Name ______________________________________**Chem 163 Section**: ______ **Team Number:** ______

ALE 1. Chemical Kinetics: Rates of Chemical Reactions

(Reference: Sections 16.1 – 16.2 + parts of 16.5 –16.6 *Silberberg 5th edition*)

How do the surface area, concentration and pressure of the reactants affect the rate of a chemical reaction?

The Model

Chemical kinetics is the part of chemistry that looks at how fast reactants are converted into products in order to establish an experimental rate law, which can be used to decide how the reaction occurs. Knowing the reaction mechanism and the factors that affect the rate of a reaction makes it possible for the chemist to plan the efficient and cost effective production of industrial, pharmaceutical, and consumer chemicals. You will find that understanding reaction rates is essential to understanding how reactions occur.

Calcium carbonate and hydrochloric acid

In the lab, *powdered* calcium carbonate reacts much faster with dilute hydrochloric acid than if the same mass was present as lumps of marble or limestone. The reaction below occurs faster with concentrated hydrochloric acid than with dilute HCl.

$$CaCO_{3(s)} + 2HCl_{(aq)} \rightarrow CaCl_{2(aq)} + H_2O_{(l)} + CO_{2(g)}$$

Catalytic converters

Catalytic converters use metals like platinum, palladium and rhodium to convert poisonous compounds in vehicle exhausts into less harmful things. For example, a reaction which removes both carbon monoxide and an oxide of nitrogen is:

$$2CO_{(g)} + 2NO_{(g)} \rightarrow 2CO_{2(g)} + N_{2(g)}$$

Because the exhaust gases are only in contact with the catalyst for a very short time, the reactions have to be very fast. The extremely expensive metals used as the catalyst are coated as a very thin layer onto a ceramic honeycomb structure to *maximize the surface area*.

The catalytic decomposition of hydrogen peroxide

Solid manganese (IV) oxide is often used as a catalyst in this reaction. Oxygen is given off at a much faster rate if the hydrogen peroxide is concentrated than if it is dilute.

$$2H_2O_{2(aq)} \xrightarrow{MnO_2} 2H_2O_{(l)} + O_{2(g)}$$

The manufacture of ammonia

The rate of reaction between the hydrogen and the nitrogen is increased by the use of very high pressures.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

In addition to increasing the rate of reaction, high pressure is used to improve the percentage of ammonia in the equilibrium mixture—a topic to be addressed when discussing Le Châtelier’s principle in our unit on chemical equilibrium.

Key Questions

Reactant molecules must collide with each other for a chemical reaction to occur. Explain *how* and *why* each of the following affects the rate of a chemical reaction. Also, for each part below, give an example from the model and a specific reaction from everyday life that illustrates the concept involved.

1. The ***surface area*** of a solid in a reaction between a solid and a gas or a solid and an aqueous solution.

2. A *decrease* in ***pressure*** in a reaction between gaseous reactants.

3. The *addition of more* ***water*** to a reaction that occurs in aqueous solution.

How does Temperature affect the rate of a chemical reaction?

Model

As the temperature of the reactants increase, the rate of reaction increases—the opposite is also true, reaction rates decrease as temperature decreases—hence we store perishable food in a refrigerator to slow down metabolic reactions in bacteria and mold that will spoil the food! As a rough approximation, for many reactions happening at around room temperature, *the rate of reaction approximately doubles for every 10°C rise in temperature*. You have to be careful not to take this too literally. It doesn't apply to all reactions. Even where it is approximately true, it may be that the rate doubles every 9°C or 11°C or whatever. The number of degrees needed to double the rate will also change gradually as the temperature increases.

Some reactions are virtually instantaneous—for example, a precipitation reaction involving the coming together of ions in solution to make an insoluble solid, or the reaction between hydrogen ions from an acid and hydroxide ions from an alkali in solution. So heating one of these won't make any noticeable difference to the rate of the reaction. However, almost any other reaction you care to name will happen faster if you heat it—either in the lab, or in industry.

For a chemical reaction to occur not only must the reactant particles collide, they must collide with sufficient kinetic energy to break reactant bonds to initiate the formation of products—this minimum amount of energy in known as the **activation energy**, E_a. The graph below represents the distribution of kinetic energy for 1.0 mole of hydrogen gas molecules at a certain temperature.

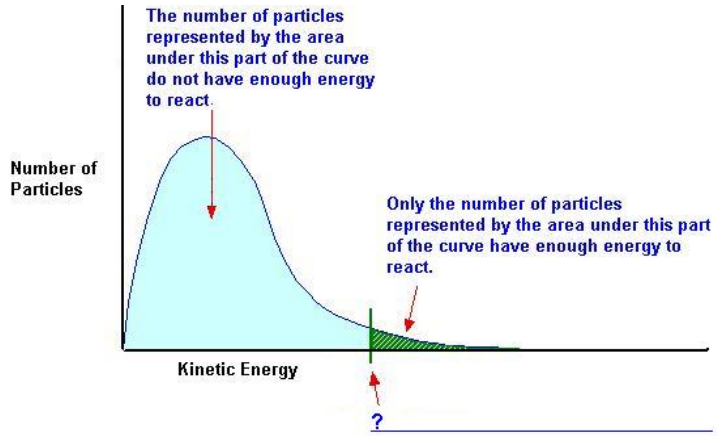


Figure 1. Kinetic energy distribution diagram for 1.0 mole of hydrogen gas

Key Questions

4. In general, by what factor does a 10 ^{o}C increase in temperature increase the rate of a chemical reaction? _________How about a 20 ^{o}C increase? ________ A 30 ^{o}C increase? ___________

5. Chemical reactions involve the breaking and making of bonds—i.e. bonds within the reactants need to be broken, while new bonds are made to form products. Is bond breaking endothermic or exothermic? (Circle your choice.) What does the kinetic energy pointed to by the arrow with the question mark in figure 1 represent? *Explain* and label the arrow in the space provided in figure 1 with the term that it represents.

6. What does the entire area under the curve in figure 1 represent?

7. Draw another curve in figure 1 for the distribution of kinetic energies for 1.0 mole of hydrogen gas at a *higher temperature* and label this curve T_{higher}.

8. Since each curve in figure 1 represents the kinetic energies of 1.0 mole of hydrogen gas, how should the area under each curve compare to each other? Why?

9. Use the line with the question mark in figure 1 together with the curves for hydrogen gas at the two different temperature to explain why an increase in temperature increases the rate of the reaction between hydrogen and nitrogen to produce ammonia: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

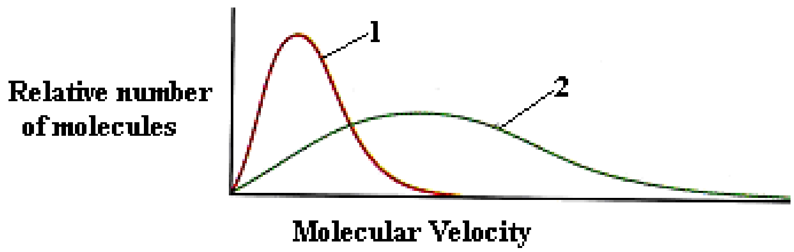


Figure 2. Molecular velocity distribution diagrams for 1.0 mol H_2 and 1.0 mol N_2 at the same temperature

10. Curves 1 and 2 in figure 2, above, represent the *molecular velocity* distribution diagrams for 1.0 mol of hydrogen gas and 1.0 mole of nitrogen gas at the *same* temperature. Which curve represents hydrogen gas? Nitrogen gas? Explain your reasoning.

    Hints: Substances at the same temperature have the same *average* kinetic energy;
    The Kinetic Energy of a particle = $E_k = \frac{1}{2} mv^2$, where m = mass of the particle, v = velocity of the particle

What is meant by "rate of a chemical reaction"?

The Model

Suppose we are interested in the generic chemical reaction as a way to synthesize the product D:

$$\boldsymbol{a}\,\mathbf{A} + \boldsymbol{b}\,\mathbf{B} \rightarrow \boldsymbol{d}\,\mathbf{D} + \boldsymbol{e}\,\mathbf{E} \qquad \mathbf{(1)}$$

(This is read: "*a* moles of A react with *b* moles of B to yield *d* moles of D and *e* moles of E") If we wish to synthesize D and sell it commercially, it would be undesirable if too little of it is produced by the time we want to sell it. And (for example, if the reaction is exothermic) it would be unacceptable and perhaps dangerous for too much D to be produced per unit of time. Hence, it is necessary that we can determine and control the rate at which D is produced in the reaction vessel.

If the volume of the reaction mixture is a constant, we can define the **rate of reaction** as:

$$Rate = \frac{1}{d}\frac{\Delta[D]}{\Delta t} \qquad \textbf{(2)}$$

where **Δ[D]** is how much the molar concentration of D changed in the amount of time that passed, **Δ*t***. It may be more convenient to monitor the reaction rate in terms of how the concentration of A (or the concentration of another species in the reaction mixture) is changing with time. In that case:

$$Rate = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{e}\frac{\Delta[E]}{\Delta t} \qquad \textbf{(3)}$$

Key Questions

11. A rate that is probably more familiar to you is the speed of a moving object:

$$\text{Speed} = \frac{\text{Distance between two points}}{\text{Time it takes to move betwen two points}}$$

How is speed similar to the rate of a reaction? How are they different?

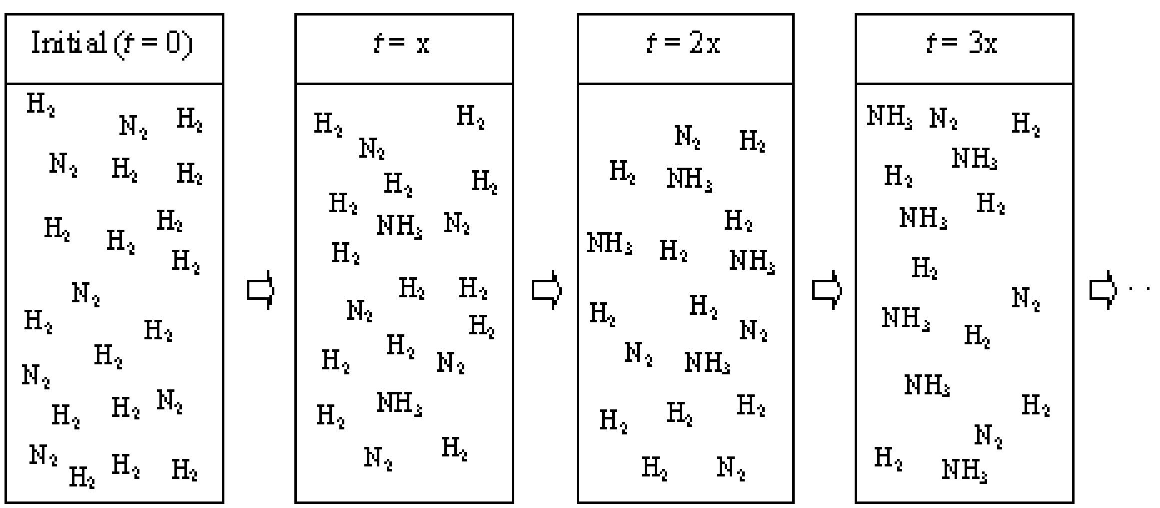
12. The rate for equation 1, above, can be expressed in several different but equivalent ways:

$$Rate = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t} = \frac{1}{e}\frac{\Delta[E]}{\Delta t}$$

When the rate is expressed in terms of the rate of change of the concentration of A or B (*e.g.* -Δ[A]/Δ*t*), the expression is written with a negative sign, but when the rate is expressed in terms of the concentration of D or E it is expressed with a positive sign (*e.g.* Δ[D]/Δ*t*),. *Explain why*.

13. As a specific example, consider the consumption of nitrogen and hydrogen gases to produce ammonia gas:

$$\mathbf{N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)}$$



Initial (t = 0)	t = x	t = 2x	t = 3x
____ N_2's	____ N_2's	____ N_2's	____ N_2's
____ H_2's	____ H_2's	____ H_2's	____ H_2's
____ NH_3's	____ NH_3's	____ NH_3's	____ NH_3's

a. Enter in the spaces above the number of molecules of each substance present. For every unit of time “x”, how many molecules of N_2 are *consumed*? _______ how many molecules of H_2 are *consumed*? _______ how many molecules of NH_3 are *produced*? _________

b. Fill in the blanks below with numbers that relate the following rates of changes of the numbers of particles, *N*.

i.) $\_\_\_\_\_ \frac{\Delta[N_{N_2}]}{\Delta t} = \_\_\_\_\_ \frac{\Delta[N_{H_2}]}{\Delta t}$ ii.) $\_\_\_\_\_ \frac{\Delta[N_{N_2}]}{\Delta t} = \_\_\_\_\_ \frac{\Delta[N_{NH_3}]}{\Delta t}$

Exercises

A. Initially at some temperature, the only substance present in a 10.0 L reaction vessel is 50.0 mol of NH_3 gas. An excess of O_2 gas is quickly pumped into the reaction vessel without changing either the vessel’s volume or the system’s temperature. After 10.0 seconds time, there are only 26.0 mol of NH_3 remaining. (There is still some left over O_2, and the reaction is still proceeding.) What is the average rate of change of the molar concentration of NH_3 over this 10.0 second interval of time? Include the correct sign and units. *Hints*: ① What is the initial molar concentration of NH_3? ② What is the final molar concentration of NH_3? ③ What is the change in the molar concentration of NH_3? ④ What is the change in time? ⑤ What is the rate of change of the molar concentration of NH_3?). *Circle your answers* and *clearly show your work with units and sig. figs.*

$[NH_3]_i =$

$[NH_3]_f =$

$\Delta[NH_3] =$

$\Delta t =$

Rate = $\Delta[NH_3]/\Delta t =$

B. The reaction between ammonia and oxygen at the temperature of the reaction vessel is:

$$\mathbf{4\ NH_3}_{(g)} + \mathbf{5\ O_2}_{(g)} \rightarrow \mathbf{4\ NO}_{(g)} + \mathbf{6\ H_2O}_{(g)}$$

Use your answer to Exercise A to determine the rate of change of the concentrations of O_2, of NO, and of H_2O in M/s. *Circle your answers and include the correct sign, units and sig. figs. for each.*

Hints:

Rate = ____ $\Delta[NH_3]/\Delta t$ = ____ $\Delta[O_2]/\Delta t$

$\Delta[O_2]/\Delta t =$

Rate = ____ $\Delta[NH_3]/\Delta t$ = ____ $\Delta[NO]/\Delta t$

$\Delta[NO]/\Delta t =$

Rate = ____ $\Delta[NH_3]/\Delta t$ = ____ $\Delta[H_2O]/\Delta t$

$\Delta[H_2O]/\Delta t =$

C. When aqueous bromine is added to an aqueous solution of acetone (CH_3COCH_3), the following reaction occurs:

$$\mathbf{Br_2}\,_{(aq)} + \mathbf{CH_3COCH_3}\,_{(aq)} \rightarrow \mathbf{CH_3COCH_2Br}\,_{(aq)} + \mathbf{HBr}\,_{(aq)}$$

Since only elemental bromine is colored, the reaction kinetics can be monitored using a spectrophotometer to measure the absorbance of visible light. A decrease in the absorbance indicates a decrease in the amount of bromine that remains in the solution. The following concentration data were obtained using a spectrophotomer. What is the rate of the reaction between bromine and acetone? _Hints_: Plot the data in the grid below. What does the slope ($\Delta y/\Delta x$) represent?

Show your work here with units and correct sig. figs.

Time (s)	[Br_2] (*M*)
30.0	0.00271
60.0	0.00266
90.0	0.00259
120.0	0.00251
150.0	0.00244
180.0	0.00240