4.9: Exercises on Chemical Kinetics

These are homework exercises to accompany the Textmap created for "General Chemistry: Principles and Modern Applications " by Petrucci et al. Complementary General Chemistry question banks can be found for other Textmaps and can be accessed here. In addition to these publicly available questions, access to private problems bank for use in exams and homework is available to faculty only on an individual basis; please contact Delmar Larsen for an account with access permission.

Q4

In the reaction $A \rightarrow \text{products}$, at $t = 0$, $[A] = 0.1563\,M$. After 1.00 minute, $[A] = 0.1496\,M$, and after 2.00 minutes, $[A] = 0.1431\,M$.

a. Calculate the average rate of reaction during the first minute and during the second minute.
b. Why are these two rates not equal?

Q5

In the reaction $A \rightarrow \text{products}$, 4.50 minutes after the reaction is started, $[A] = 0.587\,M$. The rate of reaction at this point is $\text{rate} = -\dfrac{\Delta[A]}{\Delta t} = 2.1 \times 10^{-2}\ M\,\text{min}^{-1}$. Assume that this rate remains constant for a short period of time.

a. What is $[A]$ 6.00 minutes after the reaction is started?
b. At what time after the reaction is started with $[A] = 0.56\,M$?

Q6.

Refers to figure in book. What do we do????

Q7

For the reaction $A + 2B \rightarrow 2C$, the rate of reaction is 1.75 x 10^{-5} M s^{-1} at the time when $[A] = 0.3575\,M$.

a. What is the rate of formation of C?
b. What will $[A]$ be 1 minute later?
c. Assume the rate remains at 1.75 x 10^{-5}M s^{-1}. How long would it take for $[A]$ to change from 0.3580 to 0.3500M?

Q8.

Refers to figure in book. What do we do????

Q10

At 65°, the half-life for the first-order decomposition of $N_2O_5(g)$ is 2.35 minutes.

$$N_2O_5(g) \rightarrow 2\,NO_2(g) + \frac{1}{2}O_2(g)$$

If 1.00g of N_2O_5 is introduced into an evacuated 10L flask at 65°C,

a. What is the initial partial pressure, in mmHg, of $N_2O_5(g)$?
b. What is the initial partial pressure, in mmHg, of $N_2O_5(g)$ after 2.35 minutes?
c. What is the total gas pressure, in mmHg, after 2.35 minutes?

Q11

The initial rate of the reaction $A + B \rightarrow C + D$ is determined for different initial conditions, with the results listed in the table.

a. What is the order of reaction with respect to A and to B?
b. What is the overall reaction order?
c. What is the value of the rate constant, k?

Expt	$[A]$,**M**	$[B]$,**M**	**Initial Rate, M s^{-1}**
1	0.185	0.144	3.35×10^{-4}
2	0.185	0.288	1.35×10^{-3}
3	0.370	0.144	6.75×10^{-4}
4	0.370	0.288	2.70×10^{-3}

Q12

For the reaction $A + B \rightarrow C + D$ the following initial rate of reaction were found. What is the rate law for this reaction?

Expt	$[A]$,**M**	$[B]$,**M**	**Initial Rate, M min^{-1}**
1	0.60	1.80	4.2×10^{-3}
2	1.80	1.80	1.3×10^{-2}
3	3.60	3.60	5.2×10^{-2}

Q13.

The following rates of reaction were obtained in three experiments with the reaction $2\,NO(g) + Cl_2(g) \rightarrow 2\,NOCl(g)$.

Expt	**Initial** $[NO]$, **M**	**Initial** $[Cl_2]$, **M**	**Initial Rate of Reaction, M s^{-1}**
1	0.0125	0.0260	2.23×10^{-5}
2	0.0125	0.0510	4.50×10^{-5}
3	0.0250	0.0260	9.05×10^{-5}

What is the rate of law of this reaction?

Q14.

The following was obtained for the initial rates of reaction in the reaction $A + 2\,B + C \rightarrow 2\,D + E$.

Expt	**Initial** $[A]$,**M**	**Initial** $[B]$,**M**	$[C]$, **M**	**Initial Rate**
1	1.20	1.20	1.00	R_1
2	0.60	1.20	1.00	$R_2 = \frac{1}{2} \times R_1$
3	0.60	0.60	1.00	$R_3 = \frac{1}{4} \times R_2$
4	1.20	1.20	0.50	$R_4 = 16 \times R_3$
5	0.60	0.60	0.50	$R_5 = ?$

a. What are the reaction orders with respect to A, B, and C?
b. What is the value of R_5 in terms of R_1?

Q15.

One of the following statements is true and the other is false regarding the first-order reaction $A \rightarrow B + C$. Identify the true statement and the false one, and explain your reasoning.

a. The rate of the reaction decreases as more of B and C form.
b. The time required for one-half of substance A to react is directly proportional to the quantity of A present initially.

Q16.

One of the following statements is true and the other is false regarding the first-order reaction $4\,\mathrm{A} \rightarrow \mathrm{B}+\mathrm{C}$. Identify the true statement and the false one, and explain your reasoning.

a. A graph of $[\mathrm{A}]$ versus time is a straight line.
b. The rate of the reaction is one half the rate of disappearance of A.

Q33.

The reaction $\mathrm{A}+\mathrm{B} \rightarrow \mathrm{C}+\mathrm{D}$ is second order in A and zero order in B. The value of k is 0.0107 M^{-1} min^{-1}. What is the rate of this reaction when $[\mathrm{A}]=0.106\,\mathrm{M}$ and $[\mathrm{B}]=3.73\,\mathrm{M}$?

Q34.

A reaction 50% complete in 40.0 min. How long is the start will the reaction by 75% complete if it is (a) first order (b) zero order?

Q35.

The decomposition of $\mathrm{HI}\,(\mathrm{g})$ at 500K is followed for 00s, yielding the following data; at $\mathrm{t}=0$, $[\mathrm{HI}]=1.00\,\mathrm{M}$; at $\mathrm{t}=125\,\mathrm{s}$, $[\mathrm{HI}]=0.90\,\mathrm{M}$; at $\mathrm{t}=250\,\mathrm{s}$, $[\mathrm{HI}]=0.81\,\mathrm{M}$; $\mathrm{t}=375\,\mathrm{s}$, $[\mathrm{HI}]=0.74\,\mathrm{M}$; at $\mathrm{t}=500\,\mathrm{s}$, $[\mathrm{HI}]=0.68\,\mathrm{M}$. What are the reaction order and the rate constant for the reaction:

$$\mathrm{HI(g)} \rightarrow \frac{1}{2}\mathrm{H_2(g)}+\frac{1}{2}\mathrm{I_2(g)}$$

Write the rate law for the reaction at 500 K.

Q36.

For the disproportionation of p-toluenesulfinic acid,

$$3\,\mathrm{ArSO_2H} \rightarrow \mathrm{ArSO_2SAr}+\mathrm{ArSO_3H}+\mathrm{H_2O}$$

(where $\mathrm{Ar}=\mathrm{p\text{-}CH_3C_6H_4}$), the following data were obtained: $\mathrm{t}=0\,\mathrm{min}$, $[\mathrm{ArSO_2H}]=0.140\,\mathrm{M}$; $15\ \mathrm{min}, 0 \cdot 0965\ \mathrm{M}$; $30\ \mathrm{min}, 0 \cdot 0852\ \mathrm{M}$, $45\ \mathrm{min}, 0 \cdot 0740\ \mathrm{M}$; $60\ \mathrm{min}, 0 \cdot 0668\ \mathrm{M}$; $120\ \mathrm{min}, 0 \cdot 0493\ \mathrm{M}$; $180\ \mathrm{min}, 0 \cdot 0365\ \mathrm{M}$; $300\ \mathrm{min}, 0 \cdot 0196\ \mathrm{M}$.

a. Show that this reaction is second order
b. What is the value of the rate constant, k?
c. At what time would $[\mathrm{ArSO_2H}]=0.0600\,\mathrm{M}$?
d. At what time would $[\mathrm{ArSO_2H}]=0.0300\,\mathrm{M}$?
e. At what time would $[\mathrm{ArSO_2H}]=0.0150\,\mathrm{M}$?

Q45.

Explain why

a. A reaction rate cannot be calculated from solely the collision frequency.
b. The rate of a chemical reaction may increase dramatically with temperature, whereas the collision frequency rises a lot more slowly.
c. Introducing a catalyst to a reaction mixture can have such a significant impact on the rate of the reaction, even if the temperature is held constant.

Q46.

If even a small spark is introduced into a mixture of $H_2(g)$ and $O_2(g)$, a highly exothermic explosive reaction occurs. Without the spark, the mixture remains unreacted indefinitely.

a. Explain this difference in behavior.
b. Why is the nature of the reaction independent of the size of the spark?

Q47.

For the reversible reaction $A + B \leftrightarrow A + B$ the enthalpy change of the forward reaction is +11 kj/mol. The activation energy of the forward reaction is 74 kj/mol.

A + B ßàA + B

What is the activation energy for the reverse reaction?

Q48.

By an appropriate draft, indicate why there is some relationship between the enthalpy change of the activation energy for an endothermic reaction but not for the endothermic reaction.

exothermic?

Q59.

The following statements about catalysis are not stated completely correct. What slight changes would you make to them?

a. A catalyst is a substance that speeds up a chemical reaction but does not take part in the reaction.
b. The function of a catalyst is to lower the activation energy allowed for a chemical reaction.

Q60.

The following substrate's concentration $[S]$ versus time data were obtained during an enzyme-catalyzed reaction: $t = 0\ min$; $[S] = 1.00\ M$; $30\ min, 0.90\ M$; $90\ min, 0.70\ M$; $120\ min, 0.50\ M$; $180\ min, 0.20\ M$. What order is this reaction with respect to S in the concentration

Chapter 24: Chemical Kinetics

4. In the reaction A àproducts, at t = 0 [A]=0.1563M. After 1.00 minute, [A]=0.1496, and after 2.00 minutes [A]=0.1431M.

a. Calculate the average rate of reaction during the first minute and during the second minute.

First minute: -.0067Mmin^{-1}

Second minute: -.0065Mmin^{-1}

b. Why are these two rates not equal?

Since the reaction is not a zero order reaction, the rate of reaction changes as time passes.

5. In the reaction A àproducts, 4.50 minutes after the reaction is started, [A]=0.587M. The rate of reaction at this point is rate = -Δ[A]/Δt = 2.1 x 10^{-2} M min^{-1}. Assume that this rate remains constant for a short period of time.

a) What is [A] 6.00 minutes after the reaction is started?

.6185 = [A] @ 6 minutes

b) At what time after the reaction is started with [A] = 0.56M?

time = 3.21 minutes

7. For the reaction A + 2B à2C, the rate of reaction is 1.75 x 10^{-5}M s^{-1} at the time when [A] = 0.3575M.

a)What is the rate of formation of C?

3.5 x 10^{-5} Msec^{-1}

b) What will [A] be 1 minute later?

[A] = .35645M @ 1 minute

c) Assume the rate remains at 1.75 x 10^{-5}M s^{-1}. How long would it take for [A] to change from 0.3580 to 0.3500M

time = 428.5 seconds

10.At 65°, the half-life for the first-order decomposition of N_2O_5(g) is 2.35 minutes.

N_20_5(g) à2NO_2(g) + ½0_2(g)

If 1.00g of N_20_5 is introduces into an evacuated 10L flask at 65°C,

a) What is the initial partial pressure, in mmHg, of N_20_5(g)?

b) What is the initial partial pressure, in mmHg, of N_20_5(g) after 2.35 minutes?

c) What is the total gas pressure, in mmHg, after 2.35 minutes?

11. The initial rate of the reaction A + B àC + D is determined for different initial conditions, with the results listed in the table.

a) What is the order of reaction with respect to A and to B?

[A]^x ; x = 1st order

[B]^y; y = 2nd order

b) What is the overall reaction order?

3

c) What is the value of the rate constant, k?

k = .087 M^{2}s

Expt	[A],M	[B],M	Initial Rate, M s^{-1}
1	0.185	0.144	3.35 x 10^{-4}
2	0.185	0.288	1.35 x 10^{-3}
3	0.370	0.144	6.75 x 10^{-4}
4	0.370	0.288	2.70 x 10^{-3}

Q12

For the reaction A + B àC+ D the following initial rate of reaction were found. What is the rate law for this reaction?

Rate = 2.16 x 10^{-3}M^{2}min[A]^1[B]^2

Expt	[A],M	[B],M	Initial Rate, M min^{-1}
1	0.60	1.80	4.2 x 10^{-3}
2	1.80	1.80	1.3 x 10^{-2}
3	0.60	3.60	1.7 x 10^{-2}

Q13

The following rates of reaction were obtained in three experiments with the reaction 2NO(g) + Cl_2(g) à2NOCl (g).

Expt	Initial [NO], M	Initial [Cl_2], M	Initial Rate of Reaction, M s^{-1}
1	0.0125	0.0255	2.23 x 10^{-5}
2	0.0125	0.0510	4.46 x 10^{-5}

Expt	Initial [NO], M	Initial [Cl_2], M	Initial Rate of Reaction, M s^{-1}
3	0.0250	0.0255	8.92 x 10^{-5}

What is the rate law of this reaction?

Rate = 5.597 M^2sec$[NO]^2[Cl_2]^1$

14. The following was obtained for the initial rates of reaction in the reaction A + 2B + C à2D + E.

Expt	Initial [A],M	Initial [B],M	[C], M	Initial Rate
1	1.20	1.20	1.00	R_1
2	0.60	1.20	1.00	R_2= ½ x R_1
3	0.60	0.60	1.00	R_3 = ¼ x R_2
4	1.20	1.20	0.50	R_4 = 16 x R_3
5	0.60	0.60	0.50	R_5 = ?

a) What are the reaction orders with respect to A, B, and C?

[A] = 1st order

[B] = 2nd order

[C] = 1st order

b) What is the value of R_5 in terms of R_1?

R_5 = ½ R_1

15. One of the following statements is true and the other is false regarding the first-order reaction A àB + C. Identify the true statement and the false one, and explain your reasoning.

(a) The rate of the reaction decreases as more of B and C form.

True: Since rate = k$[A]^1$; if [A] decreases, the rate will drop.

(b) The time required for one-half of substance A to react directly proportional to the quantity of A present initially.

False: Since rate = k$[A]^1$; as the [A] drops, the reaction rate becomes disproportional to the concentration. Reaction starts fast at high concentrations but will slow down at low [A]

16. One of the following statements is true and the other is false regarding the first-order reaction 2A àB + C. Identify the true statement and the false one, and explain your reasoning.

(a) A graph of [A] versus time is a straight line.

False: Since rate=k$[A]^1$; as [A] decreases, time and concentration become disproportional and graph will curve.

(b) The rate of the reaction is one half the rate of disappearance of A.

True: Since rate is dependent on balanced coefficients. [A] is actually twice the amount in rate = k[A]

33. The reaction A + B àC + D is second order in A and zero order in B. The value of k is 0.0107 M^{-1} min^{-1}. What is the rate of this reaction when [A] and = 0.106 M and [B] = 3.73 M?

Rate = 1.2 x 10^{-5} $M^{-1}min^{-1}$

34. A reaction 50% complete in 40.0 min. How long is the start will the reaction by 75% complete if it is (a) first order (b) zero order?

(a) Cannot be determined without concentration of reactant(s)

(b) 60 minutes

35. The decomposition of HI(g) at 500K is followed for 500s, yielding the following data; at t = 0 [HI] = 1.00 M; at t =125 s, [HI] = 0.90M; at t = 250s, [HI] = 0.81M; t = 375s, [HI] = 0.74M; at t = 500s, [HI] = 0.68M. What are the reaction order and the rate constant for the reaction:

HI(g) à½ H_2(g) + ½ I_2(g)”

Write the rate law for the reaction at 500 K.

36. For the disproportionation of p-toluenesulfinic acid,

3ArSO_2H àAr SO_2SAr + ArSO_3H + $H_2$0

(where Ar = p-$CH_3C_6H_4$), the following data were obtained: t = 0 min, [ArSO_2H] = 0.140 M; 15 min, 0.0965 M; 30 min, 0.0852 M, 45 min, 0.0740 M; 60 min, 0.0668 M; 120 min, 0.0493 M; 180 min, 0.0365 M; 300 min, 0.0196 M.

(a) Show that this reaction is second order

(b) What is the value of the rate constant, k?

(c) At what time would [ArSO_2H] = 0.0600M?

(d) At what time would [ArSO_2H] = 0.0300M?

(e) At what time would [ArSO_2H] = 0.0150M?

45. Explain why

(a) A reaction rate cannot be calculated from the solely collision frequency.

Collision Frequency does not solely determine the rate of the reaction because in order to overcome the activation energy to react, temperature and concentrations will also dictate the rate of the reaction.

(b) The rate of a chemical reaction may increase dramatically with temperature, whereas the collision frequency rises a lot more slowly.

A rise in temperature results in higher kinetic energies in the molecules thus increasing the % chance of colliding AND reacting rather than colliding and staying inert. Having a steady collision frequency with higher kinetic energy will result in spiked rates of reactions.

(c) Introducing a catalyst to a reaction mixture can have such a significant impact on the rate of the reaction, even if the temperature is held constant.

Catalysts induce reactants to react with one another by lowering the activation energy of the chemical reaction. This can be done without any sort of flux in the enthalpy of the system.

46. If even a small spark is introduced into a mixture of H_2(g) and O_2(g) a highly exothermic explosive reaction occurs. Without the spark, the mixture remains unreacted indefinitely.

(a) Explain this difference in behavior.

Without a super increase in the temperature which acts as a sort of catalyst, the lone diatomics do not possess the energy to overcome the activation barrier.

(b) Why is the nature of the reaction independent of the size of the spark?

Once a single reaction occurs, it independently releases more heat which in turn passes on kinetic energy to its neighboring atoms resulting in a exponential chain reaction.

47. For the reversible reaction A + B ßàAB the enthalpy change of the forward reaction is +11 kj/mol. The activation energy of the forward reaction is 74 kj/mol. What is the activation energy for the reverse reaction? **63 kJ/mol**

59. The following statements about catalysis are not stated completely correct. What slight changes would you make to them?

(a) A catalyst is a substance that speeds up a chemical reaction but does not take part in the reaction.

A catalyst is a substance that speeds up a chemical reaction but does get consumed in the reaction.

(b) The function of a catalyst is to lower the activation energy allowed for a chemical reaction.

The function of a catalyst is to lower the activation energy needed for a chemical reaction.

60. The following substrates concentration [S] versus time date were obtained during an enzyme-catalyzed reaction: t = 0 min; [S] = 1.00M; 30 min, 0.90M; 90 min, 0.70M; 120 min, 0.50M; 180 min, 0.20M. What order is this reaction with respect to S in the concentratio

Q1.

For the reaction $3A + 2B \rightarrow C + 2D$ reactant A is found to disappear at the rate of 4.6 X 10^{-5} Ms^{-1}

a. What is the rate of reaction?
b. What is the rate of disappearance of the reactant B?
c. What is the rate of appearance for product D?

S1.

a. $-\frac{1}{3}\left(\frac{-\Delta[A]}{\Delta t}\right) = \frac{1}{3}(4.6 \times 10^{-5}\ Ms^{-1}) = 1.5 \times 10^{-5}\ Ms^{-1}$

b. Rate disappearance of $B = (\text{rate of reaction}) \times 2(\text{coefficient of B})$
$(1.5 \times 10^{-5}\ Ms^{-1})(2) = 3.1 \times 10^{-5}\ Ms^{-1}$

c. Same process as B) (multiply rate of reaction by 2) OR:
$\text{Rate of appearance of D} = -\frac{1}{3}(2)\left(\frac{\Delta[A]}{\Delta t}\right) = -\frac{2}{3}(4.6 \times 10^{-5}\ Ms^{-1}) = 3.1 \times 10^{-5}\ Ms^{-1}$

Q3.

In the reaction $A \rightarrow B$, $[A]$ is found to be 0.675M at $t = 51.1\ s$ and 0.605M at $t = 61.5\ s$. Find the average rate of the reaction during this time interval.

S3.

$$\text{Rate} = -\left(\frac{\Delta[A]}{\Delta t}\right) = \frac{0.675\ M - 0.605\ M}{61.5\ s - 51.1\ s} = 0.00673 = 6.73 \times 10^{-3}\ Ms^{-1}$$

Q11.

The initial rate of the reaction $A + B \rightarrow C + D$ is determined for difference initial conditions, with the results listed in the table:

Expt	**[A], M**	**[B], M**	**Initial Rates, Ms^{-1}**
1	.241	.153	1.261 X 10^{-4}
2	.241	.306	5.044 X 10^{-4}
3	.482	.153	2.522 X 10^{-4}
4	.482	.306	6.741 X 10^{-4}

a. What is the order of the reaction with respect to A and B? Write out respective rate laws for A and B
b. What is the overall reaction order?
c. What is the value of the k, the rate constant?

S11.

a. m and n are the respective orders according to A and B:
$R1 = 1.261 \times 10^{-4} = [0.241]^m[0.153]^n$
$R2 = 5.044 \times 10^{-4} = [0.241]^m[0.306]^n$
$R3 = 2.522 \times 10^{-4} = [0.482]^m[0.153]^n$
$R4 = 6.741 \times 10^{-4} = [0.482]^m[0.306]^n$
Now utilize the rate laws / solve:
Divide reaction 2 by reaction 1 (A is constant B changes concentration)
$$\frac{R2}{R1} = \frac{5.044 \times 10^{-4}}{1.261 \times 10^{-4}} = \frac{[0.241]^m[0.306]^n}{[0.241]^m[0.151]^n}$$

$$\frac{\mathrm{R2}}{\mathrm{R1}} = 4 = 2^{\mathrm{n}}$$
$\mathrm{n} = 2$

Reaction is second order with respect to B. Do the same for A. Use reactions 3 and 1 ($[\mathrm{B}]$ is constant, $[\mathrm{A}]$ changes)

$$\frac{\mathrm{R3}}{\mathrm{R1}} = \frac{2.522 \times 10^{-4}}{1.26 \times 10^{-4}} = \frac{[0.482]^{\mathrm{m}}[0.153]^{\mathrm{n}}}{[0.241]^{\mathrm{m}}[0.153]^{\mathrm{n}}}$$
$$\frac{\mathrm{R3}}{\mathrm{R1}} = 2 = 2^{\mathrm{m}}$$
$\mathrm{m} = 1$

Reaction is first order with respect to A

b. Overall reaction order = (reaction order of A + reaction order of B) = 1 + 2 = 3rder order overall

c. Substitute in for one of the reactions

$\text{Rate law} = \mathrm{k}[\mathrm{A}][\mathrm{B}]^2$

For example use reaction 1

Rate: $1.261 \times 10^{-4} = \mathrm{k}[\mathrm{A}][\mathrm{B}]^2$

$1.261 \times 10^{-4} = \mathrm{k}[0.241][0.153]^2$

$\mathrm{k} = 0.0224\,\mathrm{M}^{-2}\mathrm{s}^{-1}$

Q13.

The following rates of reactions were obtained in three experiments with the reaction $2\,\mathrm{NO(g)} + \mathrm{Cl_2} \rightarrow 2\,\mathrm{NOCl(g)}$

Expt	**Initial $[\mathrm{NO}]$, M**	**Initial $[\mathrm{Cl_2}]$, M**	**Initial Rate of reaction Ms^{-1}**
1	.362	.730	1.45 X 10 ^-5
2	.362	1.46	2.90 X 10^-5
3	.724	.730	5.80 X 10^-5

What is the order of the reaction with respect of A and B? Write out respective rate laws for A and B

S13.

m and n are the respective orders according to A and B:

$$\mathrm{R1} = 1.45 \times 10^{-5} = [0.362]^{\mathrm{m}}[0.730]^{\mathrm{n}}$$

$$\mathrm{R2} = 2.90 \times 10^{-5} = [0.362]^{\mathrm{m}}[1.46]^{\mathrm{n}}$$

$$\mathrm{R3} = 5.80 \times 10^{-5} = [0.724]^{\mathrm{m}}[0.730]^{\mathrm{n}}$$

Now utilize the rate laws and solve:

Divide R2 by R1 ($[\mathrm{A}]$ stays constant while $[\mathrm{Cl_2}]$ changes)

$$\frac{\mathrm{R2}}{\mathrm{R1}} = \frac{2.9 \times 10^{-5}}{1.45 \times 10^{-5}} = \frac{[0.362]^{\mathrm{m}}[1.46]^{\mathrm{n}}}{[0.362]^{\mathrm{m}}[0.730]^{\mathrm{n}}}$$

$$\frac{\mathrm{R2}}{\mathrm{R1}} = 2 = 2^{\mathrm{n}}$$

$\mathrm{n} = 1$

First order with respect to $\mathrm{Cl_2}$

Divide R3 by R1 ($[\mathrm{Cl_2}]$ is constant $[\mathrm{NO}]$ changes)

$$\frac{\mathrm{R3}}{\mathrm{R1}} = \frac{5.8 \times 10^{-5}}{1.45 \times 10^{-5}} = \frac{[0.724]^{\mathrm{m}}[0.730]^{\mathrm{n}}}{[0.362]^{\mathrm{m}}[0.730]^{\mathrm{n}}}$$

$$\frac{\mathrm{R3}}{\mathrm{R1}} = 4 = 2^{\mathrm{m}}$$

$\mathrm{n} = 2$

Second order with respect to $[\mathrm{NO}]$

$\mathrm{Rate\ Law} = \mathrm{k[NO]^2[Cl_2]}$

Using the rate law we can solve for k, the rate constant

Use any set of experimental data

Lets use exp. 2

$2.9 \times 10^{-5}\ \mathrm{Ms^{-1}} = \mathrm{k[NO]^2[Cl_2]} = \mathrm{k}[0.362]^2[1.46]$

$\mathrm{k} = 1.52 \times 10^{-4}\ \mathrm{M^{-2}s^{-1}[NO]^2[Cl_2]}$

Q17.

The first order reaction has $t_{1/2}$ of 250s

a. What percent of a sample of A remains unreacted 1500s after a reaction starts.
b. What if the rate of the reaction is 1/2 the rate of disappearance of A.

S17.

a. $\mathrm{k} = \dfrac{\ln 2}{\mathrm{t_{1/2}}} = \dfrac{0.693}{250\ \mathrm{s}} = 0.00277\ \mathrm{s^{-1}}$

$$\begin{aligned} \ln(\%\ \mathrm{unreacted}) &= -\mathrm{kt} \tag{4.9.1}\\ &= (-.00277\ \mathrm{s^{-1}})(1500\ \mathrm{s}) = -4.155 \tag{4.9.2}\end{aligned}$$

$\%\ \mathrm{unreacted} = 0.0157 \times 100\% = 1.57\%\ \mathrm{of\ the\ original\ quantity}$

b. $\mathrm{Rate} = \mathrm{k[A]} = 0.00277\ \mathrm{s^{-1}})(0.5\ \mathrm{M}) = 0.00139\ \mathrm{M/s}$

Q19.

The reaction A to product is first order in A.

a. If 2.4 g of A is allowed to decompose for 30 minutes, the mass of A remaining undecomposed is found to be .6g. What is the halflife, $t_{1/2}$, of this reaction.
b. Starting with 2.4g of A what is the mass of A remaining undecomposed after 1 hour

S19.

a. Mass has decreased to 1/4 of the original mass. Since $\left(\dfrac{1}{2}\right)\left(\dfrac{1}{2}\right) = \dfrac{1}{4}$. 2 halflives have elapsed. As a result

$2 \times \mathrm{t_{1/2}} = 30\ \mathrm{minutes}$
$\mathrm{t_{1/2}} = 15\ \mathrm{minutes}$

b. $\mathrm{k} = \dfrac{0.693}{15\ \mathrm{minutes}} = 0.0462\ \mathrm{min^{-1}}$

Use equation $\dfrac{\ln[\mathrm{A}]_\mathrm{t}}{\ln[\mathrm{A}]_0} = -\mathrm{kt}$

$\dfrac{\ln[\mathrm{A}]_\mathrm{t}}{\ln[\mathrm{A}]_0} = (-0.0462\ \mathrm{min^{-1}})(60\ \mathrm{min}) = -2.8$

$\dfrac{[\mathrm{A}]_\mathrm{t}}{[\mathrm{A}]_0} = \mathrm{e}^{-2.8}$

$[\mathrm{A}]_\mathrm{t} = [\mathrm{A}]_0\mathrm{e}^{-2.8}$

$[\mathrm{A}]_\mathrm{t} = (2.4\ \mathrm{g})(\mathrm{e}^{-2.8}) = 0.146\ \mathrm{g\ A}$

Q21.

In the first order reaction $\mathrm{D} \rightarrow \mathrm{products}$ it is found that 90% of the original amount of reactant D decomposes in 140 minutes. Find the half life of the decomposition reaction.

S21.

Use the equation. $\frac{\ln[A]_t}{\ln[A]_0} = -kt$

$100\% - 90\% = 10\%\text{ left}$

$\frac{\ln[0.1]}{1.00} = -k(140\text{ min})\ k = 0.0164\text{ min}^{-1}$

$\text{Half life} = \frac{\ln(2)}{0.0164} = 42.3\text{ min}$

Q23.

Acetoacetic acid, $CH_3COCH_2COOH(aq)$, a reagent used in organic synthesis, decomposes in acidic solution, producing acetone and carbon dioxide gas: $CH_3COCH_2COOH(aq) \rightarrow CH_3COCH_3(aq) + CO_2(g)$

This is a first-order decomposition with a halflife of 144 minutes.

How long with it take for a sample of acetoacetic acid to be 55% decomposed?

S23.

Start with the decomposed $= 100\% - 55\% = 45\%$ decomposed

$$\ln\frac{\frac{45}{100}[A]_0}{[A]_0} = \ln 0.45 = -kt$$

Find the value of $k \rightarrow k = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{144\text{ minutes}} = 0.00481\text{ min}^{-1}$

Plug the k value back in

$\ln 0.45 = (-0.00481\text{ min}^{-1})(t)$

$t = 166\text{ seconds}$

Q27.

Which sets of data correspond to a:

a. Zero order reaction
b. First order reaction
c. Second order reaction

I		**II**		**III**	
Time(s)	[A], **M**	**Time(s)**	[B], **M**	**Time(s)**	[C], **M**
25	1	0	5	0	2.23
50	.85	25	2.5	25	1.82
75	.70	50	1.67	50	1.49
100	.55	75	1.25	75	1.21
125	.40	100	1	-	-
150	.25	-	-	-	-
200	.10	-	-	-	-

S27.

Graph out each graph for:

1) Concentration vs Time

2) ln(Concentration) vs Time

3) $\frac{1}{\text{Concentration}}$ vs Time

Whichever one gives a straight linear line will correlate with the correct order of the reaction:

If Concentration vs Time straight: Zero Order

If ln(Concentration) vs Time straight: First Order

If $\frac{1}{\text{Concentration}}$ vs Time straight: Second Order

The correct graphs are shown below for each set of data points provided:

I:

II:

III:

Q29.

What is the approximate half life of the first order reaction?

S29.

Set III is first order. We can analyze the data points to get the half life. Since at the 100 second time period, the concentration decreased by a little more than half. Around 70 seconds. We can obtain a more accurate half life by obtaining a value for k from the relation of $\ln \frac{[\mathrm{A}]_\mathrm{t}}{[\mathrm{A}]_0} = -\mathrm{kt}$ and $\mathrm{t}_{1/2} = \frac{0.693}{\mathrm{k}}$

$$\ln \frac{0.77}{100} = -\mathrm{k}(25\ \mathrm{s})$$

$$\mathrm{k} = 9.92 \times 10^{-3}\ \mathrm{s}^{-1}$$

thus $\mathrm{t}_{1/2} = \frac{0.693}{9.92 \times 10^{-3}\ \mathrm{s}^{-1}} = \text{around } 70 \text{ seconds}$.

Q33.

The reaction $\mathrm{A} + \mathrm{B} \rightarrow \mathrm{C} + \mathrm{D}$ is second order and first order with respect to B. The value of k is .0351 M^-1min^-1. What is the rate of this reaction when $[\mathrm{A}] = 0.120\ \mathrm{M}$ and $[\mathrm{B}] = 4.6\ \mathrm{M}$?

S33.

Simply substitute in the values for the rate equation to get the rate of reaction:

$$\mathrm{Rate} = \mathrm{k}[\mathrm{A}]^2[\mathrm{B}] = (0.0351\ \mathrm{M}^{-1}\mathrm{min}^{-1})[0.12]^2[4.6] = 0.0023\ \mathrm{M/min}$$

Q35.

The decomposition of $\mathrm{HF(g)}$ at 750 degrees kelvin is followed for 500s, yielding the following data: at t:0 $[\mathrm{HF}] = 1.05$ M. t:100s $[\mathrm{HF}] = 1.25$ M. t: 200s $[\mathrm{HF}] = 1.54$ M. t=300s $[\mathrm{HF}] = 2$ M.

What are the reaction order and the rate constant for the reaction? $\mathrm{HF(g)} \rightarrow \frac{1}{2}\mathrm{H_2(g)} + \frac{1}{2}\mathrm{F_2(g)}$

Write the rate law for the reaction at 750 degrees K.

S35.

Make a table as follows:

Time(s)	$[\mathrm{HF}]$**, M**	**ln** $[\mathrm{HF}]$	$\frac{1}{[\mathrm{HF}]}$**, M^-1**
0	1.05	.049	.95
100	1.25	.223	.80
200	1.54	.432	.65
300	2	.693	.50

From the above data, plot time vs $[\mathrm{HF}]$, $\ln[\mathrm{HF}]$, and $\frac{1}{[\mathrm{HF}]}$. Which ever one gives a straight linear line with a positive slope is the correct corresponding order.

If Concentration vs Time straight: Zero Order

If ln(Concentration) vs Time straight: First Order

If $\frac{1}{\text{Concentration}}$ vs Time straight: Second Order

$\frac{1}{[\mathrm{HF}]}$. Which ever one gives a straight linear line with a positive slope is the correct corresponding order. will provide a straight line with a positive slope. The decomposition of From the above data, plot time vs $[\mathrm{HF}]$ is a ***<u>second order reaction.</u>***

Zero order?

First order?

Second order:

In order to calculate the value of k, the rate constant, you must find the slope of the line:

$$\frac{2\,\mathrm{M}-1.05\,\mathrm{M}}{300\,\mathrm{s}-0\,\mathrm{s}}=0.0032\ \mathrm{M^{-1}s^{-1}}$$

Rate law: $0.0032\ \mathrm{M^{-1}s^{-1}}\ [\mathrm{HF}]$

Q37.

For the reaction $\mathrm{F}\rightarrow\mathrm{products}$, the following data was obtained. $\mathrm{t}=0\,\mathrm{s}$ $[\mathrm{F}]=0.79\,\mathrm{M}$, $\mathrm{t}=50\,\mathrm{s}$ $[\mathrm{F}]=0.67\,\mathrm{M}$, $\mathrm{t}=100\,\mathrm{s}$ $[\mathrm{F}]=0.55\,\mathrm{M}$, $\mathrm{t}=150\,\mathrm{s}$ $[\mathrm{F}]=0.43\,\mathrm{M}$

a. Find the order of the reaction
b. Find the half life of the reaction

S37.

a. Make a table like the following:

Time(s)	$[\mathbf{F}]$, M	$\ln[\mathbf{F}]$

			$\frac{1}{[F]}$, M^-1
0	.790	.236	1.26
50	.670	.400	1.49
100	.550	.598	1.82
150	.430	.844	2.33

For this reaction $[\mathrm{F}]$ is decreasing consistantly .12M overtime. Plot $[\mathrm{A}]$, M versus time(s), $\ln[\mathrm{F}]$ versus time(s) and $\frac{1}{[\mathrm{F}]}$ versus time(s).

Only $[\mathrm{F}]$ versus time will gve a straight line with a negative slope: ***<u>Zero order reaction</u>***

Zero order:

First order?:

Second order?:

b. The half life will need one half of the initial $[\mathrm{F}]$ to react

$$\Delta[\mathrm{F}]=\frac{0.79\,\mathrm{M}}{2}=0.395\,\mathrm{M}\text{ and }\mathrm{t}_{1/2}=\frac{0.395\,\mathrm{M}}{\text{Slope}}$$

$$\text{Slope} = \frac{0.430\,\text{M} - 0.790\,\text{M}}{150\,\text{s} - 0\,\text{s}} = 0.0024\,\text{M}^{-1}\text{s}^{-1}$$

Plug the rate constant k back into the half life equation:

$$t_{1/2} = \frac{0.395\,\text{M}}{-0.0024} = 165 \text{ seconds}$$

Q43.

Although initially the rate laws of first order and second order reactions may seem similar, they are also very different. Write out the equations of the two half life equations and explain why the situation aren't the same for two different reactions rates.

S43.

First Order: $t_{1/2} = \frac{0.693}{k}$

Second order: $t_{1/2} = \frac{1}{[A]_0 k}$

Based on the formula, a first order reaction's half-life stays constant and this depends on the value of the rate constant, k. A second order reaction on the other hand has a half-life that fluctuates and varies inversely proportional to $[A]_0$. As $[A]_0$ increase, the half-life decreases. In a second order reaction the rate of reaction increases as the $[A]$ does and so the higher the concentration of initial A, the higher the rate, and the lower the concentration the lower the rate of reaction. For a reaction order of one, all that is taken into account if the value of the rate constant, k. This means that the half-life of this order is constant and will not depend on the concentration of initial A.

Q45.

Explain why:

a. Even though the necessary components collide together, a reaction may not occur
b. The addition of a catalyst doesn't cause it to be included in the chemical equation.
c. Temperature increases the rate of a chemical reaction.

S45.

a. This is due to the fact that rates of a reaction depend on at least two factors other than the frequency of collisions. One of the most important aspects is whether of the not the collisions have enough energy to get over the energy barriers to the products. The higher the activation energy, the less frequencies of the collisions being energetic enough. Second of all the molecules in a given collision have to be orientated in a certain way. The more complex the molecules are, the more motion the molecules can have. This will result in a lower fraction o the collisions being correctly orientated.
b. Addition of a catalyst merely speeds up the reaction due to the lowering of the activation energy. It enables an alternate mechanism. The lower activation energy will mean a larger fraction of the molecules having the sufficient energy to react (leading to increased r
c. This is due to the increase frequency of the collisions(more chances of a reaction occurring). In addition, the molecules collide with more force and is able to overcome the activation energy necessary for the process to proceed.

Q47.

For the reversible reaction $A + B \leftrightarrow A + B$ the enthalpy change of the forward reaction is +20kj/mol. The activation energy of the forward reaction is 84 kj/mol.

a. What is the activation energy of the reverse reaction?
b. Sketch the reaction plot for this reaction

S47.

a. The products are 20kj/mol closer in energy to the energy activated complex than that of the reactants(the activation energy of the reverse):
   $84\text{ jk/mol} - 20\text{ kj/mol} = 64\text{ kj/mol}$
b.

Q49.

a. How many intermediates are there in this reaction?
b. How many transition states are there?
c. What is the fastest step?
d. Is the reaction exothermic or endothermic?
e. Is the second step exothermic or endothermic?
f. What is the slowest step?

S49.

a. 4
b. There are 5 peaks/min max: 5
c. E has the lowest activation energy required
d. Endothermic reaction absorbs energy from A-F
e. Endothermic
f. First step, the activation energy is the highest

Q51.

The rate constant for the reaction $\mathrm{H_2(g) + F_2(g) \rightarrow 2\,HF}$ has been determined at the following temperatures 650 degrees k, $\mathrm{k = 4.8 \times 10^{-4}\ M^{-1}s^{-1}}$; 700 degrees K, $\mathrm{k = 3.0 \times 10^{-2}\ M^{-1}s^{-1}}$. Calculate the activation energy for the reaction.

S51.

Use the Arrhenius equation:

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) = \ln \frac{4.80 \times 10^{-4}\ \mathrm{M^{-1}s^{-1}}}{3.00 \times 10^{-2}\ \mathrm{M^{-1}s^{-1}}} = \frac{E_a}{R}\left(\frac{1}{700\mathrm{K}} - \frac{1}{650\mathrm{K}}\right)$$

$$(E_a)(-1.099 \times 10^{-4}) = -4.135R \quad R = 8.314\ \mathrm{j/(mol\ k)}$$

$$\mathrm{E_a} = \frac{(-4.135)(8.314\ \mathrm{J/(mol\ k)})}{-1.099 \times 10^{-4}} = 313\ \mathrm{kj/mol}$$

Q59.

True or false? Modify the statement so it is more accurate:

a. Catalysts speed up a reaction Describe what a catalyst is
b. Catalysts remain part of the overall equation

S59.

a. True; Catalysts are able to speed up a reaction. They lower the activation energy and let the reaction proceed at a lower energy level. Not all catalyst quickens a reaction. Some catalysts, called inhibitors, actually slow down the rate of reaction.
b. False. Although catalysts are part of the reaction, they are not part of the chemical equation. It "takes part" in the reaction but is only there to change the mechanism of a reaction. Catalysts are not included in the equation, they only change the activation energy.

Q61.

What are the similarities and differences between the catalytic activity and properties of an enzyme and that of a metal such as platinum or other metallic catalyst or ever activated carbon?

S61.

Platinum and enzymes both have a center that acts as the active site where reactions occur. There are two types of catalysts: heterogeneous and homogenous. While platinum(hetero) doesn't dissolve into the mixture, enzymes(homo) are usually soluable. The most important aspect that enzymes are very specific while platinum catalyzes almost everything. Enzymes have certain configurations and shapes that are unique to each one. They will only catalyze certain reactions if it is is the correct one.

Q63.

Describe the effect of enzyme concentration on the rate of the enzyme reaction. What effect is going on?

GRAPH:

S63.

Although enzyme concentration increase resulted in an increase in reaction initially, the increase leveled out eventually. This is due to the fact that substrate may be running out. The leveling off shows that the reactions are at their maximum capacity upon the catalyst. This may be due to the limited amount of the substrate.

Q67.

The reaction $2\mathrm{A} + 2\mathrm{B} \leftrightarrow 2\mathrm{C} + 2\mathrm{D}$ is second order in respect to $[\mathrm{A}]$ and first order in respect to $[\mathrm{B}]$. A three step mechanism has been proposed. The third fast step is the $\text{second intermediate} + \mathrm{B} \rightarrow 2\mathrm{C} + \mathrm{D}$. The first step is $2\mathrm{A} \rightarrow \text{first intermediate}$. Propose an entire three step mechanism to show that it conforms to experimentally determined reaction order.

S67.

Write out the proposed three set of reactions:

1. $\mathrm{2A \leftrightarrow Intermediate\ 1 \quad (Fast)}$
2. Unknown (Slow)
3. $\mathrm{Intermediate\ 2 + B \rightarrow C + D \quad (Fast)}$

First: Find the rate law for this reaction: $\mathrm{Rate = k[A]^m[B]^n}$

m=2nd order n=1st order

as a result: $\mathrm{Rate = k[A]^2[B]^1}$

Consider the three equations and calculate step 2:

1. $\mathrm{2A \leftrightarrow Intermediate\ 1 \quad (Fast)}$
2. $\mathrm{Intermediate\ 1 + B \rightarrow D + Intermediate\ 2 \quad (Slow)}$
3. $\mathrm{Intermediate\ 2 + B \rightarrow C + D \quad (Fast)}$

Crossing out:

1. $\mathrm{2A \leftrightarrow \cancel{Intermediate\ 1} \quad (Fast)}$
2. $\mathrm{\cancel{Intermediate\ 1} + B \rightarrow D + \cancel{Intermediate\ 2} \quad (Slow)}$
3. $\mathrm{\cancel{Intermediate\ 2} + B \rightarrow C + D \quad (Fast)}$

$\mathrm{= 2A + 2B \leftrightarrow 2C + 2D}$

Through the concepts of mechanism and reactions, we know that the rate determining step is going to be the slowest one.

The rate law of reaction 1 is $\mathrm{Rate = k_1[A]^2}$

The rate law of reaction 2 is $\mathrm{Rate = k_2[B][I_1]}$

The rate law of reaction 3 is $\mathrm{Rate = k_3[B][I_2]}$

We can not have intermediates in our reaction rate law

Step 1 can also be written as $\mathrm{Rate = k_{-1}[I_1]}$

The two reaction 1 equations are equal, set them equal to each other:

$\mathrm{k_1[A]^2 = k_{-1}[I_1]}$

$\mathrm{[I_1] = \dfrac{k_1}{k_{-1}}[A]^2}$

let $\mathrm{\dfrac{k_1}{k_{-1}} = k}$

$\mathrm{[I_1] = k[A]^2}$

Substitute this back into the rate determining step. Combine the k value like the previous part of this problem

As a result, the rate $\mathrm{= k[A]^2[B]}$

note that this is the same as the original equation.

Q78.

For a second order reaction what are the units of k

$\mathrm{rate = \dfrac{-d[A]}{A} = k[A][A] = k[A]^2}$

S78.

=> k has units of M/sec

Q87.

Find the general rate law and the magnitude of k for the overall reaction.

1. $\mathrm{2\,(N_2O_5 \rightarrow NO_2 + NO_3)}$

2. $NO_2 \rightarrow NO_3 \rightarrow NO_2 + O_2 + NO$
3. $NO + NO_3 \rightarrow 2\,NO_2$

S87.

$2\,N_2O_5 + NO_2 + NO_3 + NO + NO_3 \rightarrow 2\,NO_2 + 2\,NO_3 + NO_2 + O_2 + NO + 2\,NO_2$
$\Rightarrow 2\,N_2O_5 \rightarrow 4\,NO_2 + O_2$ (overall reaction)

1. $NO + Br_2 \leftrightarrow NOBr_2$ [Fast, revers·]
2. $NOBr_2 + NO \rightarrow 2\,NOBr$ [Slow, RDS]

$$\Rightarrow \mathrm{Rate} = \mathrm{Rate}_2 = k_2[NO][NOBr_2]$$
$$\rightarrow \mathrm{Rate}_1 = \mathrm{Rate}_{-1} \rightarrow k_1[NO][Br_2] = k - 1[NOBr_2]$$
$$\rightarrow [NOBr_2] = \frac{k_1}{k_{-1}}[NO][Br_2]$$
$$\Rightarrow \mathrm{Rate} = k_2[NO][NOBr_2] = k_2[NO]\frac{k_1}{k_{-1}}[NO][Br_2]$$
$$\Rightarrow \mathrm{Rate} = \frac{k_2k_1}{k_{-1}}[NO]^2[Br_2] = k[NO]^2[Br_2]$$
$$\rightarrow \text{Experimental rate law: Rate} = k[NO]^2[Br_2]$$
$$\rightarrow \text{Consistent with the exp. rate law } (k = \frac{k_2k_1}{k_{-1}})$$

Q1

In the reaction $3\,A + B \rightarrow 3\,C + 3\,D$, A has a disappearance rate of 3.4×10^{-3} Ms^{-1}.

a. What is the rate of reaction at point A?
b. What is the rate of disappearance of B?
c. What is the rate of formation of C?

S1

For more help see: The Rate of a Chemical Reaction

a. $-\frac{1}{3}\left(-\frac{\Delta[A]}{\Delta t}\right) = \frac{1}{3}(3.4 \times 10^{-3}\ Ms^{-1}) = 1.13 \times 10^{-3}\ Ms^{-1}$
b. $\text{Rate of disappearance of B} = \text{reaction rate} \times \text{coefficient of B}$
$(1.13 \times 10^{-3}\ Ms^{-1})(1) = 1.13 \times 10^{-3}\ Ms^{-1}$
c. $\text{Rate of formation of C} = \text{reaction rate} \times \text{coefficient of C}$
$(1.13 \times 10^{-3}\ Ms^{-1})(2) = 2.26 \times 10^{-3}\ Ms^{-1}$

Q3.

What is the average rate of reaction over a time interval for $[A]$ if it is 0.455 M at $t = 80.25$ s and 0.474 M at $t = 82.4$ s?

S3.

For more help see: The Rate of a Chemical Reaction

$$-\frac{\Delta[A]}{\Delta t} = \frac{0.474\,M - 0.455\,M}{82.4\,s - 80.25\,s} = 8.8 \times 10^{-3}\ Ms^{-1}$$

Q11.

Use the table below to answer the following questions:

a. Find the order of the reaction A vs. B
b. Find the overall order
c. Find the rate constant

EXPT	$[A]$,M	$[B]$,M	Initial Rates, Ms^{-1}

EXPT	[A],M	[B],M	Initial Rates, Ms^{-1}
1	0.175	0.138	3.75×10^{-4}
2	0.175	0.185	1.25×10^{-3}
3	0.365	0.138	3.75×10^{-4}
4	0.365	0.185	1.25×10^{-3}

S11.

For more help see: The Rate of a Chemical Reaction

$\text{Reaction 1} = 3.75 \times 10^{-4} = k \times [0.175]^m[0.138]^n$

$\text{Reaction 2} = 1.25 \times 10^{-3} = k \times [0.175]^m[0.185]^n$

$\text{Reaction 3} = 3.75 \times 10^{-4} = k \times [0.365]^m[0.138]^n$

$\text{Reaction 4} = 1.25 \times 10^{-3} = k \times [0.365]^m[0.185]^n$

a. Order of reaction with respect to B:
   1. Find where A is constant and B changes (Reaction 1 and Reaction 2)
   2. Divide: $\frac{\text{Reaction 2}}{\text{Reaction 1}} = \frac{1.25 \times 10^{-3}}{3.75 \times 10^{-4}} = \frac{[0.175]^m[0.185]^n}{[0.175]^m[0.138]^n}$
   $\frac{\text{Reaction 2}}{\text{Reaction 1}} = 4 = 2^n \rightarrow n = 2$
   3. Therefore the reaction is second order with respect to B.

   Order of reaction with respect to A:
   1. Find where B is constant and A changes (Reaction 3 and Reaction 1)
   2. Divide: $\frac{\text{Reaction 3}}{\text{Reaction 1}} = \frac{4.41 \times 10^{-4}}{2.205 \times 10^{-4}} = \frac{[0.406]^m[0.662]^n}{[0.203]^m[0.662]^n}$
   $\frac{R3}{R1} = 2 = 2^m$
   $m = 1$
   3. Thus the reaction is first order with respect to A

b. $\text{Reaction order} = \text{reaction order of } A + \text{reaction order of } B = 3^{rd}$ order reaction

c. $2.205 \times 10^{-4} = k \times [0.331][0.203]^2$
   $k = 1.6 \times 10^{-2}$

Q13.

Use the date table below to determine the rate law of the reacton: $A + B \rightarrow 2\,D$

Experiment	Initial [A],M	Initial [B],M	Initial Rate of Reaction, Ms^{-1}
1	1.5	1.5	4.3×10^{-3}
2	1.5	3.0	8.6×10^{-3}
3	3.0	3.0	1.12×10^{-2}

S13.

For more help see: The Rate of a Chemical Reaction

From looking at the table, [A] is first order and [B] is first order

overall rxn is 2nd order

$R = k[A][B]$

$4.3\text{E-3 } Ms^{-1} = k(1.5\,M)(1.5\,M)$

$k = 1.2\text{E-3}\ (M^{-1})(s^{-1})$

Q17.

A first order reaction $A \rightarrow \text{products}$ has a half life of 120 seconds calculate the following:

a. What percentage of A remains unreacted after 800 seconds of reaction.
b. What is the rate of reaction at $[A] = 0.25\ M$?

S17.

For more help see: The Rate Law

a. $t_{1/2}(\text{first order}) = \dfrac{\ln 2}{k}$
   $k = \dfrac{\ln 2}{t_{1/2}} = \dfrac{\ln 2}{120\ s} = 5.77 \times 10^{-3}$
   percent unreacted defined by $\dfrac{[A]_t}{[A]_0}$

$$\frac{[A]_t}{[A]_0} = e^{-kt} \tag{4.9.3}$$

$$= e^{(-5.77\times10^{-3}\times800)} \times 100 = 0.98\% \text{ remains unreached.} \tag{4.9.4}$$

b. For a first order reaction, $\text{rate} = k[C]$
   $= 0.0046/s \times 0.25$
   $= 1.15 \times 10^{-3}\ M/s$

Q19.

Consider another first order reaction $A \rightarrow \text{products}$.

a. 5g of A is allowed to decompose for 45 minutes leaving 0.8 grams excess. What is the half life?
b. If we start with 1.8g of A how much is remaining after 1 hour?

S19.

For more help see: The Rate Law

a. First we determine the value of k
   $\ln\dfrac{[A]_t}{[A]_0} = -kt$
   $\ln\dfrac{[0.8]}{[5]} = -k(45\ \text{min})$
   $k = 4.07\text{E-2}\ \text{min}^{-1}$
   Next, we find the half life

$$t_{1/2} = \frac{0.693}{k} \tag{4.9.5}$$

$$= \frac{0.693}{4.07\text{E-2}} \tag{4.9.6}$$

$$= 17\ \text{mins} \tag{4.9.7}$$

Q21.

$A \rightarrow \text{products}$ is a first order reaction. 97% of reactants decompose in 137 minutes. What is the half-life, $t_{1/2}$, of this decomposition?

S21.

For more help see: Half-lives and Pharmacokinetics

$0.03 = \dfrac{[A]_t}{[A]_0} = e^{-kt}$

$\ln(0.03) = \ln e^{-kt}$

$\ln(0.03) = -kt$

$\ln(0.03) = -k(137\text{ minutes})$

$= \frac{\ln 2}{-0.0255}$

= ln 2/ -.0255

$= 27\text{ minutes}$

Q23.

The decomposition reaction of 5g of reactant A has a half-life of 50 minutes. Given the reaction is first order, how long will it take for reactant A to decompose 40%?

Use the following data sets for questions 27 and 29.

Data Set 1 $k = 4.56E\text{-}2$

Time, seconds	$[A]$, M
0	2.00
50	1.77
100	1.65
150	1.34
200	1.00
250	0.95
300	0.50
350	0.08

Data Set 2 $k = 5.87E\text{-}2$

Time, seconds	$[A]$, M
0	2.0
50	1.5
100	1.3
150	0.5
200	0

Data Set 3 $k = 6.2E\text{-}2$

Time, seconds	$[A]$, M
0	2.0
50	1.8
100	0.67
150	0.57
200	0.3
250	0.2
300	0.1
350	0

S23.

For more help see: Half-lives and Pharmacokinetics

If 40% of reactant A decomposes, that means that 60% of reactant A is remaining 60% of 5g is 3g

Next we find k,

$$\mathrm{t}_{1/2}=\frac{0.693}{\mathrm{k}}$$
$$\mathrm{k}=0.01386\ \mathrm{min}^{-1}$$

Next we solve for t,

$$\ln\left(\frac{3}{5}\right)=-(0.01386)(\mathrm{t})$$
$$\mathrm{t}=36.86\ \mathrm{min}$$

Q27.

Determine the orders of the above data sets. In other words whether they are zero, first, or second order.

S27.

For more help see: The Rate of a Chemical Reaction

Data Set 1 is First Order

Data set 2 is Zero Order

Data set 3 is Second Order

Q29.

Find the half-life, $\mathrm{t}_{1/2}$ of the first order reaction.

S29.

For more help see:

Set 1 :

$\mathrm{t}_{1/2}=\dfrac{0.693}{\mathrm{k}}$

$\mathrm{t}_{1/2}=\dfrac{0.693}{4.56\mathrm{E}\text{-}2}$

$\mathrm{t}_{1/2}=15.2\ \mathrm{s}$

Set 2:

$$\begin{aligned}\mathrm{t}_{1/2}&=\frac{[\mathrm{A}]_0}{2\mathrm{k}} &(4.9.8)\\&=\frac{2}{(2)(5.87\mathrm{E}\text{-}2)} &(4.9.9)\\&=17.0\ \mathrm{s} &(4.9.10)\end{aligned}$$

Set 3:

$$\begin{aligned}\mathrm{t}_{1/2}&=\frac{1}{[\mathrm{A}]_0\mathrm{k}} &(4.9.11)\\\mathrm{t}_{1/2}&=\frac{1}{(2.0)(6.2\mathrm{E}\text{-}2)} &(4.9.12)\\&=8.06\ \mathrm{s} &(4.9.13)\end{aligned}$$

Q33.

The reaction $\mathrm{A+B \rightarrow C+D}$ is a first order in A and first order in B. K is equal to 0.0234 $\mathrm{M^{-1}min^{-1}}$. What is the rate of this reaction when $[\mathrm{A}] = 0.245\ \mathrm{M}$ and $[\mathrm{B}] = 4.45\ \mathrm{M}$?

S33.

For more help see: Half-lives and Pharmacokinetics

$$\begin{aligned} \mathrm{R} &= \mathrm{k[A][B]} \qquad (4.9.14) \\ &= (0.0234\ \mathrm{M^{-1}\ min^{-1}})(0.245\ \mathrm{M})(4.45\ \mathrm{M}) \qquad (4.9.15) \\ &= 0.0255\ \mathrm{M\ min^{-1}} \qquad (4.9.16) \end{aligned}$$

Q35.

A common decomposition reaction is observed at constant temperature for 600s with the following data recorded: at $\mathrm{t} = 0$, $[\mathrm{Reactant}] = 2.00\ \mathrm{M}$; at $\mathrm{t} = 200\ \mathrm{s}$, $[\mathrm{Reactant}] = 1.80\ \mathrm{M}$; at $\mathrm{t} = 400\ \mathrm{s}$, $[\mathrm{Reactant}] = 1.62\ \mathrm{M}$; at $\mathrm{t} = 600\ \mathrm{s}$, $[\mathrm{Reactant}] = 1.48\ \mathrm{M}$; at $\mathrm{t} = 800\ \mathrm{s}$, $[\mathrm{Reactant}] = 1.36\ \mathrm{M}$. Please provide the reaction order, rate constant, and the rate law for this reaction at this temperature.

S35.

For more help see:by graphing the reaction in a log vs x plot we see that it is a second order reaction.

$$\mathrm{k} = \frac{0.617\ \mathrm{M^{-1}} - 0.500\ \mathrm{M^{-1}}}{400\ \mathrm{s} - 0\ \mathrm{s}} = 5.77 \times 10^{-3}$$

Q37.

A reaction $\mathrm{A \rightarrow products}$ resulted in the following data. What is the order of the reaction? What is the half life?

Time, s	**[A],M**
0	0.333
46	0.045
55	0.033
120	0.0196

S37.

For more help see: The Rate of a Chemical Reaction

Second Order:

Solve for k using this equation:

$$\frac{1}{[\mathrm{A}]_t} = \mathrm{kt} + \frac{1}{[\mathrm{A}]_0}$$

Evidently, all the k values for the 3 different times will come out to equal approximately 0.400

Q43.

Half lives of zeroth and second order reactions are dependent on half life. The situations are different in both cases. Explain why this is so.

S43?

Q45.

Explain the following:

a. Why can a reaction rate not be determined from a collision rate.
b. Why is it that rates of reactions change with temperature quickly whereas collision is slower.
c. Why does addition of catalyst effect the reaction even without change in temperature.

S45

a. reactions must have collision rates higher than the activation energy.
b. just because there is an increase in collisions does not mean that the reactions occur more frequently.
c. when we increase concentration although we increase the collisions we do not really increase the energy.

Q47.

Consider a reversible reaction with a enthalpy change of the forward reaction of 28kJ/mol, and a activation energy of the forward reaction of 75 kJ/mol.

a. Find the activation energy of the reverse reaction.
b. Sketch a reaction profile for the above reaction.

S47.

a. -75
b. a graph with k as the slope and $[A]$ as the y intercept. Should have a negative slope.

Q49.

Visually analyze the following graph.

a. Count the intermediates of the reaction.
b. How many transition states are present?
c. Which segment in the reaction is the fastest?
d. Which step has the smallest rate constant?
e. Is step A endothermic or exothermic?
f. What is the energy change of the overall reaction: endothermic or exothermic

S49.

For more help see:

a. 3
b. 2
c. 3
d. exothermic
e. overall exothermic

Q51.

The following observations of a reaction’s rate constant have been made: at $T = 325\,K$, $k = 3.2 \times 10^{-6}\ M^{-1}s^{-1}$; at $T = 456\,K$, $k = 2.8 \times 10^{-5}\ M^{-1}s^{-1}$. What is the activation energy of this reaction?

S51.

For more help see: Section on Ahraneous's equation

Solution: use $\ln\frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

$$\ln\frac{2.8 \times 10^{-5}}{3.2 \times 10^{-6}} = \frac{E_a}{8.3145\ J/mol\,K}\left(\frac{1}{325} - \frac{1}{456}\right)$$

$$-4.21=\frac{E_a(-2.22\times 10^{-4})}{8.314}$$
$$-35.004=E_a(-2.22\times 10^{-4})$$
$$E_a=2.25\times 10^4\ J/mol\text{ or }159\ kJ/mol$$

Q59.

The following statements are incorrect. What slight modifications would you make to them?

a. A catalyst speeds up a reaction but dues not take part in it.
b. A catalyst functions to effectively lower the activation energy of a reaction.

S59.

For more help see:

a. Catalysts do not go throught permenent change.
b. This only applies to homogeneous catalysts.

Q61.

Name some of the similarities and differences between the catalytic activity of platinum metal and of an enzyme?

S61.

For more help see:

Similarities: Metal activity site

Differences: Platinum is a universal catalyst where as enzymes are specific.

Q63.

What reaction conditions are required to produce a straight-line graph of reaction rate vs. enzyme concentration?

S63.

For more help see:

The catalyst took a different pathway in order to lower activation energy more effectively. Both graphs are accurate.

Q1.

In the reaction $4\,A+3\,B\rightarrow 2\,C+3\,D$ reaction A is found to disappear at a rate of 5.1 X 10^{-5} Ms^{-1}

a. What is the rate of reaction?
b. What is the rate of disappearance of B?
c. What is the rate of formation of C?

Kinetics

S1.

a. $-\frac{1}{4}\left(\frac{-\Delta[A]}{\Delta t}\right)=\frac{1}{4}(5.1\times 10^{-5}\ Ms^{-1})=1.3\times 10^{-5}\ Ms^{-1}$
b. Rate of disappearance of B = reaction rate X coefficient of B
   $(1.3\times 10^{-5}\ Ms^{-1})(3)=3.9\times 10^{-5}\ Ms^{-1}$
c. Rate of formation of C = reaction rate X coefficient of C
   $(1.3\times 10^{-5}\ Ms^{-1})(2)=2.6\times 10^{-5}\ Ms^{-1}$

Q3.

In the reaction $A\rightarrow B$, $[A]$ is found to be 0.750 M at $t=61.2\,s$ and 0.704 M at $t=73.5\,s$. Determine the average rate of the reaction during this time interval.

S3.

$$-\frac{\Delta[\mathrm{A}]}{\Delta \mathrm{t}}=\frac{0.704\ \mathrm{M}-0.750\ \mathrm{M}}{61.2\ \mathrm{s}-73.5\ \mathrm{s}}=3.7\times10^{-3}\ \mathrm{Ms}^{-1}$$

Q11.

The initial rate of the reaction $\mathrm{A}+\mathrm{B}\rightarrow\mathrm{C}+\mathrm{D}$ is determined for different initial conditions, with the results listed in the table:

Expt	$[\mathrm{A}]$, **M**	$[\mathrm{B}]$, **M**	**Initial Rate, Ms^{-1}**
1	0.331	0.203	2.205 X 10^{-4}
2	0.331	0.406	8.82 X 10^{-4}
3	0.662	0.203	4.41 X 10^{-4}
4	0.662	0.406	1.7 X 10^{-3}

a. What is the order of reaction with respect to A and B?
b. What is the overall reaction order?
c. What is the value of the rate constant k?

The Rate of a Chemical Reaction

S11.

a. $\mathrm{Reaction}\ 1=2.205\times10^{-4}=\mathrm{k}\times[0.331]^{\mathrm{m}}[0.203]^{\mathrm{n}}$
$\mathrm{Reaction}\ 2=8.82\times10^{-4}=\mathrm{k}\times[0.331]^{\mathrm{m}}[0.406]^{\mathrm{n}}$
$\mathrm{Reaction}\ 3=4.41\times10^{-4}=\mathrm{k}\times[0.662]^{\mathrm{m}}[0.203]^{\mathrm{n}}$
$\mathrm{Reaction}\ 4=1.7\times10^{-3}=\mathrm{k}\times[0.662]^{\mathrm{m}}[406]^{\mathrm{n}}$

<u>Order of Reaction with respect to B:</u>

1. Find where A is constant and B changes (Reaction 1 and Reaction 2)
2. Divide: $\frac{\mathrm{Reaction}\ 2}{\mathrm{Reaction}\ 1}=\frac{8.82\times10^{-4}}{2.205\times10^{-4}}=\frac{[0.331]^{\mathrm{m}}[0.406]^{\mathrm{n}}}{[0.331]^{\mathrm{m}}[0.203]^{\mathrm{n}}}$
$\frac{\mathrm{Reaction}\ 2}{\mathrm{Reaction}\ 1}=4=2^{\mathrm{n}}\rightarrow\mathrm{n}=2$
3. Thus the reaction is second order with respect to B.

<u>Order of Reaction with respect to A:</u>

1. Find where B is constant and A changes (Reaction 3 and Reaction 1)
2. Divide: $\frac{\mathrm{Reaction}\ 3}{\mathrm{Reaction}\ 1}=\frac{4.41\times10^{-4}}{2.205\times10^{-4}}=\frac{[0.406]^{\mathrm{m}}[0.662]^{\mathrm{n}}}{[0.203]^{\mathrm{m}}[0.662]^{\mathrm{n}}}$
$\frac{\mathrm{R}3}{\mathrm{R}1}=2=2^{\mathrm{m}}$
$\mathrm{m}=1$
3. Thus the reaction is first order with respect to A

b. Reaction order = reaction order of A + reaction order of B = 3rd order reaction
c. $2.205\times10^{-4}=\mathrm{k}\times[0.331][0.203]^{2}$
$\mathrm{k}=1.6\times10^{-2}$

Q13.

The following rates of reactions were obtained in three experiments with the reaction $2\ \mathrm{NO(g)}+\mathrm{Cl_2(g)}\rightarrow2\ \mathrm{NOCl(g)}$

Expt	Initial $[\mathrm{NO}]$, M	Initial $\mathrm{Cl_2}$, M	Initial rate of reaction, Ms^{-1}
1	.145	.405	1.24 X 10^{-5}
2	.145	.81	2.48 X 10^{-5}

3	.29	.405	4.96 X 10^{-5}

What is the rate law for this reaction?

Kinetics

S13.

<u>Order of Reaction with respect to [Cl_2]</u>:

1. Find where $[NO]$ is constant and $[Cl_2]$ changes (Reaction 1 and Reaction 2)
2. Divide: Reaction 2 by Reaction 1
   $$\frac{2.48\times10^{-5}}{1.24\times10^{-5}}=\frac{[0.145]^m[0.81]^n}{[0.145]^m[0.405]^n}\rightarrow 2=2^n$$
3. Thus $[Cl_2]$ is first order

<u>Order of Reaction with respect to [NO]:</u>

1. Find where $[Cl_2]$ is constant and $[NO]$ changes (Reaction 1 and Reaction 3)
2. Divide: Reaction 3 by Reaction 1
   $$\frac{4.96\times10^{-5}}{1.24\times10^{-5}}=\frac{[0.29]^m[0.405]^n}{[0.145]^m[0.405]^n}\rightarrow 4=2^m$$
3. Thus $[NO]$ is second order

<u>Rate Law:</u>

$\text{Rate Law}=k[NO]^2[Cl_2]$

Q17.

The first-order reaction $A\rightarrow\text{products}$ has $t_{1/2}=300\,s$

a. What percent of sample A remains <u>unreacted</u> 1000 s after the reaction starts?
b. What is the rate of reaction when $[A]=0.25\,M$

Kinetics

S17.

a. $\ln(\%\,\text{unreacted})=-kt$
   $$k=\frac{\ln 2}{t_{1/2}}=\frac{\ln 2}{300\,s}=0.0023\,s^{-1}$$
   $\ln(\%\,\text{unreacted})=-(0.0023\,s^{-1})(1000\,s)=-2.3$
   $e^{-2.3}=0.1\times100\%=10\%\,\text{unreacted}$
b. $\text{Rate}=k[A]$
   $\text{Rate}=0.0023\,s^{-1}[0.25\,M]=5.74\times10^{-4}\,Ms^{-1}$

Q19.

The reaction $A\rightarrow\text{products}$ is first order in A

a. If 4.2g A decomposes for 45 minutes, the undecomposed A is measured to be 1.05g. What is the half-life, $t_{1/2}$, of this reaction?
b. Starting with the same 4.2 g, what is the mass of undecomposed A after 75 minutes?

S19.

a. $(4.2\,g)\left(\frac{1}{4}\right)=1.05\,g\rightarrow 2\,\text{halflives have passed}\rightarrow\frac{45\text{ minutes}}{2}=t_{1/2}=22.5\text{ minutes}$
b. $\frac{\ln[A]_t}{\ln[A]_0}=-kt$
   $$k=\frac{\ln 2}{t_{1/2}}=\frac{\ln 2}{22.5\text{ minutes}}=0.0308\,\text{min}^{-1}$$

$$\frac{\ln[\mathrm{A}]_t}{\ln[\mathrm{A}]_0} = (-0.0308\,\mathrm{min}^{-1})(75\,\mathrm{min}) = -2.31$$
$$[\mathrm{A}]_t = [\mathrm{A}]_0 e^{-2.31}$$
$$[\mathrm{A}]_t = (4.2\,\mathrm{g})(0.09926) = 0.417\,\mathrm{g\ A}$$

Q21.

In a first order reaction, 95% of the original amount of reactant decomposes in 122 minutes. What is the half-life of this reaction?

S21.

In order to determine the half-life of the first-order reaction, we first need to determine the rate constant, k. $[\mathrm{Reactant}]_t = 0.05$ if $[\mathrm{Reactant}]_0 = 1.00$ since only 5% of the original reactant remains after 122 minutes.

$$\ln\frac{[\mathrm{Reactant}]_t}{[\mathrm{Reactant}]_0} = -kt = \ln\frac{0.05}{1} = -2.996 = -k(122\,\mathrm{min})$$
$$k = \frac{-2.996}{-122\,\mathrm{min}} = 0.024555\,\mathrm{min}^{-1}$$
$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.024555\,\mathrm{min}^{-1}} = 28.2\,\mathrm{min}$$

Q23a.

If a first order decomposition reaction has a half-life of 107 minutes, in what amount of time will the original reactant be ¼ of its original concentration?

S23a.

In order to determine the amount of time for this decomposition reaction to occur, we must first determine the rate constant k by using the half-life.

$$t_{1/2} = \frac{0.693}{k}$$
$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{107\,\mathrm{min}} = 0.00648\,\mathrm{min}^{-1}$$
$$\ln\frac{[\mathrm{Reactant}]_t}{[\mathrm{Reactant}]_0} = -kt = \ln\frac{0.25}{1} = -1.386 = -0.00648\,\mathrm{min}^{-1}t$$
$$t = \frac{-1.386}{-0.00648\,\mathrm{min}^{-1}} = 214\,\mathrm{min}$$

Table A

I		II		III	
Time, s	[Reactant], M	Time, s	[Reactant], M	Time, s	[Reactant], M
0	4.00	0	4.00	0	4.00
10	3.20	10	3.52	10	3.00
20	2.68	20	3.03	20	2.00
30	2.28	30	2.49	30	1.00
40	2.00	40	2.01	40	0.00
50	1.80	50	1.76		
60	1.60	60	1.52		
70	1.47	70	1.24		
80	1.33	80	0.99		

Q27.

Using Table A, determine whether each set is zero-order, first-order, or third-order.

S27.

I. Data set I must be second-order because $\frac{1}{[\text{Reactant}]_t} - \frac{1}{[\text{Reactant}]_0} = \mathrm{kt}$. For the first 40s in set I, $\frac{1}{2.00\,\mathrm{M}} - \frac{1}{4.00\,\mathrm{M}} = 0.25\,\mathrm{L\,mol^{-1}} = \mathrm{k}(40\,\mathrm{s})\,,\, \mathrm{k} = 0.00625\,\mathrm{L\,mol^{-1}\,s^{-1}}$.
For the first 80s in set I, $\frac{1}{1.33\,\mathrm{M}} - \frac{1}{4.00\,\mathrm{M}} = 0.5\,\mathrm{L\,mol^{-1}} = \mathrm{k}(80\,\mathrm{s})\,,\, \mathrm{k} = 0.00625\,\mathrm{L\,mol^{-1}\,s^{-1}}$.
Since both give the same rate constant, k, using the second-order kinetics equation, set I must be a second-order reaction.

II. Data set II must be first-order because the half-life is constant. The first half-life is approximately 40s because the reactant concentration goes from 4.00M to 2.01M (about half). The second half-life is also 40s because the reactant concentration goes from 2.01M to 0.99M (about half) from 40s to 80s.

III. Data set II must be zero-order because it is decomposing at a constant rate. Every single ten seconds, the reactant concentration decreases by another 1M.

Q29.

With the information given in Table A, are you able to find the half-life of the first-order reaction? If so, give $t_{1/2}$.

S29.

Yes, we can determine the half-life of the first-order reaction of data set II.

$$\ln\frac{[\text{Reactant}]_t}{[\text{Reactant}]_0} = -\mathrm{kt} = \ln\frac{2.01}{4.00} = -\mathrm{k}(40\,\mathrm{s})\ ,\ \mathrm{k} = 0.0172\,\mathrm{s^{-1}}$$

$$t_{1/2} = \frac{0.693}{\mathrm{k}} = \frac{0.693}{0.0172\,\mathrm{s^{-1}}} = 40.3\,\mathrm{s}$$

Q33.

The reaction $\mathrm{W + X \rightarrow Y + Z}$ is zero order in X and second order in W. The rate constant, k, is found to be 0.0115 $\mathrm{M^{-1}min^{-1}}$. What is the rate of the reaction when $[\mathrm{W}] = 0.095\,\mathrm{M}$ and $[\mathrm{X}] = 2.67\,\mathrm{M}$?

S33.

Using the rate equation, $\mathrm{Rate} = \mathrm{k}[\mathrm{W}]^2[\mathrm{X}]^0 = (0.0115\,\mathrm{M^{-1}min^{-1}})(0.095\,\mathrm{M})^2(2.67\,\mathrm{M})^0 = 0.00109\,\mathrm{M/min}$

Q35.

A decomposition reaction is observed at constant temperature for 800s, and the following data is recorded: at t=0, $[\text{Reactant}] = 2.00\,\mathrm{M}$; at t=200 s, $[\text{Reactant}] = 1.80\,\mathrm{M}$; at t=400 s, $[\text{Reactant}] = 1.62\,\mathrm{M}$; at t=600 s, $[\text{Reactant}] = 1.48\,\mathrm{M}$; at t=800 s, $[\text{Reactant}] = 1.36\,\mathrm{M}$. Please provide the reaction order, rate constant, and the rate law for this reaction at this temperature.

S35.

This reaction is of second-order because a plot of $\frac{1}{[\text{Reactant}]}$ vs. t gives a straight line.

Time (s)	[Reactant] (M)	$\frac{1}{[\text{Reactant}]}$ ($\mathrm{M^{-1}}$)
0	2.00	0.500
200	1.80	0.556
400	1.62	0.617
600	1.48	0.676
800	1.36	0.735

The rate constant, k, is given by the slope of this straight line.

$$\mathrm{k} \approx \frac{0.617\,\mathrm{M}^{-1} - 0.500\,\mathrm{M}^{-1}}{400\,\mathrm{s} - 0\,\mathrm{s}} \approx 2.925\mathrm{E}\text{-}4\mathrm{M}^{-1}\mathrm{s}^{-1}.$$

$$\mathrm{Rate} = \mathrm{k}[\mathrm{Reactant}]^2.$$

Q37.

For a certain decomposition reaction, the following observations have been made: at $\mathrm{t} = 0\,\mathrm{s}$, $[\mathrm{Reactant}] = 1.43\,\mathrm{M}$; at $\mathrm{t} = 44\,\mathrm{s}$, $[\mathrm{Reactant}] = 1.21\,\mathrm{M}$; at $\mathrm{t} = 148\,\mathrm{s}$, $[\mathrm{Reactant}] = 0.69\,\mathrm{M}$; and at $\mathrm{t} = 264\,\mathrm{s}$, $[\mathrm{Reactant}] = 0.11\,\mathrm{M}$. Determine the order and half-life of this reaction.

S37.

This reaction is of zero-order because a plot of $[\mathrm{Reactant}]$ vs. t gives a straight line.

The rate constant, k, is given by the slope of this straight line.

$$\mathrm{k} = \frac{0.69\,\mathrm{M} - 1.43\,\mathrm{M}}{148\,\mathrm{s} - 0\,\mathrm{s}} = -0.00500\,\mathrm{M/s}.$$

$$[\mathrm{Reactant}]_\mathrm{t} = \frac{[\mathrm{Reactant}]_0}{2} = \frac{1.43\,\mathrm{M}}{2} = 0.715\,\mathrm{M}$$

$$\mathrm{t}_{1/2} = \frac{0.715\,\mathrm{M}}{0.00500\,\mathrm{M/s}} = 143\,\mathrm{s}.$$

Q43.

Does the half-life of a reaction get longer or shorter as initial reactant concentration increases and why? Please answer for a) zero-order reactions b) second-order reactions.

S43.

a. $\mathrm{t}_{1/2} = \dfrac{[\mathrm{Reactant}]_0}{2\mathrm{k}}$
   In a zero-order reaction, half-life is proportional to initial reactant concentration, so the half-life of a zero-order reaction would get longer if the initial reactant concentration increased.

b. $\mathrm{t}_{1/2} = \dfrac{1}{\mathrm{k}[\mathrm{Reactant}]_0}$
   In a second-order reaction, half-life is inversely proportional to initial reactant concentration, so the half-life of a second-order reaction would get shorter if the initial reactant concentration increased.

Q45.

Answer the following:

a. What two factors does the rate of a reaction depend on other than the frequency of collisions?
b. Why does the rate of reaction increase dramatically with temperature?
c. What is the net effect of the addition of a catalyst?

S45.

a. 1) Whether or not the collisions occurring have enough energy to get over the activation energy and become products. 2) Whether or not the molecules involved in the collisions are situated properly for the reaction to occur.
b. Collision frequency does not increase dramatically with temperature; however, the percentage of molecules with enough energy to get over the activation energy and become products does.
c. The net effect of the addition of a catalyst is the decreasing of the energy barrier to products. The catalyst does so by enabling an alternative mechanism with a lower activation energy.

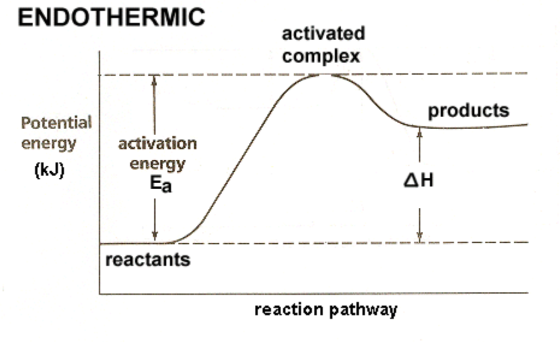
Q47.

For a reversible reaction, the enthalpy change of the forward reaction is 37kJ/mol, and the activation energy of the forward reaction is 96kJ/mol.

a. With the information provided, are you able to determine the activation energy of the reverse reaction? If so, please determine it.
b. Provide a sketch of the potential energy vs. progress of reaction.

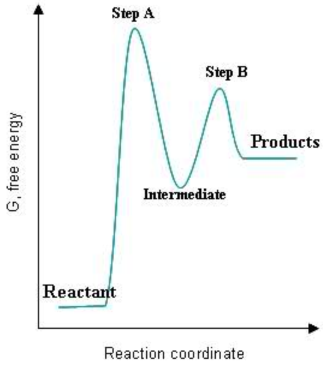
S47.

a. Yes we are able to determine the activation energy of the reverse reaction. Because the enthalpy change of the forward reaction is 37kJ/mol, the products are 37kJ/mol closer to the transition state than the reactants. The activation energy for the reverse reaction is $96\,\mathrm{kJ/mol} - 37\,\mathrm{kJ/mol} = 59\,\mathrm{kJ/mol}$
b. $\Delta\mathrm{H} = +37\,\mathrm{kJ}$
$\mathrm{E_a(forward)} = 96\,\mathrm{kJ}$
$\mathrm{E_a(reverse)} = 59\,\mathrm{kJ}$



Q49.

Given the following graph:



Please answer the following,

a. How can you tell where the intermediate is on the graph?
b. How can you tell where the transition state(s) is/are on the graph?
c. How can you tell where the fastest step of the reaction is on the graph?
d. How can you tell which step has the smallest rate constant?
e. How can you tell whether the steps of the reaction are exothermic or endothermic?
f. How can you tell whether the entire reaction is exothermic and endothermic?

S49.

a. The intermediate is a local minimum and must be brought back up to a transition state before becoming the final product(s).
b. The transition states, labeled Step A and Step B, are local maxima of the graph because they have reached the activation energy state needed to become intermediates/products.
c. The fastest step of the reaction is the one with the smallest activation energy, which in this case would be Step B because the energy gap between the intermediate and the Step B transition step is much smaller than the gap between the original reactant and the Step A transition state.
d. The smallest rate constant would correspond to the slowest reaction, which would correspond to the largest activation energy. In this case, Step A would have the smallest rate constant.
e. The steps are exothermic if their intermediates/products are lower in energy than their reactants, and the steps are endothermic if their intermediates/products are higher in energy than their reactants. Step A and Step B are endothermic because their intermediates/products are higher in energy than their reactants.
f. The overall reaction is exothermic if the initial reactant is higher in energy than the final products, and it is endothermic if the initial reactant is lower in energy than the final products. This reaction is endothermic because the reactant is lower in energy than the final products.

Q51.

The following observations of a reaction's rate constant have been made: at $\mathrm{T = 325\,K}$, $\mathrm{k = 3.2E\text{-}6 M^{-1} s^{-1}}$; at $\mathrm{T = 456\,K}$, $\mathrm{k = 2.8E\text{-}5 M^{-1} s^{-1}}$. What is the activation energy of this reaction?

S51.

$$\ln\frac{\mathrm{k_1}}{\mathrm{k_2}}=\frac{\mathrm{E_a}}{\mathrm{R}}\left(\frac{1}{\mathrm{T_2}}-\frac{1}{\mathrm{T_1}}\right)=\ln\frac{\mathrm{3.2E-6M^{-1}s^{-1}}}{\mathrm{2.8E-5M^{-1}s^{-1}}}=\frac{\mathrm{E_a}}{\mathrm{8.3145\,J\,mol^{-1}K^{-1}}}\left(\frac{1}{\mathrm{456\,K}}-\frac{1}{\mathrm{325\,K}}\right)$$

$$-2.2=-1.06\,\mathrm{mol\,J^{-1}}(\mathrm{E_a}),\ \mathrm{E_a}=\mathrm{2.1E4\,J\,mol^{-1}}$$

Q59.

a. Do catalysts take part in the reaction they catalyze? Do catalysts always speed up a reaction? Explain.
b. What is the function of a catalyst?

S59.

a. No, catalysts do not take part in the reactions they catalyze. No, catalysts do not always speed up a reaction; some negative catalysts, called inhibitors, can slow down the rate of a reaction.
b. Catalysts main function is to provide an alternative pathway for a reaction. By changing the mechanism for a reaction, a catalyst provides a pathway with a lower activation energy, resulting in a faster reaction.

Q61.

Please answer the following about the catalytic activity of both platinum metal and enzymes:

a. Where are there active sites?
b. Are they heterogeneous or homogeneous?
c. Are they specific or nonspecific?

S61.

a. The active site of platinum and of enzymes are at a metal center.
b. Enzymes are usually homogeneous, meaning they are soluble in the reactant; platinum, however, is heterogeneous, meaning it cannot be dissolved in the reactant.
c. Enzymes are extremely specific to their substrates, while platinum is usually more nonspecific.

Q63.

What reaction conditions are necessary to produce a straight-line graph of reaction rate vs. enzyme concentration?

S63.

An excess of reactant (substrate) must be available.

Q67.

The following reaction, $2W + 2X \rightarrow Y + Z$, consists of a three-step mechanism. The first step is fast, and is as follows: $W + W \leftrightarrow A$. The third step is fast as well, and is as follows: $B + X \rightarrow Z$. Comprise a three-step mechanism that conforms to W being of second order and X being of first order.

S67.

The first criterion for the reaction mechanism is that it must add up to produce the overall reaction $2W + 2X \rightarrow Y + Z$. We already have two of the three steps of the mechanism, so in order to find the second step, all we need to do is subtract the first and third steps from the overall reaction.

Overall Reaction: $2W + 2X \rightarrow Y + Z$

-First Step: $-(W + W \leftrightarrow A)$

-Third Step: $-(B + X \rightarrow Z)$

____

$X + A \leftrightarrow Y + B$ for the second step.

$r_2 = k_2[X][A]$

$r_f = k_f[W]^2$

$r_r = k_r[A]$

At equilibrium, rate forward=rate reverse so,

$k_f[W]^2 = k_r[A]$

$$[A] = \frac{k_f}{k_r}[W]^2$$

$$r = k_2\frac{k_f}{k_r}[W]^2[X]; \; k = k_2\frac{k_f}{k_r}$$

Rate Law: $r = k[W]^2[X]$, which conforms to W being of second order and X being of first order.

Q78.

Find an expression to describe the units of rate constant, k, for a reaction in terms of order of the reaction (n) , concentration (M), and time (s). Then use this expression to find the units of the rate constant, k, for a zero, first, and second order reaction.

S78.

The rate equation is $\text{rate} = k[\text{Reactant}]_n$. Rate has the units of M/s, $[\text{Reactant}]$ has the units of M, so when substituting in units for the rate equation you get, $M/s = (\text{units of } k)M_n$. By rearranging this equation you get, $(\text{units of } k) = \dfrac{Ms^{-1}}{M_n} = M_{1-n}s^{-1}$.

When $n = 0$,

$(\text{units of } k) = M_{1-0}s^{-1} = M/s$

When $n = 1$,

$(\text{units of } k) = M_{1-1}s^{-1} = s^{-1}$

When $n = 2$,

$(\text{units of } k) = M_{1-2}s^{-1} = M^{-1}s^{-1}$

Q87.

The overall reaction $H_2 + Br_2 \rightarrow 2\,HBr$ occurs in the following three step mechanism:

i. $Br_2 \xleftrightarrow[k_{-1}]{k_1} 2Br$ (forward and reverse reactions are fast)

ii. $Br + H_2 \xrightarrow{k_2} HBr + H$ (slow)

iii. $H + Br_2 \xrightarrow{k_3} HBr + Br$ (fast)

$k_1 = 5.7E4$; $k_{-1} = 4.5E4$; $k_2 = 2.7E\text{-}1$; $k_3 = 1.6E3$. What is the rate constant, k, and the rate law for the entire reaction?

S87.

Because step ii is the slow step, it is the rate determining step and the rate law should be derived according to it.

$$\frac{1}{2}\left(\frac{d[HBr]}{dt}\right) = k_2[Br][H_2]$$

The ½ coefficient is needed to account for the two HBr being made. $[Br]$ is an intermediate, so its rate of formation must equal its rate of decomposition:

$$k_1[Br_2] = k_{-1}[Br]^2\,,\ [Br] = \frac{k_1}{k_{-1}}[Br_2]^{1/2}$$

We can now replace $[Br]$ in the original rate law expression, giving:

$$\text{Rate} = k_2\left(\frac{k_1}{k_{-1}}\right)^{1/2}[H_2][Br_2]^{1/2}$$

$$\text{Meaning } k = k_2\left(\frac{k_1}{k_{-1}}\right)^{1/2} = (2.7E-1)\left(\frac{5.7E4}{4.5E4}\right)^{1/2} = 0.30$$
