

# Chemical Kinetics 1

Reading: Ch 13, sections 1 - 2      Homework: Chapter 13: 3, 5, 25\*, 27, 29\*, 31\*

\* = 'important' homework question

## Factors that Affect Reaction Rates

General Discussion: Fundamentally speaking, what must happen at the microscopic level during a chemical reaction for 'new' chemical(s) to be formed?



Remember Dr. Mills favorite saying.....



One time British soccer icon  
'Gazza' with a gyro

**“Chemistry is a bit like  
Scottish soccer – it’s  
basically a bunch of round  
things bumping into one  
another”**



Gazza playing out his career  
with Glasgow Rangers



A ***fixed*** fraction of all molecular collisions are fruitful.

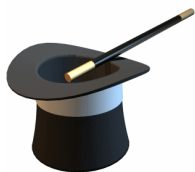
These ***fruitful collisions*** result in the formation of ‘new’ product species



Question: What would happen to the ***rate of reaction*** (i.e. the speed of the reaction) if the number of molecular scale collisions among the reactants were:

a. Increased?

b. Decreased?



***Always remember that the speed (or rate) of a chemical reaction is directly proportional to the number of molecular\* collisions per second occurring among the reactants – some fixed fraction of which will be fruitful***

Discussion: Which ***macro*** scale variables (i.e. in lab) can chemists alter to ultimately ***increase the number of molecular collisions*** among chemical reactants per second; thereby increasing the reaction rate? List them:

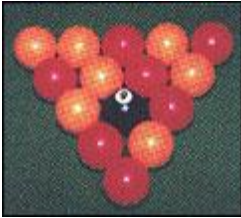
1.

2.

3.

4.

## 1. Concentration of Reactants



Observation: Which would result in a greater number of ball-on-ball collisions – your break in 9-ball or ‘regular’ 15-ball pool? Why?



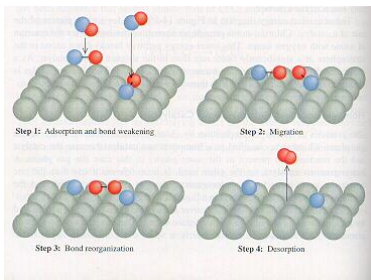
## 2. Presence of a catalyst

Discussion: What is a catalyst / what does a catalyst do?

Example: the Pt/Pd catalyst in your car's muffler, a two-way catalyst



Questions: Which *two* 'unpleasant' gasses are produced through the incomplete combustion of gasoline? How are these gases converted to more benign products?



### 3. Temperature at which the reaction occurs

Discussion: What happens to the rate of molecular collisions (therefore the rate of reaction) when the temperature of the reaction vessel is increased? Why?



The kinetic energy (K.E.) of a molecular\* species is proportional to the ambient temperature.

Molecular KE =  $\frac{1}{2} mv^2 = kT$  (k is the Boltzmann constant)

**i.e. Temp  $\propto v^2 \propto$  (reaction rate)<sup>2</sup>**

#### 4. Surface Area of a Solid Reactant



Why does powdered sugar dissolve much more quickly than ‘trendy’ crystalline sugar swizzles? What’s happening on the micro scale?



#### **Definition of Reaction Rate**

##### Discussion Questions

1. How do you know that a reaction is occurring or has finished?
  
  
  
  
  
  
  
  
  
  
2. How then, would you measure the speed (or rate) of reaction? Hint: How is rate of distance traveled (speed) measured by your car’s ‘speedo’?

#### Definition of Reaction Rate

3. How would you define 'reaction rate' or 'rate of reaction' mathematically? Hint: Think about expressing rate of change in calculus.

Example: The decomposition of dinitrogen pentoxide



The rate of reaction can be expressed in terms of *either* the decrease in  $[\text{N}_2\text{O}_5]$  with time *or* the increase of  $[\text{NO}_2]$  or  $[\text{O}_2]$  with time.

Task: write calculus style relationships illustrating the above

Rate of formation wrt.  $\text{O}_2 =$

Rate of formation wrt.  $\text{NO}_2 =$

Rate of loss wrt.  $\text{N}_2\text{O}_5 =$

Application: AVERAGE reaction rates



**Average reaction rates are ‘as advertised’ - the average speed (rate) of a reaction over an extended (measurable) period of time**

Worked Example: If it takes 32 seconds to see the appearance of 2 moles O<sub>2</sub> (g) (within a 1.0 L container) from the above reaction, what is the average rate of reaction over this time period?



***Difference* is always found by subtracting the initial condition from the final condition in chemistry problems**

**i.e:  $\Delta(\text{variable}) = \text{final value variable} - \text{initial value variable}$**

Calculations

$$\Delta [\text{O}_2] =$$

$$\Delta t =$$

$$\Rightarrow \text{Average rate of reaction} = \frac{\Delta [\text{O}_2]}{\Delta t} =$$

Note: The unit for rate of reaction is always  $\text{mols L}^{-1}/\text{s}$  ( $\text{mols L}^{-1} \text{ s}^{-1}$ )

## Instantaneous Rates of Reaction

Analogy: The difference between *average* and *instantaneous* rates



Average rate analogy: It takes ~60 minutes to travel the 60 miles from JJC to downtown Chicago. What is the average speed during the journey?



Instantaneous rate analogy: Is it likely that you will travel at exactly 60 miles/hr for the entire duration of the journey?



Open road speed  $\approx$

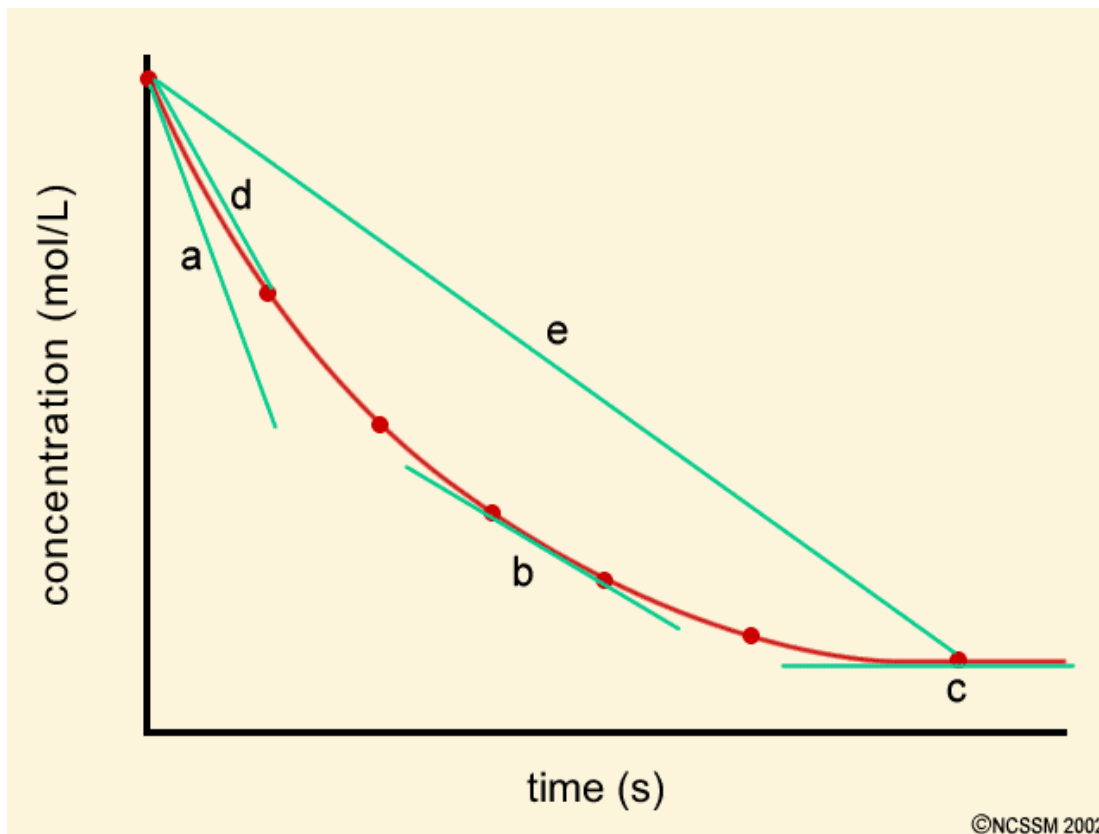
Congested expressway speed  $\approx$

Discussion: How would you expect the instantaneous rate of reaction to vary through the course of any reaction? What molecular level events are responsible for this trend?



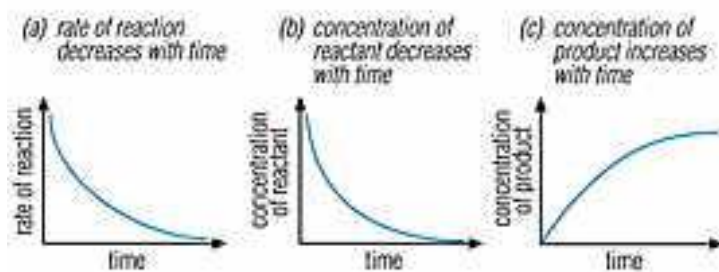


Generic Graph of Concentration *Reactant* v Time for a chemical reaction

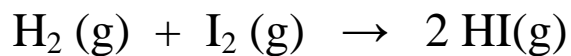


Features of the graph

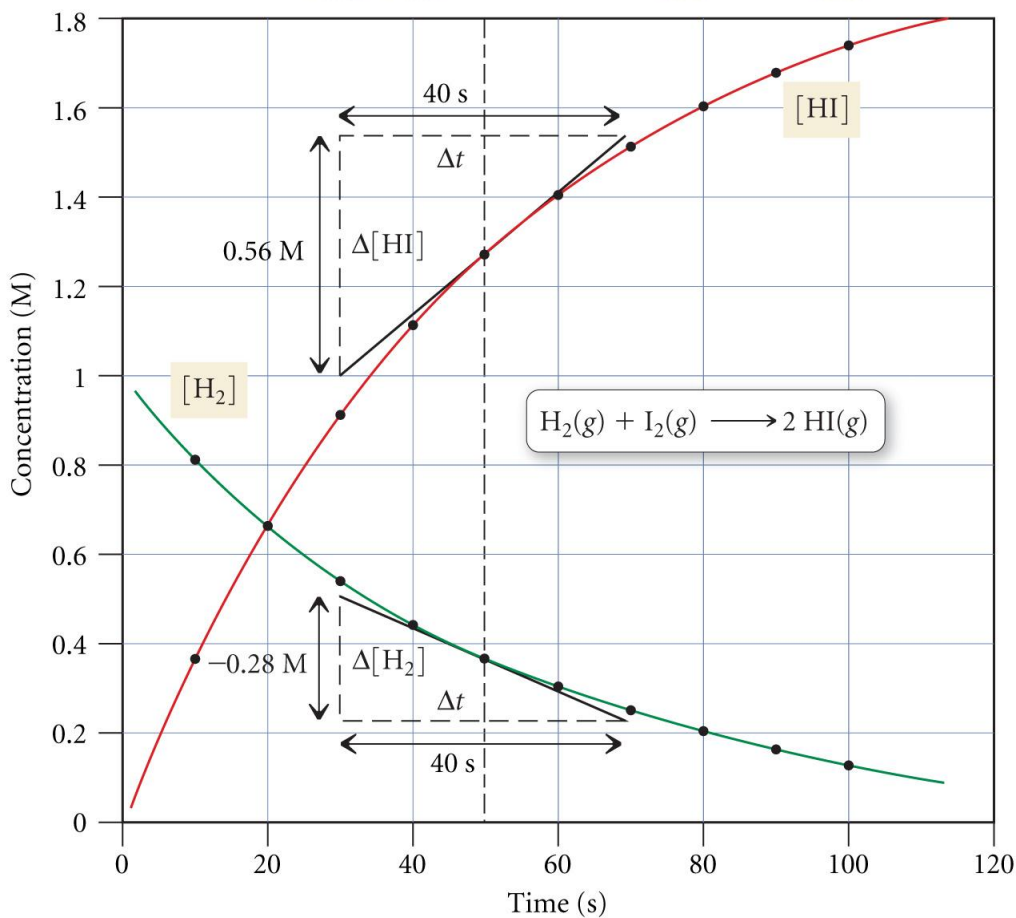
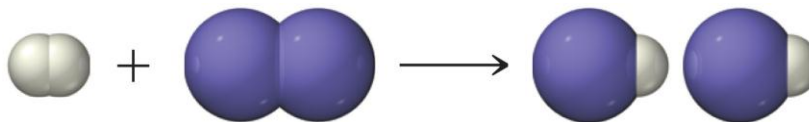
Discussion: If the [reactants] *decreases* with time for any reaction (above), then: 1) How does [products] vary with time? 2) How does the *rate of formation* of products vary with time?



Overview Example: Graph of product conc. v time – measuring the rate of HI (g) formation and the rate of H<sub>2</sub> (g) disappearance for the reaction:



i.e.



General Features of the graphs

## Calculating the *instantaneous* rates of reaction

Recap: While a ‘true’ instantaneous rate can only be found by determining the *exact* gradient (slope) of the rate of reaction ([conc] v time) graph at a specified time (how?), a good approximation can be found through

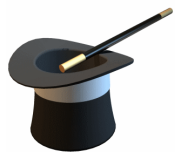
*either*:

Graphical Method: Draw a tangent line to the experimental rate of reaction graph at the time of interest, and then find its gradient (by hand, or modern computer programs and/or graphical calculators can also do this)

Task: Use the ‘graphical’ method to find the instantaneous rate of reaction at  $t = 50$  seconds in terms of change in [HI] with time

*or*

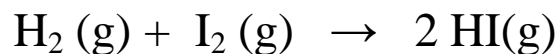
Equation of a Line Method: Use the equation of a line equation, i.e.  $y_2 - y_1 = m(x_2 - x_1)$ , to solve for the gradient of the curve ( $m$ ) given a pair of adjacent experimental data points



**Determine  $\Delta[\text{conc}]$  and  $\Delta t$  values using ‘equidistant’ data points either side of the required time. Divide these determined values to find the instantaneous rate at the desired time**

Task: Use the ‘equation’ method to find the instantaneous rate of reaction at  $t = 50$  seconds in terms of change in  $[\text{H}_2]$  with time (see p 566 or appendix for data table). Discussion: why are your two answers different (more later)?

Wrap Up Example: Consider our previous example (see p 566 and appendix for graph and data table).



Experimental: As you will discover in lab, for most kinetic studies the concentration of a reactant, *or* product, is monitored with time; i.e. [conc] values are recorded at for a series of regular time intervals during the experiment. This raw data is then either used directly or plotted as a standard 'reaction rate' or [conc] v time graph shown here – see HWK for examples.

Wrap up: Using the tabulated experimental data and/or graph from p 566 of *Tro* (see appendix too), determine the instantaneous rate of the reaction, with respect to the disappearance of  $\text{H}_2(\text{g})$ , at  $t = 80 \text{ s}$ .



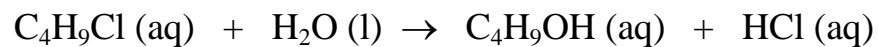
Summary:

The instantaneous rate of reaction is a measure of either the *rate of change* of [reactant] or [product] at a fixed point in time (some fixed time after the reactants are mixed)

The instantaneous rate is found by determining the slope (gradient) of the [conc] v time reaction rate graph at a specified time after the reaction has commenced.

## Reaction Rates and Stoichiometry

Discussion: For the reaction:



Is the rate of appearance  $\text{C}_4\text{H}_9\text{OH (aq)}$  = rate of appearance  $\text{HCl (aq)}$ ? How do you know? Write a rate expression illustrating this relationship

Is the rate of disappearance  $\text{C}_4\text{H}_9\text{Cl (aq)}$  = rate of disappearance  $\text{H}_2\text{O (l)}$ ? Write a rate expression illustrating this relationship

Write a rate expression illustrating the relationship between the rate of disappearance  $\text{C}_4\text{H}_9\text{Cl (aq)}$  and the rate of appearance  $\text{HCl (aq)}$



**Stoichiometric factors (balancing numbers) indicate the relative number of molecules ( $\propto$  [conc]) of a reactant or product that are consumed or formed, respectively, per unit time for any reaction**

Example: For the reaction:



The rate of reaction can be expressed in terms of either  $[\text{N}_2\text{O}_5]$ ,  $[\text{NO}_2]$  or  $[\text{O}_2]$

Does  $[\text{NO}_2]$  increase at a faster, slower, or at the same rate as  $[\text{O}_2]$ ? Express this relationship as a rate expression

Does  $[\text{N}_2\text{O}_5]$  decrease at a faster, slower, or at the same rate as  $[\text{O}_2]$ ? Express this relationship as a rate expression



**Balanced chemical equations and rates of reaction are related via the following generic expressions:**



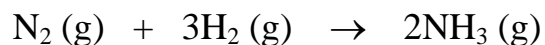
$$\text{Rate} = \frac{-1}{a} \frac{\Delta[\text{A}]}{\Delta t} = \frac{-1}{b} \frac{\Delta[\text{B}]}{\Delta t} = \frac{1}{c} \frac{\Delta[\text{C}]}{\Delta t} = \frac{1}{d} \frac{\Delta[\text{D}]}{\Delta t}$$



*“Expressing reaction rates”*

The following question was taken from your 1<sup>st</sup> practice midterm:

The reaction between hydrogen and nitrogen to form ammonia is known as the Haber process:



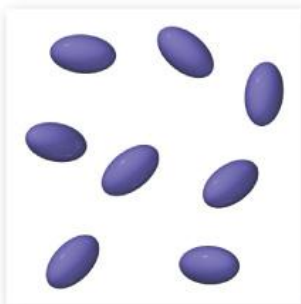
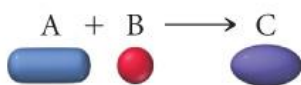
Question 1a (3 points each): Express the rate of the above reaction in terms of changes in  $[\text{N}_2]$  with time,  $[\text{H}_2]$  with time, and  $[\text{NH}_3]$  with time.

Question 1b (16 points): When  $[\text{H}_2]$  is decreasing at  $0.175 \text{ molL}^{-1}\text{s}^{-1}$ , at what rate is  $[\text{NH}_3]$  increasing?



## Appendix

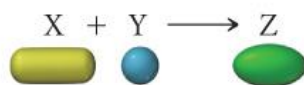
A reaction with a fast rate



Time



A reaction with a slow rate



Time (s)	[H <sub>2</sub> ] (M)	Δ[H <sub>2</sub> ]	Δt	
0.000	1.000	}		
10.000	0.819		-0.181	10.000
20.000	0.670		-0.149	10.000
30.000	0.549		-0.121	10.000
40.000	0.449		-0.100	10.000
50.000	0.368		-0.081	10.000
60.000	0.301		-0.067	10.000
70.000	0.247		-0.054	10.000
80.000	0.202		-0.045	10.000
90.000	0.165		-0.037	10.000
100.000	0.135	-0.030	10.000	

