, so the sugar will dissolve more quickly (there is more water available to surround the sugar molecules)
10. Use the Kinetic Molecular Theory to explain why reaction rates vary with temperature.
- when temperature is increased, the particles in the system move faster (on average). This means that reactant particles will collide with more force (increased kinetic energy) so there will be more effective collisions
  - because the particles are moving faster, there will also be more **frequent** collisions between reactants. If there are more collisions, the reaction will happen more quickly and the reaction rate will increase
  - so, increasing the temperature increases the reaction rate for two reasons: more collisions and harder collisions

11. For the reaction:  $4 \text{HBr (g)} + \text{O}_2 \text{(g)} \rightarrow 2 \text{H}_2\text{O (g)} + 2 \text{Br}_2 \text{(l)}$ , the reaction mechanism is:



- a) What is the rate-determining step for this reaction? Explain.
- the slowest step in a reaction mechanism is the RDS; for this mechanism, it is the first step
  - as fast as the RDS produces HOBr, it is consumed in the second elementary step, so the overall reaction can only proceed as quickly as the slowest step
- b) **Sketch** a potential energy diagram for this reaction mechanism.
- the potential energy diagram will have three “bumps”
  - the first bump will be the highest because it is the slowest step so it has the highest  $E_a$ . The curve will drop below the original level of enthalpy of the reaction because  $\Delta H$  is negative
  - the second bump will only be small because the second step has a fast rate (low  $E_a$ ). The curve will end above the enthalpy level of the first step
  - the third bump will also be small because of the fast rate. The curve will end up below the enthalpy level of the second step
  - we do not know if the reaction is endothermic or exothermic overall
- c) In general terms, compare the  $E_a$  values for each of the elementary steps.
- the  $E_a$  for the first step is quite large because the rate of that step is slow
  - the  $E_a$  for the second and third steps are quite low because these steps have fast rates
- d) Is the rate law  $\text{rate} = k [\text{HBr}]^4 [\text{O}_2]^1$  reasonable for the reaction? Explain.
- no, this rate law is not reasonable for the proposed reaction mechanism
  - the RDS for the reaction shows one molecule of HBr reacting with one molecule of  $\text{O}_2$
  - this rate mechanism would suggest that the rate law should be:  $\text{rate} = k[\text{HBr}] [\text{O}_2]$
- e) What would be the effect on the reaction rate of increasing the concentration of HOBr ?
- increasing the concentration of HOBr would have no effect on the reaction rate of the overall reaction because HOBr is not involved in the RDS
  - to make the reaction happen more quickly, the concentration of either HBr or  $\text{O}_2$  must be increased
- f) Suggest two variables that could be used to measure the rate of this reaction.
- the rate of this reaction could be measured by the appearance of the orange colour of  $\text{Br}_2\text{(l)}$
  - the rate could also be monitored by measuring the rate of decrease in pressure in a closed system. Pressure will decrease because there are five molecules of gases on the reactant side of the reaction, but only one two molecules of gas (vapour) on the product side.

12. The following represent the elementary steps in a reaction mechanism.



- a) Assume that the enthalpy of the reactants is 50 kJ. Sketch an energy profile for this mechanism.
- the first bump goes from 50 kJ up to 120 kJ, then drops down to 20 kJ
  - the second bump goes from 20 kJ up to 110 kJ, then drops down to 30 kJ
  - the third bump goes from 30 kJ up to 50 kJ, then down to 15 kJ
- b) What is the rate-determining step for this reaction?
- step 1 is the RDS
  - it has the highest peak measured from the original enthalpy of the reactants
- c) Write the equation for the overall reaction:  $X_2 + 2 Z \rightarrow 2 XZ$
- d) Find the values of  $\Delta H$  and  $E_a$  for the overall reaction.
- $\Delta H = -35 \text{ kJ}$
  - $E_a = 70 \text{ kJ}$  (from reactants to highest peak)
- e) Identify one reaction intermediate in the reaction. How do you know it is a reaction intermediate?
- XY and X are both reaction intermediates
  - these species are produced in one elementary step, but then consumed in another
- f) Identify one catalyst in the reaction. How do you know it is a catalyst?
- Y is a catalyst
  - it is a catalyst because it is used in an early elementary step then regenerated in a later step and it does not show up in the overall reaction equation