

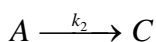
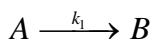
Chapter 21 Homework Questions

- 21.1** The rate of formation of C in the reaction $2 A + B \rightarrow 2 C + 3 D$ is 2.7 Ms^{-1} . State the reaction rate, and the rates of formation or consumption of A, B, and D.
- 21.2** The rate law for the reaction, $A + B \rightarrow \text{Products}$, is of the form, $r = k[A]^x[B]^y$. From the initial rate data for this reaction given below, determine the reaction orders, “x” and “y”, and the rate constant, k (give units).
- | [A] ₀ | [B] ₀ | r ₀ |
|------------------|------------------|------------------------|
| 0.10 M | 2.0 M | 8.50 Ms^{-1} |
| 0.30 | 2.0 | 2.83 |
| 0.30 | 3.0 | 7.80 |
- 21.3** At 518 °C, the half-life for the decomposition of gaseous acetaldehyde (aka ethanal, CH_3CHO) is 410 s when the initial pressure is 363 torr. The half-life is 880 s when the initial pressure is 169 torr. Determine the order of the reaction.
- 21.4** The reaction, $A \rightarrow P$, is of order “x”; i.e. $\text{Rate} = k[A]^x$. When $[A]_0 = 0.4 \text{ M}$, the half-life of the reaction is 200 s. When $[A]_0 = 0.2 \text{ M}$, the half-life of the reaction is 50 s. What is the order of this reaction (i.e. what is “x”)?
- 21.5** The reaction, $A \rightarrow P$, is of order “x”; i.e. $\text{Rate} = k[A]^x$. When $[A]_0 = 0.1 \text{ M}$, the half-life of the reaction is 200 s. When $[A]_0 = 0.25 \text{ M}$, the half-life of the reaction is 126 s. What is the order of this reaction (i.e. what is “x”)?
- 21.6** Consider a second order reaction, $A \rightarrow \text{Products}$. When $[A]_0 = 1.30 \text{ M}$, the half life of the reaction is 42 seconds.
- What is the rate constant, k, for this reaction?
 - When $[A]_0 = 1.30 \text{ M}$, what will the concentration be 60 seconds after the start of the reaction.
 - When $[A]_0 = 1.30 \text{ M}$, how long will it take for the concentration of A to decrease to 0.80 M?
- 21.7** Consider a third order reaction, $A \rightarrow \text{Products}$. When the initial concentration is $[A]_0 = 0.80 \text{ M}$, it takes 6.40 seconds for the concentration to decrease to $[A] = 0.50 \text{ M}$.
- Calculate the rate constant, k.
 - When $[A]_0 = 0.80 \text{ M}$, what is the concentration after 20 seconds.
 - When $[A]_0 = 0.80 \text{ M}$, how long does it take for the concentration to decrease to 0.30 M

21.8 Consider a reaction, $A \rightarrow \text{Products}$, which is of order $3/2$; i.e. $\text{Rate} = -\frac{d[A]}{dt} = k[A]^{3/2}$. The rate constant for this reaction is $k = 0.03 \text{ M}^{-1/2}\text{s}^{-1}$.

- Determine the half-life for this reaction when $[A]_0 = 0.50 \text{ M}$
- If the initial concentration of A is 0.50 M , what will the concentration of A be after 25 s ?
- If the initial concentration of A is 0.50 M , how long will it take for the concentration to decrease to 0.20 M ?

21.9 Consider the competitive first-order reactions,



- If one begins an experiment with $[A]_0 = 1.20 \text{ M}$, it is found that $[B] = 0.90 \text{ M}$ at the conclusion of the experiment.
What is the ratio of the two rate constants, k_1/k_2 ?
- It is found that the rate constant for the first reaction is $k_1 = 0.60 \text{ s}^{-1}$. what is the concentration, $[C]$, 2.0 seconds after the start of the reaction?

21.10 The rate constant for a first order reaction is $1.5 \times 10^{-3} \text{ s}^{-1}$ at 40°C and $8.6 \times 10^{-2} \text{ s}^{-1}$ at 80°C .

- Calculate the Arrhenius parameters, A and E_a , for this reaction.
- Calculate the rate constant of this reaction at 130°C .
- Calculate the temperature at which the half-life of this reaction is 200 s .

21.11 The Transition State Theory Equation for the rate constant is:

$$k = \frac{RT}{N_A h} e^{\frac{\Delta S^\ddagger}{R}} e^{-\frac{\Delta H^\ddagger}{RT}} \quad R, N_A \text{ and } h \text{ are universal constants:}$$

$$\frac{R}{N_A h} = \frac{8.31}{(6.02 \times 10^{23})(6.63 \times 10^{-34})} = 2.1 \times 10^{10}$$

For a given kinetics experiment, a plot of $\ln(k/T)$ vs. $1/T$ was a straight line with Slope = -5450 K and Intercept = $+12.80$

Calculate the reaction's Activation Enthalpy, ΔH^\ddagger (in kJ/mol), and the Activation Entropy, ΔS^\ddagger (in J/mol-K).

21.12 One theory of rate constants for bimolecular gas phase reactions is “Collision Theory”. The collision theory form for the rate constant is: $k = C\sqrt{T}e^{-\frac{E_0}{RT}}$, where C is a constant, and E_0 is the threshold energy for reaction.

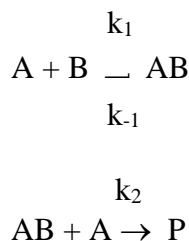
Develop an expression relating the threshold energy, E_0 , to the Arrhenius Activation Energy.

21.13 The reaction mechanism for the reaction, $A_2 + 2 B \rightarrow 2 P$ is:



Deduce the rate law for $d[P]/dt$ for this mechanism.

21.14 The reaction, $2 A + B \rightarrow P$ (P is the product) proceeds by the following mechanism.



“AB” is an intermediate present in steady-state concentration. Use the steady-state approximation on [AB] to develop an expression for the rate of formation of P as a function of [A], [B], k_1 , k_{-1} and k_2 .

Note: For Photochemistry questions: On an exam, you would be given the following relationship between photon wavelength (λ) and energy (E_{ph}):

$$E_{ph} = \frac{hc}{\lambda} \quad h = 6.63 \times 10^{-34} \text{ J s} , \quad c = 3.00 \times 10^8 \text{ m/s}$$

21.15 In a photochemical reaction, $A \rightarrow 2 B + C$, the quantum yield with 500 nm light is 210 mol A reacted/mol photon absorbed. After exposure of 300 mmol of A to light, 2.28 mmol of B is formed.

How many photons were absorbed?

21.16 In an experiment to determine the reaction quantum yield of a photochemical reaction, $A \rightarrow \text{Products}$, the reactant was exposed to 490 nm radiation from a 100 W source for 45 min. The intensity of the transmitted light was 40% of the intensity of the incident light. As a result of the radiation, 0.344 mol of the reactant decomposed.

Determine the quantum yield, Φ_R , for this reaction.

- 21.17** Consider the quenching of an organic fluorophore with a fluorescent lifetime, $\tau_0 = 6.0$ ns. A quenching agent with a quenching rate constant, $k_Q = 3.0 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$, is added to the solution.
- Predict the quencher concentration, $[Q]$, required to obtain 60% quenching of the fluorescence.
- 21.18** In a pulsed laser fluorescence experiment on Naphthalene (dissolved in hexane), the fluorescence intensity 35 ns after the experiment begins is 65% of the intensity at the beginning of the experiment.
- In a separate experiment, it was determined that the fluorescence rate constant is:
 $k_F = 4.8 \times 10^6 \text{ s}^{-1}$.
- Calculate (a) the singlet state lifetime, τ_0 (in ns), and (b) the fluorescence quantum yield of naphthalene.
- 21.19** The hydrolysis of the substrate, N-glutaryl-L-phenylalanine-p-nitroanilide [GPNA], to p-nitroaniline and N-glutaryl-L-phenylalanine is catalyzed by α -chymotrypsin.
- When $[E]_0 = 4.0 \times 10^{-6} \text{ M}$, it is found that $v_0 = 3.7 \times 10^{-8} \text{ M/s}$ when $[S] = 2.5 \times 10^{-4} \text{ M}$ and $v_0 = 9.8 \times 10^{-8} \text{ M/s}$ when $[S] = 1.0 \times 10^{-3} \text{ M}$.
- Determine the slope and intercept of the Lineweaver-Burk plot and, from these, K_M , V_m , and k_2 for this reaction.
- 21.20** Consider an enzyme catalyzed reaction with $[E]_0 = 2 \text{ mM}$, $K_M = 20 \text{ mM}$, and $V_M = 80 \text{ mM/s}$
- (a) The slope of the Lineweaver-Burk plot is
 (A) 0.013 s/mM (B) 4 s^{-1} (C) $6.3 \times 10^{-4} \text{ mM/s}$ (D) 0.25 s
- (b) The intercept of the Lineweaver-Burk plot is
 (A) 0.013 s/mM (B) 4 s^{-1} (C) $6.3 \times 10^{-4} \text{ mM/s}$ (D) 0.25 s
- (c) The “turnover number”, k_2 , is
 (A) 10 (B) 0.10 s^{-1} (C) 40 s^{-1} (D) 0.025 s