AP CHEMISTRY

Unit 3: Chemical Kinetics

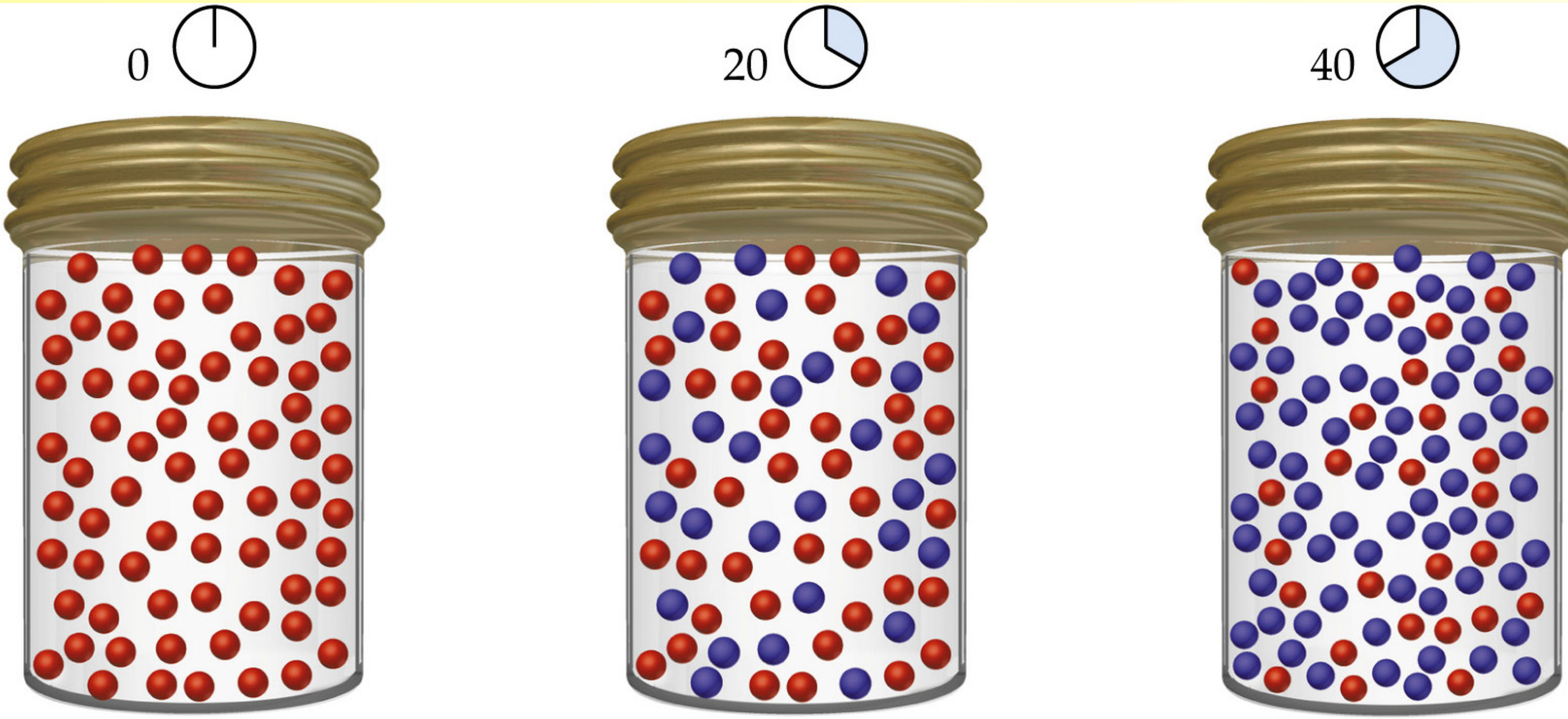
Jeff Venables
Northwestern High School

Reaction Rates

- Speed of a reaction is measured by the change in amount of a substance with time.
  - Volume
  - Mass or moles
  - Concentration (molarity)
- For a reaction A → B

$$\text{Average rate} = \frac{\text{change in number of moles of B}}{\text{change in time}}$$

$$= \frac{\Delta(\text{moles of B})}{\Delta t}$$


0
20
40

- Suppose A reacts to form B. Let us begin with 1.00 mol A.
  - At $t = 0$ (time zero) there is 1.00 mol A (100 red spheres) and no B present.
  - At $t = 20$ min, there is 0.54 mol A and 0.46 mol B.
  - At $t = 40$ min, there is 0.30 mol A and 0.70 mol B.
  - Calculating,

$$\text{Average rate} = \frac{\Delta(\text{moles of B})}{\Delta t}$$

$$= \frac{(\text{moles of B at } t = 40) - (\text{moles of B at } t = 0)}{40 \text{ min} - 0 \text{ min}}$$

$$= \frac{0.70 \text{ mol} - 0 \text{ mol}}{40 \text{ min} - 0 \text{ min}} = 0.0175 \text{ mol/min}$$

- For the reaction A → B there are two ways of measuring rate:
  - the speed at which the products appear (i.e. change in moles of B per unit time), or
  - the speed at which the reactants disappear (i.e. the change in moles of A per unit time).

$$\text{Average rate with respect to A} = \frac{\Delta(\text{moles of A})}{\Delta t}$$

Change of Rate with Time

- Most useful units for rates are to look at molarity. Since volume is constant, molarity and moles are directly proportional.
- Consider:

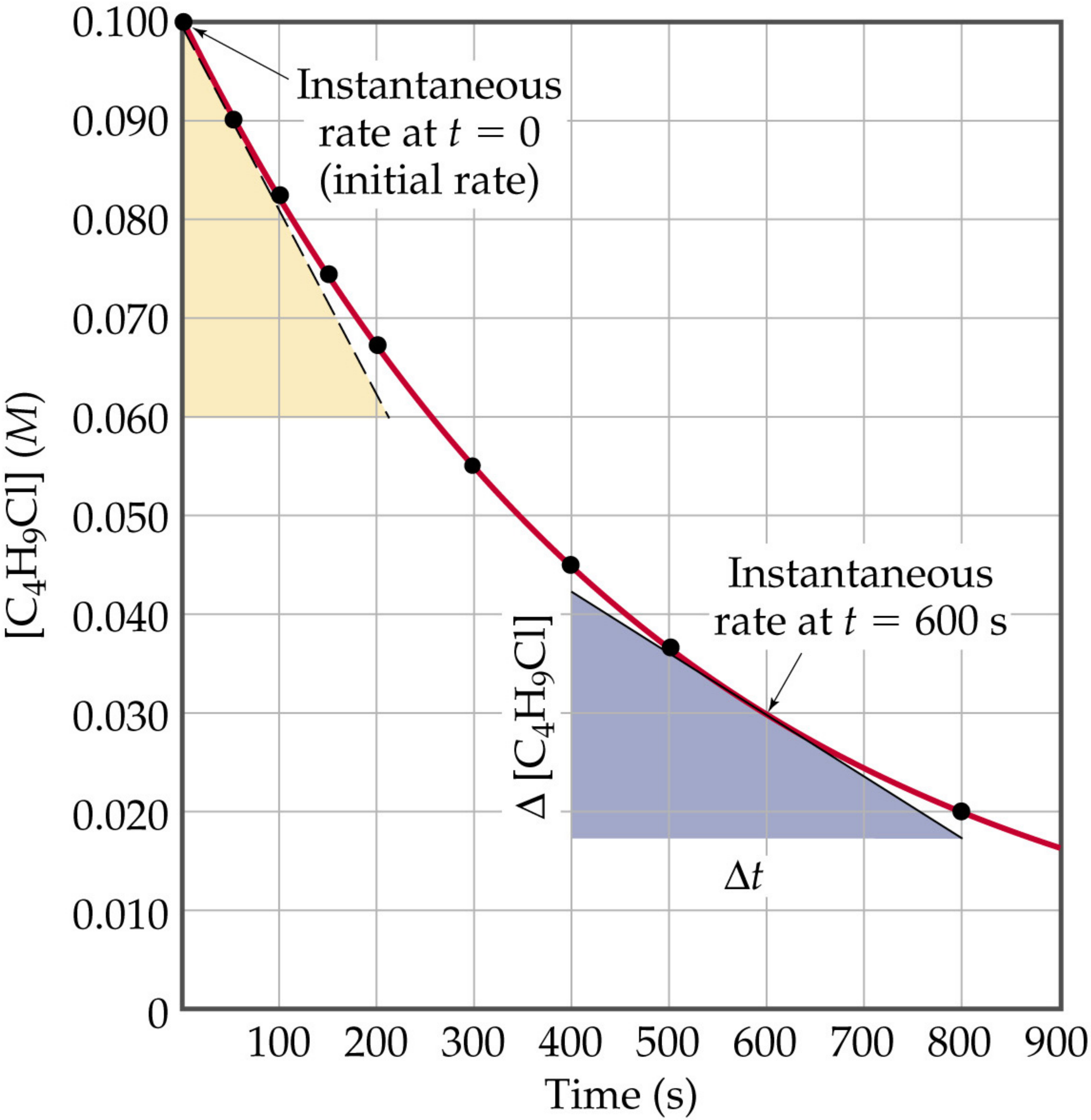
$$C_4H_9Cl(aq) + H_2O(l) \rightarrow C_4H_9OH(aq) + HCl(aq)$$

TABLE 14.1 Rate Data for Reaction of C_4H_9Cl with Water

Time, t (s)	$[C_4H_9Cl]$ (M)	Average Rate (M/s)
0.0	0.1000	
		1.9×10^{-4}
50.0	0.0905	
		1.7×10^{-4}
100.0	0.0820	
		1.6×10^{-4}
150.0	0.0741	
		1.4×10^{-4}
200.0	0.0671	
		1.22×10^{-4}
300.0	0.0549	
		1.01×10^{-4}
400.0	0.0448	
		0.80×10^{-4}
500.0	0.0368	
		0.560×10^{-4}
800.0	0.0200	
10,000	0	

$$C_4H_9Cl(aq) + H_2O(l) \rightarrow C_4H_9OH(aq) + HCl(aq)$$

- We can calculate the average rate in terms of the disappearance of C_4H_9Cl.
- The units for average rate are **mol L^{-1} s^{-1}** or *M/s*.
- The average rate decreases with time.
- We plot $[C_4H_9Cl]$ versus time.
- The rate at any instant in time (instantaneous rate) is the slope of the tangent to the curve.
- Instantaneous rate is different from average rate.
- We usually call the instantaneous rate the rate.



Instantaneous
rate at t = 0
(initial rate)
Instantaneous
rate at t = 600 s
Δ [C4H9Cl]
Δt
[C4H9Cl] (M)
0.100
0.090
0.080
0.070
0.060
0.050
0.040
0.030
0.020
0.010
0
100
200
300
400
500
600
700
800
900
Time (s)

Reaction Rate and Stoichiometry

- For the reaction

$$C_4H_9Cl(aq) + H_2O(l) \rightarrow C_4H_9OH(aq) + HCl(aq)$$

we know

$$\text{Rate} = -\frac{\Delta[C_4H_9Cl]}{\Delta t} = \frac{\Delta[C_4H_9OH]}{\Delta t}$$

- In general for

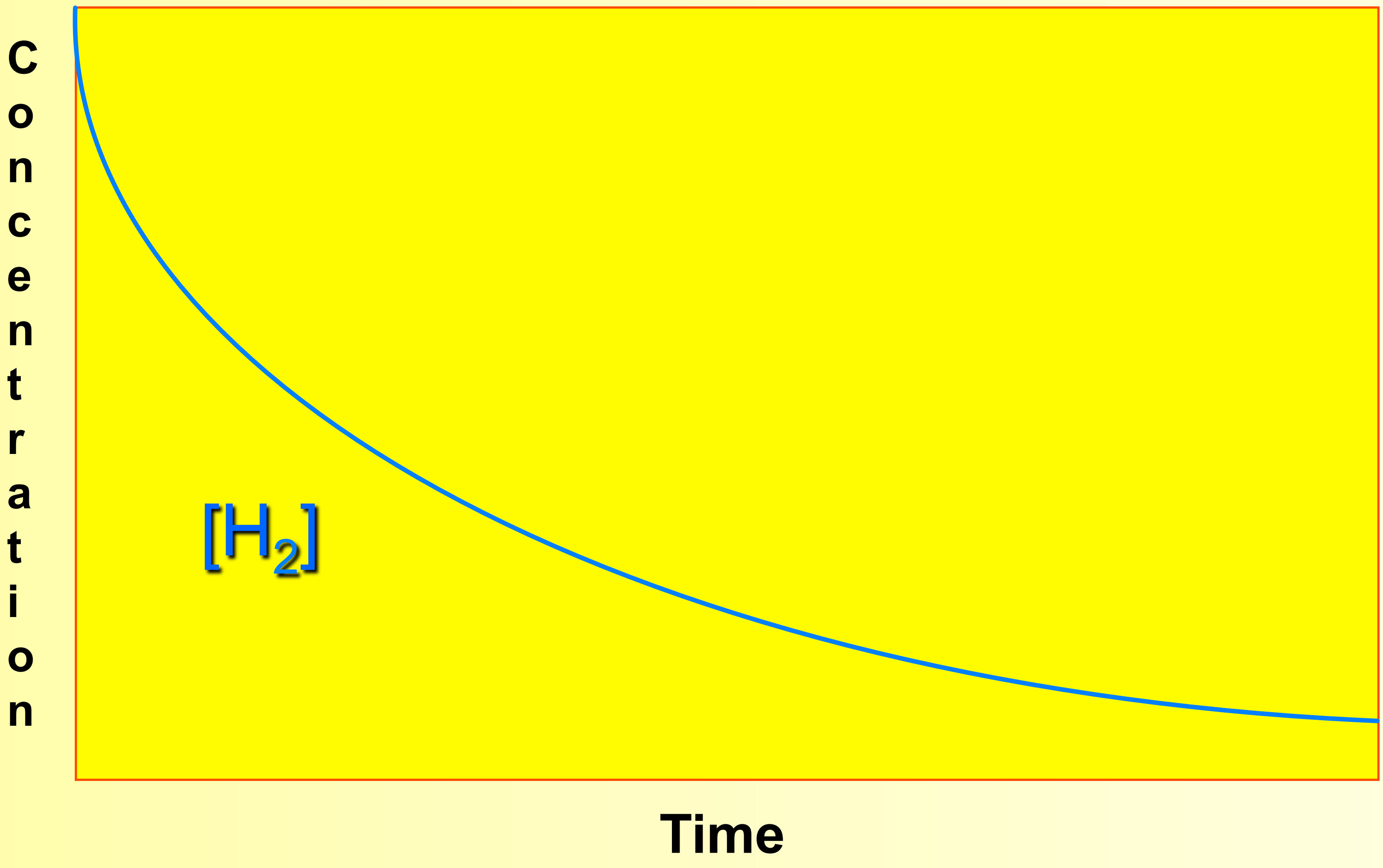
$$a\text{A} + b\text{B} \rightarrow c\text{C} + d\text{D}$$

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

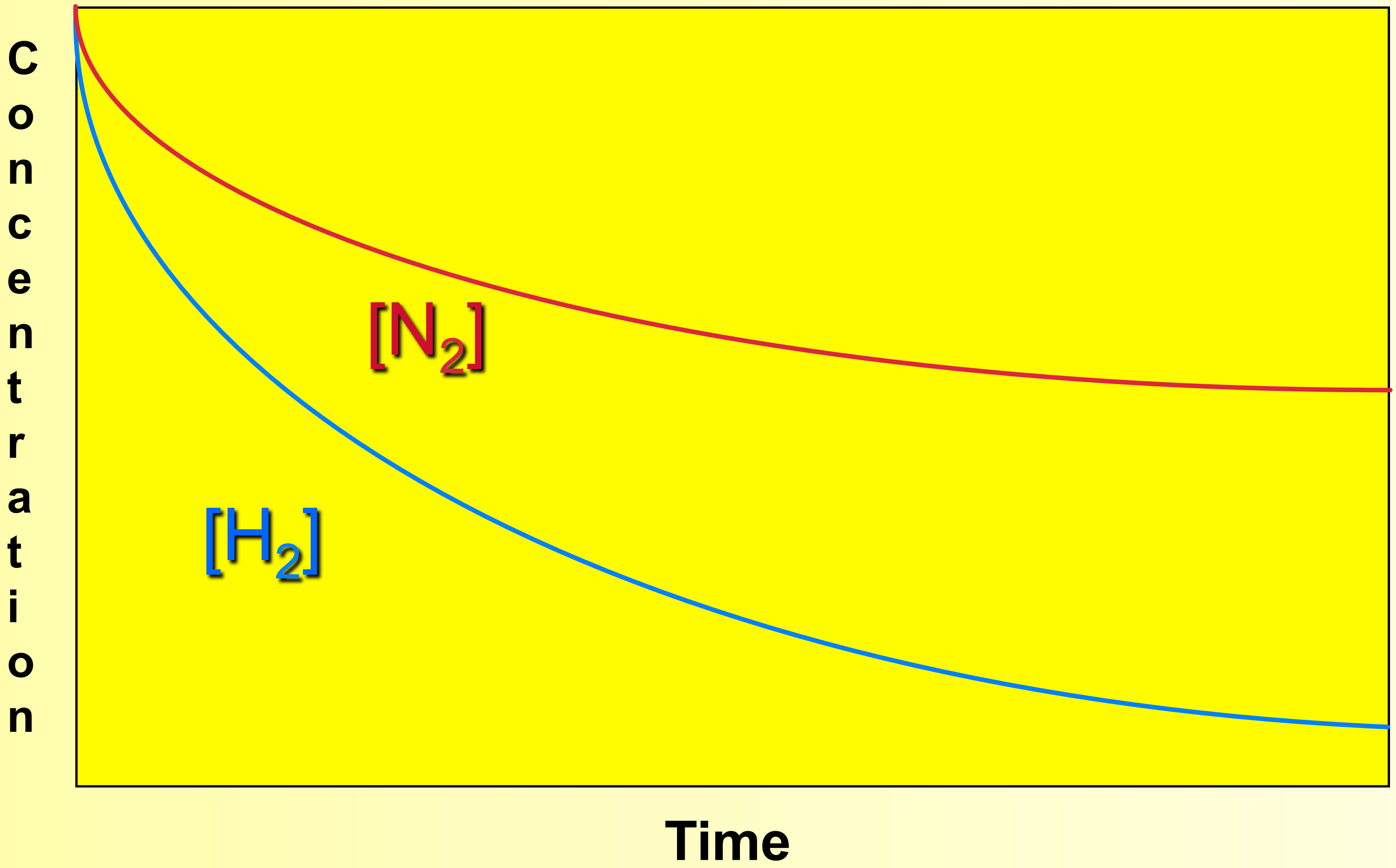
Reaction Rate

- $\text{Rate} = \dfrac{\text{Conc. of A at } t_2 - \text{Conc. of A at } t_1}{t_2 - t_1}$
- $\text{Rate} = \dfrac{\Delta [A]}{\Delta t}$
- Change in concentration per unit time
- For this reaction
- $N_2 + 3H_2 \longrightarrow 2NH_3$

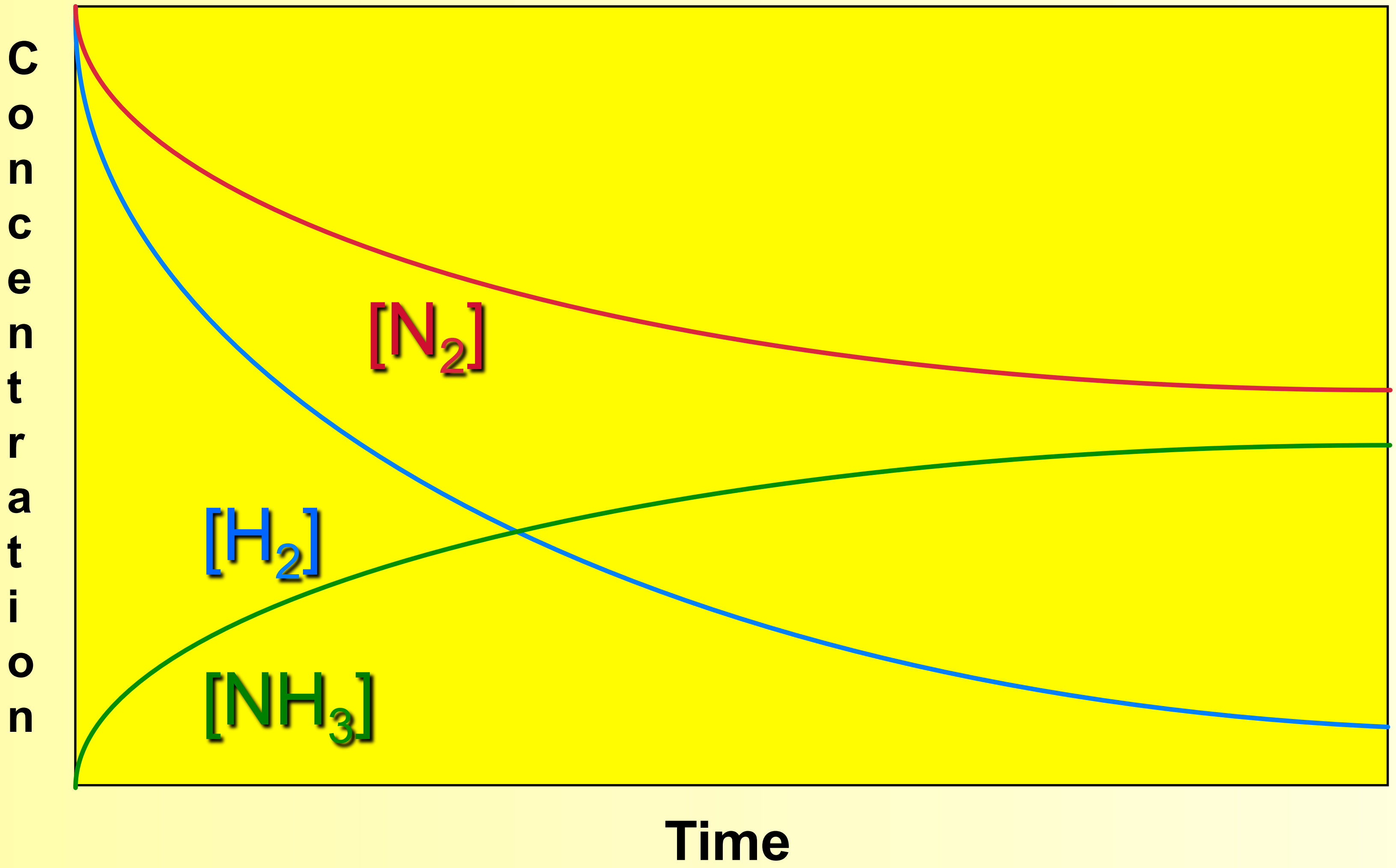
- As the reaction progresses the concentration H_2 goes down



- As the reaction progresses the concentration N_2 goes down 1/3 as fast



- As the reaction progresses the concentration NH_3 goes up.



Example

$$N_2 + 3H_2 \longrightarrow 2NH_3$$

At a certain temperature, the rate of this reaction is -0.13 mol N_2 L^{-1} s^{-1}. What is the rate in mol H_2 L^{-1} s^{-1}? What is the rate in mol NH_3 L^{-1} s^{-1}?

Example

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At a certain temperature, the rate of this reaction is -0.13 mol N_2 L^{-1} s^{-1}. What is the rate in mol H_2 L^{-1} s^{-1}? What is the rate in mol NH_3 L^{-1} s^{-1}?

-0.39 mol H_2 L^{-1} s^{-1}

0.26 mol NH_3 L^{-1} s^{-1}

Factors that Affect Reaction Rates

- Kinetics is the study of how fast chemical reactions occur.
- There are 4 important factors which affect rates of reactions:
  - reactant concentration,
  - temperature,
  - action of catalysts, and
  - surface area/particle size.
- Goal: to understand chemical reactions at the molecular level.

Concentration and Rate

In general rates increase as reactant concentrations increase.

$$NH_4^+(aq) + NO_2^-(aq) \rightarrow N_2(g) + 2H_2O(l)$$

TABLE 14.2 Rate Data for the Reaction of Ammonium and Nitrite Ions in Water at 25°C

Experiment Number	Initial NH_4^+ Concentration (*M*)	Initial NO_2^- Concentration (*M*)	Observed Initial Rate (*M*/s)
1	0.0100	0.200	5.4×10^{-7}
2	0.0200	0.200	10.8×10^{-7}
3	0.0400	0.200	21.5×10^{-7}
4	0.0600	0.200	32.3×10^{-7}
5	0.200	0.0202	10.8×10^{-7}
6	0.200	0.0404	21.6×10^{-7}
7	0.200	0.0606	32.4×10^{-7}
8	0.200	0.0808	43.3×10^{-7}

- For the reaction

$$NH_4^+(aq) + NO_2^-(aq) \rightarrow N_2(g) + 2H_2O(l)$$

we note
  - as $[NH_4^+]$ doubles with $[NO_2^-]$ constant the rate doubles,
  - as $[NO_2^-]$ doubles with $[NH_4^+]$ constant, the rate doubles,
  - We conclude rate $\propto [NH_4^+][NO_2^-]$.
- Rate law:

$$\text{Rate} = k[NH_4^+][NO_2^-]$$

- The constant k is the rate constant.

$$2\,NO_2 \longrightarrow 2\,NO + O_2$$

- You will find that the rate will only depend on the concentrations of the reactants.
- Rate = $k[NO_2]^n$
- This is called a **rate law expression**.
- *k* is called the rate constant.
- n is the order of the reactant -usually a positive integer.

Types of Rate Laws

- Differential Rate law - describes how rate depends on concentration (Referred to as simply "rate law").
- Integrated Rate Law - Describes how concentration varies with time.
  - For each type of differential rate law there is an integrated rate law and vice versa.
- Rate laws can help us better understand reaction mechanisms.

Exponents in the Rate Law

- For a general reaction with rate law

$$\text{Rate} = k[\text{reactant}\,1]^m[\text{reactant}\,2]^n$$

  we say the reaction is *m*th order in reactant 1 and *n*th order in reactant 2.
- The overall order of reaction is $m + n + \ldots$.
- A reaction can be zeroth order if m, n, … are zero.
  - This means that the rate does not depend on the concentration of (a) reactant(s)
- Note: the values of the exponents (orders) have to be determined experimentally. They are not simply related to stoichiometry.