Chapter 3: Chemical Kinetics

Exercises — Exercises

Q1 From the rate expression for the following reactions, determine their order of reaction and the dimensions of the rate constants.

(i) $3NO(g) \rightarrow N_2O(g)$ Rate = $k[NO]^2$

(ii) $H_2O_2(aq) + 3I^-(aq) + 2H^+ \rightarrow 2H_2O(l) + I_3^-$ Rate = $k[H_2O_2][I^-]$

(iii) $CH_3CHO(g) \rightarrow CH_4(g) + CO(g)$ Rate = k[CH3CHO]^(3/2)

(iv) $C_2H_5Cl(g) \rightarrow C_2H_4(g) + HCl(g)$ Rate = $k[C_2H_5Cl]$

SOLUTION

For any rate expression Rate = k[A]^x[B]^y, the order = x + y, and k units = (mol L^{-1} s^{-1}) / (mol L^{-1})^(total order).

(i) Rate = $k[NO]^2$
Order = 2 (second order).
Units of k: k = Rate/$[NO]^2$ = (mol L^{-1} s^{-1}) / (mol L^{-1})^2 = L mol^{-1} s^{-1}.

(ii) Rate = $k[H_2O_2][I^-]$
Order = 1 + 1 = 2 (second order).
Units of k: k = Rate/($[H_2O_2][I^-]$) = (mol L^{-1} s^{-1}) / (mol L^{-1})^2 = L mol^{-1} s^{-1}.

(iii) Rate = k[CH3CHO]^(3/2)
Order = 3/2 = 1.5 (pseudo three-halves order).
Units of k: k = Rate/[CH3CHO]^(3/2) = (mol L^{-1} s^{-1}) / (mol L^{-1})^(3/2) = L^(1/2) mol^(-1/2) s^{-1}.

(iv) Rate = $k[C_2H_5Cl]$
Order = 1 (first order).
Units of k: k = Rate/$[C_2H_5Cl]$ = (mol L^{-1} s^{-1}) / (mol L^{-1}) = s^{-1}.

Answer: (i) Order = 2, k: L mol^{-1} s^{-1}; (ii) Order = 2, k: L mol^{-1} s^{-1}; (iii) Order = 3/2, k: L^(1/2) mol^(-1/2) s^{-1}; (iv) Order = 1, k: s^{-1}

Q2 For the reaction: $2A + B \rightarrow A_2B$
the rate = $k[A][B]^2$ with $k = 2.0 \times 10^{-6}$ mol^{-2} L^2 s^{-1}. Calculate the initial rate of the reaction when [A] = 0.1 mol L^{-1}, [B] = 0.2 mol L^{-1}. Calculate the rate of reaction after [A] is reduced to 0.06 mol L^{-1}.

SOLUTION

Given: rate = $k[A][B]^2$, $k = 2.0 \times 10^{-6}$ mol^{-2} L^2 s^{-1}.
$[A]_0 = 0.1$ mol L^{-1}, $[B]_0 = 0.2$ mol L^{-1}.

Initial rate:
$Rate_0 = k \times [A]_0 \times [B]_0^2 = 2.0 \times 10^{-6} \times 0.1 \times (0.2)^2$
$Rate_0 = 2.0 \times 10^{-6} \times 0.1 \times 0.04 = 8.0 \times 10^{-9}$ mol L^{-1} s^{-1}.

When [A] is reduced to 0.06 mol L^{-1}:
Decrease in [A] = 0.1 - 0.06 = 0.04 mol L^{-1}.
From stoichiometry $2A + B \rightarrow A_2B$: for every 2 mol of A consumed, 1 mol of B is consumed.
Decrease in [B] = 0.04/2 = 0.02 mol L^{-1}.
Remaining [B] = 0.20 - 0.02 = 0.18 mol L^{-1}.

Rate = $k \times [A] \times [B]^2 = 2.0 \times 10^{-6} \times 0.06 \times (0.18)^2$
Rate = $2.0 \times 10^{-6} \times 0.06 \times 0.0324 = 3.89 \times 10^{-9}$ mol L^{-1} s^{-1}.

Answer: Initial rate = 8.0×10^{-9} mol L^{-1} s^{-1}; Rate after [A] = 0.06 mol L^{-1}: 3.89×10^{-9} mol L^{-1} s^{-1}

Q3 The decomposition of NH_3 on platinum surface is zero order reaction. What are the rates of production of N_2 and H_2 if $k = 2.5 \times 10^{-4}$ mol L^{-1} s^{-1}?

SOLUTION

The balanced equation is: $2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$.

For a zero order reaction, the rate equals the rate constant k.
Rate of reaction = $k = 2.5 \times 10^{-4}$ mol L^{-1} s^{-1}.

The rate of reaction is defined as:
$Rate = -1/2 \times d[NH_3]/dt = d[N_2]/dt = 1/3 \times d[H_2]/dt$

Rate of production of N_2:
$d[N_2]/dt = Rate = 2.5 \times 10^{-4}$ mol L^{-1} s^{-1}.

Rate of production of H_2:
$d[H_2]/dt = 3 \times Rate = 3 \times 2.5 \times 10^{-4} = 7.5 \times 10^{-4}$ mol L^{-1} s^{-1}.

Answer: Rate of production of N_2 = 2.5 × 10^{-4} mol L^{-1} s^{-1}; Rate of production of H_2 = 7.5 × 10^{-4} mol L^{-1} s^{-1}

Q4 The decomposition of dimethyl ether leads to the formation of CH_4, H_2 and CO and the reaction rate is given by Rate = k[CH_3OCH_3]^(3/2). The rate of reaction is followed by increase in pressure in a closed vessel, so the rate can also be expressed in terms of the partial pressure of dimethyl ether, i.e., Rate = k(p_CH_3OCH_3)^(3/2). If the pressure is measured in bar and time in minutes, then what are the units of rate and rate constants?

SOLUTION

Rate is expressed as change in pressure per unit time.
Units of rate = bar min^{-1}.

Rate = k × (p_CH_3OCH_3)^(3/2)
k = Rate / (p_CH_3OCH_3)^(3/2)

Units of k = (bar min^{-1}) / (bar)^(3/2)
= bar^(1 - 3/2) min^{-1}
= bar^(-1/2) min^{-1}.

Answer: Units of rate = bar min^{-1}; Units of rate constant k = bar^(-1/2) min^{-1}

Q5 Mention the factors that affect the rate of a chemical reaction.

SOLUTION

The following factors affect the rate of a chemical reaction:

1. Concentration of reactants: Rate generally increases with increasing concentration of reactants (except for zero order reactions).

2. Temperature: An increase in temperature increases the rate constant k (usually, rate doubles for every 10 K rise in temperature).

3. Nature of reactants: Physical state (solid < liquid < gas), bond type, and reactivity of reactants influence the rate.

4. Presence of a catalyst: A catalyst provides an alternative pathway with lower activation energy, increasing the reaction rate without being consumed.

5. Surface area (for heterogeneous reactions): Greater surface area leads to a faster rate.

6. Exposure to radiation (photochemical reactions): Certain reactions are initiated or accelerated by light.

Answer: Factors: (1) Concentration of reactants, (2) Temperature, (3) Nature of reactants (physical state and chemical nature), (4) Presence of catalyst, (5) Surface area (for heterogeneous reactions), (6) Radiation (for photochemical reactions)

Q6 A reaction is second order with respect to a reactant. How is the rate of reaction affected if the concentration of the reactant is (i) doubled (ii) reduced to half?

SOLUTION

For a second order reaction: Rate = $k[A]^2$.

(i) When concentration [A] is doubled ([A] -> 2[A]):
New rate = $k(2[A])^2 = 4k[A]^2 = 4 \times$ original rate.
The rate increases 4 times (becomes four times the original).

(ii) When concentration [A] is reduced to half ([A] -> [A]/2):
New rate = $k([A]/2)^2 = k[A]^2/4 = (1/4) \times$ original rate.
The rate decreases to one-fourth (1/4) of the original rate.

Answer: (i) Rate becomes 4 times; (ii) Rate becomes 1/4 of the original

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Q7 What is the effect of temperature on the rate constant of a reaction? How can this effect of temperature on rate constant be represented quantitatively?

SOLUTION

Effect of temperature on rate constant:
The rate constant k increases with increase in temperature. Generally, the rate of a reaction (and hence k) approximately doubles for every 10 K rise in temperature.

Quantitative representation — The Arrhenius equation:
$k = A \times e^{(-Ea/RT)}$

where:
k = rate constant
A = pre-exponential factor (frequency factor / Arrhenius factor)
Ea = activation energy (J mol^{-1})
R = gas constant = 8.314 J mol^{-1} K^{-1}

T = absolute temperature (K)

Taking logarithm:
ln k = ln A - Ea/(RT)
or log k = log A - Ea/(2.303 RT)

A plot of log k vs 1/T gives a straight line with slope = -Ea/(2.303R) and intercept = log A.
Higher temperature -> smaller Ea/RT -> larger k.

Answer: Rate constant increases with temperature. Arrhenius equation: k = A × e^(-Ea/RT), where A = frequency factor, Ea = activation energy, R = 8.314 J mol^{-1} K^{-1}, T = absolute temperature (K).

Q8 In a pseudo first order reaction in water, the following results were obtained:
t/s: 0, 30, 60, 90
[A]/mol L^{-1}: 0.55, 0.31, 0.17, 0.085
Calculate the average rate of reaction between the time interval 30 to 60 seconds.

SOLUTION

Average rate of reaction = -d[A]/dt ≈ -Δ[A]/Δt.

Between t = 30 s and t = 60 s:
Δ[A] = [A]_60 - [A]_30 = 0.17 - 0.31 = -0.14 mol L^{-1}.
Δt = 60 - 30 = 30 s.

Average rate = -Δ[A]/Δt = -(-0.14)/30 = 0.14/30
= 4.67×10^{-3} mol L^{-1} s^{-1}.

Answer: Average rate = 4.67×10^{-3} mol L^{-1} s^{-1}

Q9 A reaction is first order in A and second order in B.
(i) Write the differential rate equation.
(ii) How is the rate affected on increasing the concentration of B three times?
(iii) How is the rate affected when the concentrations of both A and B are doubled?

SOLUTION

(i) Differential rate equation:
Rate = -d[A]/dt = k[A][B]².

(ii) When [B] is increased three times ([B] -> 3[B]):

New rate = $k[A](3[B])^2 = 9k[A][B]^2 = 9 \times$ original rate.
The rate increases 9 times.

(iii) When both [A] and [B] are doubled ([A] -> 2[A], [B] -> 2[B]):
New rate = $k(2[A])(2[B])^2 = k \times 2[A] \times 4[B]^2 = 8k[A][B]^2 = 8 \times$ original rate.
The rate increases 8 times.

Answer: (i) Rate = $k[A][B]^2$; (ii) Rate becomes 9 times; (iii) Rate becomes 8 times

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Q10 In a reaction between A and B, the initial rate of reaction (r_0) was measured for different initial concentrations of A and B as given below:

A/mol L^{-1}	0.20	0.20	0.40
B/mol L^{-1}	0.30	0.10	0.05
r_0/mol L^{-1} s^{-1}	5.07×10^{-5}	5.07×10^{-5}	1.43×10^{-4}

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

SOLUTION

Let rate = k[A]^m[B]^n.

Order with respect to B (Experiments 1 and 2, [A] is constant at 0.20 mol L^{-1}):
$r_1/r_2 = ([B]_1/[B]_2)^n$
$5.07 \times 10^{-5} / 5.07 \times 10^{-5} = (0.30/0.10)^n$
$1 = 3^n$
n = 0 (zero order with respect to B).

Order with respect to A (Experiments 2 and 3, using n=0 so B has no effect):
$r_3/r_2 = ([A]_3/[A]_2)^m$
$1.43 \times 10^{-4} / 5.07 \times 10^{-5} = (0.40/0.20)^m$
$2.821 = (2)^m$
Taking log: m = log(2.821)/log(2) = 0.4505/0.3010 = 1.5.
m = 3/2 (order = 1.5 with respect to A).

Overall order = m + n = 1.5 + 0 = 1.5.

Answer: Order w.r.t. A = 3/2 (1.5); Order w.r.t. B = 0; Overall order = 1.5

Q11 The following results have been obtained during the kinetic studies of the reaction: 2A + B -> C + D

Exp I: [A]=0.1, [B]=0.1, rate=6.0×10^{-3} mol L^{-1} min^{-1}

Exp II: [A]=0.3, [B]=0.2, rate=7.2×10^{-2} mol L^{-1} min^{-1}

Exp III: [A]=0.3, [B]=0.4, rate=2.88×10^{-1} mol L^{-1} min^{-1}

Exp IV: [A]=0.4, [B]=0.1, rate=2.40×10^{-2} mol L^{-1} min^{-1}

Determine the rate law and the rate constant for the reaction.

SOLUTION

Let rate = k[A]^m[B]^n.

Order with respect to B (Experiments II and III, [A] = 0.3 mol L^{-1}):

r_III/r_II = ([B]_III/[B]_II)^n

$2.88 \times 10^{-1} / 7.2 \times 10^{-2} = (0.4/0.2)^n$

4.00 = 2^n

n = 2 (second order with respect to B).

Order with respect to A (Experiments I and IV, [B] = 0.1 mol L^{-1}):

r_IV/r_I = ([A]_IV/[A]_I)^m

$2.40 \times 10^{-2} / 6.0 \times 10^{-3} = (0.4/0.1)^m$

4.00 = 4^m

m = 1 (first order with respect to A).

Rate law: Rate = $k[A][B]^2$.

Calculate k using Experiment I:

$k = \text{Rate} / ([A][B]^2) = 6.0 \times 10^{-3} / (0.1 \times (0.1)^2)$

$k = 6.0 \times 10^{-3} / (0.1 \times 0.01) = 6.0 \times 10^{-3} / 10^{-3}$

k = 6.0 L^2 mol^{-2} min^{-1}.

Verification with Exp II: $k = 7.2 \times 10^{-2}/(0.3 \times 0.04) = 7.2 \times 10^{-2}/0.012 = 6.0$. Confirmed.

Answer: Rate law: Rate = $k[A][B]^2$; Rate constant k = 6.0 L^2 mol^{-2} min^{-1}

Q12 The reaction between A and B is first order with respect to A and zero order with respect to B. Fill in the blanks in the following table:
Exp I: [A]=0.1, [B]=0.1, rate=2.0×10^{-2} mol L^{-1} min^{-1}
Exp II: [A]=?, [B]=0.2, rate=4.0×10^{-2} mol L^{-1} min^{-1}
Exp III: [A]=0.4, [B]=0.4, rate=?
Exp IV: [A]=?, [B]=0.2, rate=2.0×10^{-2} mol L^{-1} min^{-1}

SOLUTION

Rate = $k[A]^1[B]^0 = k[A]$ (zero order in B, first order in A).

From Experiment I: $k = \text{Rate}/[A] = 2.0 \times 10^{-2} / 0.1 = 0.2\ min^{-1}$.

Experiment II: $[A] = \text{Rate}/k = 4.0 \times 10^{-2} / 0.2 = 0.2$ mol L^{-1}.

Experiment III: $\text{Rate} = k[A] = 0.2 \times 0.4 = 8.0 \times 10^{-2}$ mol L^{-1} min^{-1}.

Experiment IV: $[A] = \text{Rate}/k = 2.0 \times 10^{-2} / 0.2 = 0.1$ mol L^{-1}.

Summary of completed table:
Exp I: [A]=0.1, [B]=0.1, rate=2.0×10^{-2} mol L^{-1} min^{-1}
Exp II: [A]=0.2, [B]=0.2, rate=4.0×10^{-2} mol L^{-1} min^{-1}
Exp III: [A]=0.4, [B]=0.4, rate=8.0×10^{-2} mol L^{-1} min^{-1}
Exp IV: [A]=0.1, [B]=0.2, rate=2.0×10^{-2} mol L^{-1} min^{-1}

Answer: Exp II: [A] = 0.2 mol L^{-1}; Exp III: rate = 8.0×10^{-2} mol L^{-1} min^{-1}; Exp IV: [A] = 0.1 mol L^{-1}

Q13 Calculate the half-life of a first order reaction from their rate constants given below:
(i) 200 s^{-1}
(ii) 2 min^{-1}
(iii) 4 $years^{-1}$

SOLUTION

For a first order reaction: $t_{(1/2)} = 0.693/k$.

(i) $k = 200\ s^{-1}$:
$t_{(1/2)} = 0.693/200 = 3.46 \times 10^{-3}$ s.

(ii) $k = 2\ min^{-1}$:
$t_{(1/2)} = 0.693/2 = 0.346$ min = 0.35 min.

(iii) $k = 4\ years^{-1}$:
$t_{(1/2)} = 0.693/4 = 0.173$ years.

Answer: (i) 3.46×10^{-3} s; (ii) 0.346 min; (iii) 0.173 years

Q14 The half-life for radioactive decay of ^{14}C is 5730 years. An archaeological artifact containing wood had only 80% of the ^{14}C found in a living tree. Estimate the age of the sample.

SOLUTION

Radioactive decay is a first order process.
Given: $t_{1/2} = 5730$ years; $N/N_0 = 0.80$.

$k = 0.693/t_{1/2} = 0.693/5730 = 1.209 \times 10^{-4}\ yr^{-1}$.

For first order: $\ln(N_0/N) = kt$
$t = \ln(N_0/N)/k = \ln(1/0.80)/k = \ln(1.25)/k$

$\ln(1.25) = 0.22314$
$t = 0.22314 / (1.209 \times 10^{-4}) = 1845$ years.

Alternatively using log form:
$t = 2.303/k \times \log(N_0/N) = 2.303/(1.209 \times 10^{-4}) \times \log(1.25)$
$= 2.303/(1.209 \times 10^{-4}) \times 0.09691 = 1845$ years.

Answer: Age of the sample ≈ 1845 years

Q15 The experimental data for decomposition of N_2O_5 [$2N_2O_5 \rightarrow 4NO_2 + O_2$] in gas phase at 318 K are given below:
t/s: 0, 400, 800, 1200, 1600, 2000, 2400, 2800, 3200
$10^2 \times [N_2O_5]$/mol L^{-1}: 1.63, 1.36, 1.14, 0.93, 0.78, 0.64, 0.53, 0.43, 0.35
(i) Plot $[N_2O_5]$ against t. (ii) Find the half-life period for the reaction. (iii) Draw a graph between log$[N_2O_5]$ and t. (iv) What is the rate law? (v) Calculate the rate constant. (vi) Calculate the half-life period from k and compare it with (ii).

SOLUTION

Data table:

t(s)	$[N_2O_5]$(mol/L)	log$[N_2O_5]$
0	0.0163	-1.788
400	0.0136	-1.866
800	0.0114	-1.943
1200	0.0093	-2.031
1600	0.0078	-2.108

2000	0.0064	-2.194
2400	0.0053	-2.276
2800	0.0043	-2.367
3200	0.0035	-2.456

(i) A plot of $[N_2O_5]$ vs t gives a curve (exponential decay), confirming the concentration decreases non-linearly with time.

(ii) Initial $[N_2O_5]_0 = 1.63 \times 10^{-2}$ mol L^{-1}.
Half of $[N_2O_5]_0 = 0.815 \times 10^{-2}$ mol L^{-1}.
From the $[N_2O_5]$ vs t graph, $[N_2O_5] = 0.815 \times 10^{-2}$ mol L^{-1} at approximately t ≈ 1440 s.
t_(1/2) ≈ 1440 s (from graph).

(iii) A plot of $\log[N_2O_5]$ vs t gives a straight line, confirming first order kinetics.

(iv) Since $\log[N_2O_5]$ vs t is linear (straight line), the reaction is first order.
Rate law: Rate = $k[N_2O_5]$.

(v) For first order: $\log[N_2O_5] = \log[N_2O_5]_0 - kt/2.303$
Slope of $\log[N_2O_5]$ vs t = $-k/2.303$
Using endpoints: slope = $(\log(0.0035) - \log(0.0163))/(3200 - 0)$
$= (-2.456 - (-1.788))/3200 = -0.668/3200 = -2.088 \times 10^{-4}$ s^{-1}
$k = -\text{slope} \times 2.303 = 2.088 \times 10^{-4} \times 2.303 = 4.81 \times 10^{-4}$ s^{-1}.

(vi) t_(1/2) from $k = 0.693/k = 0.693/(4.81 \times 10^{-4}) = 1440$ s.
This agrees well with the graphical value of ~1440 s in (ii).

Answer: (iv) Rate = $k[N_2O_5]$ (first order); (v) $k = 4.81 \times 10^{-4}$ s^{-1}; (vi) t_(1/2) = 1440 s (matches graphical value)

Q16 The rate constant for a first order reaction is 60 s^{-1}. How much time will it take to reduce the initial concentration of the reactant to its 1/16th value?

SOLUTION

Given: $k = 60$ s^{-1}; $[A] = [A]_0/16$.

For a first order reaction: $t = (1/k) \times \ln([A]_0/[A])$
$t = \ln([A]_0/([A]_0/16)) / 60$
$t = \ln(16) / 60$

Note: $\ln(16) = \ln(2^4) = 4 \times \ln(2) = 4 \times 0.693 = 2.772$
This corresponds to 4 half-lives.

t = 2.772 / 60 = 4.62 × 10^{-2} s.

Alternatively: t = 4 × t_(1/2) = 4 × (0.693/60) = 4 × 0.01155 = 4.62 × 10^{-2} s.

Answer: t = 4.62 × 10^{-2} s

Q17 During nuclear explosion, one of the products is ^{90}Sr with half-life of 28.1 years. If 1 mg of ^{90}Sr was absorbed in the bones of a newly born baby instead of calcium, how much of it will remain after 10 years and 60 years if it is not lost metabolically.

SOLUTION

Radioactive decay is first order: N = N_0 × e^(-kt).
t_(1/2) = 28.1 years; k = 0.693/28.1 = 2.466 × 10^{-2} yr^{-1}.
N_0 = 1 mg.

After 10 years:
N = 1 × e^(-0.02466 × 10) = e^(-0.2466) = 0.7814 mg.

After 60 years:
N = 1 × e^(-0.02466 × 60) = e^(-1.4796) = 0.2278 mg.

Using logarithmic form:
After 10 years: N = 1 × (1/2)^(10/28.1) = (1/2)^(0.3559) = 0.781 mg.
After 60 years: N = 1 × (1/2)^(60/28.1) = (1/2)^(2.135) = 0.228 mg.

Answer: After 10 years: 0.781 mg remains; After 60 years: 0.228 mg remains

Q18 For a first order reaction, show that time required for 99% completion is twice the time required for the completion of 90% of reaction.

SOLUTION

For a first order reaction: t = (2.303/k) × log($[A]_0$/[A])

Time for 90% completion (10% remaining):
t_(90%) = (2.303/k) × log($[A]_0$/(0.10 × $[A]_0$))
= (2.303/k) × log(10)
= (2.303/k) × 1
= 2.303/k.

Time for 99% completion (1% remaining):
t_(99%) = (2.303/k) × log($[A]_0$/(0.01 × $[A]_0$))

= (2.303/k) × log(100)
= (2.303/k) × 2
= 2 × (2.303/k).

Therefore: t_(99%) = 2 × t_(90%).
The time required for 99% completion is exactly twice the time for 90% completion. (Proved)

Answer: t_(99%) = 2 × t_(90%) is proved; both equal (2.303/k) × log(100) and (2.303/k) × log(10) respectively.

Q19 A first order reaction takes 40 min for 30% decomposition. Calculate t_(1/2).

SOLUTION

Given: t = 40 min; 30% decomposed, so 70% remains: [A] = 0.70[A]$_0$.

For first order: k = (2.303/t) × log([A]$_0$/[A])
k = (2.303/40) × log(1/0.70)
k = (2.303/40) × log(1.4286)
k = (2.303/40) × 0.15490
k = 0.05758 × 0.15490
k = 8.918 × 10^{-3} min^{-1}.

t_(1/2) = 0.693/k = 0.693/(8.918 × 10^{-3}) = 77.7 min.

Answer: t_(1/2) = 77.7 min

Q20 For the decomposition of azoisopropane to hexane and nitrogen at 543 K, the following data are obtained:
t(sec): 0, 360, 720
P(mm Hg): 35.0, 54.0, 63.0
Calculate the rate constant.

SOLUTION

The decomposition reaction:
$(CH_3)_2CHN{=}NCH(CH_3)_2(g) \rightarrow C_6H_{14}(g) + N_2(g)$
1 mole of reactant gives 2 moles of gaseous products.

At t = 0: only reactant A at pressure P_0 = 35.0 mm Hg.
At time t: if pressure of A decreases by x, product pressures each increase by x.
Total pressure P = (P_0 - x) + x + x = P_0 + x

Therefore: $x = P - P_0$ and $P_A = P_0 - x = 2P_0 - P$.

At t = 360 s: P = 54.0 mm Hg
$P_A(360) = 2 \times 35.0 - 54.0 = 70.0 - 54.0 = 16.0$ mm Hg.

At t = 720 s: P = 63.0 mm Hg
$P_A(720) = 2 \times 35.0 - 63.0 = 70.0 - 63.0 = 7.0$ mm Hg.

For first order kinetics: $k = (2.303/t) \times \log(P_0/P_A)$

$k_{(360)} = (2.303/360) \times \log(35.0/16.0)$
$= (2.303/360) \times \log(2.1875)$
$= (2.303/360) \times 0.3399$
$= 2.175 \times 10^{-3}\ s^{-1}$.

$k_{(720)} = (2.303/720) \times \log(35.0/7.0)$
$= (2.303/720) \times \log(5.0)$
$= (2.303/720) \times 0.6990$
$= 2.235 \times 10^{-3}\ s^{-1}$.

Average $k = (2.175 + 2.235) \times 10^{-3} / 2 = 2.21 \times 10^{-3}\ s^{-1}$.

Answer: Rate constant $k = 2.21 \times 10^{-3}\ s^{-1}$

Q21 The following data were obtained during the first order thermal decomposition of SO_2Cl_2 at a constant volume:
$SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$
Expt 1: Time = 0 s, Total pressure = 0.5 atm
Expt 2: Time = 100 s, Total pressure = 0.6 atm
Calculate the rate of the reaction when total pressure is 0.65 atm.

SOLUTION

Reaction: $SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$
1 mole -> 2 moles of gas.

At t = 0: $P_0 = 0.5$ atm (only SO_2Cl_2).
At t = 100 s: $P_{total} = 0.6$ atm.
If $P_{SO_2Cl_2}$ decreases by x: $P_{SO_2Cl_2} = P_0 - x$; $P_{SO_2} = x$; $P_{Cl_2} = x$.
$P_{total} = (P_0 - x) + x + x = P_0 + x$.
$x = P_{total} - P_0 = 0.6 - 0.5 = 0.1$ atm.
$P_{SO_2Cl_2}$ at t=100 s = 0.5 - 0.1 = 0.4 atm.

Rate constant (first order):

k = (2.303/100) × log(0.5/0.4)
= (2.303/100) × log(1.25)
= (2.303/100) × 0.09691
= 2.231 × 10^{-3} s^{-1}.

When P_total = 0.65 atm:
x = 0.65 - 0.5 = 0.15 atm.
P_SO_2Cl_2 = 0.5 - 0.15 = 0.35 atm.

Rate = k × P_SO_2Cl_2 = 2.231 × 10^{-3} × 0.35
= 7.81 × 10^{-4} atm s^{-1}.

Answer: Rate = 7.81 × 10^{-4} atm s^{-1}

Q22 The rate constant for the decomposition of N_2O_5 at various temperatures is given below:
T/°C: 0, 20, 40, 60, 80
10^5 × k/s^{-1}: 0.0787, 1.70, 25.7, 178, 2140
Draw a graph between ln k and 1/T and calculate the values of A and Ea. Predict the rate constant at 30°C and 50°C.

SOLUTION

Convert temperatures to Kelvin and calculate ln k:

T(°C)	T(K)	k(s^{-1})	ln k
0	273	7.87×10^{-7}	-14.06
20	293	1.70×10^{-5}	-10.98
40	313	2.57×10^{-4}	-8.27
60	333	1.78×10^{-3}	-6.33
80	353	2.14×10^{-2}	-3.84

The Arrhenius equation: ln k = ln A - Ea/(RT).
A plot of ln k vs 1/T gives a straight line with slope = -Ea/R.

Using linear regression on the data:
Slope = -Ea/R = -12115 K
Ea = 12115 × 8.314 = 1.007 × 10^5 J mol^{-1} = 100.6 kJ mol^{-1}.

Intercept = ln A = 30.31
A = e^{30}.31 = 1.43 × 10^{13} s^{-1}.

Prediction at 30°C (303 K):

ln k = 30.31 - 12115/303 = 30.31 - 39.98 = -9.67
k(30°C) = e^(-9.67) = 6.3 × 10^{-5} s^{-1}.

Prediction at 50°C (323 K):
ln k = 30.31 - 12115/323 = 30.31 - 37.51 = -7.20
k(50°C) = e^(-7.20) = 7.4 × 10^{-4} s^{-1}.

Answer: Ea = 100.6 kJ mol^{-1}; A = 1.43 × 10^{13} s^{-1}; k at 30°C = 6.3 × 10^{-5} s^{-1}; k at 50°C = 7.4 × 10^{-4} s^{-1}

Q23 The rate constant for the decomposition of hydrocarbons is 2.418 × 10^{-5} s^{-1} at 546 K. If the energy of activation is 179.9 kJ/mol, what will be the value of pre-exponential factor.

SOLUTION

Given: k = 2.418 × 10^{-5} s^{-1}, T = 546 K, Ea = 179.9 kJ mol^{-1} = 179900 J mol^{-1}.
R = 8.314 J mol^{-1} K^{-1}.

Arrhenius equation: k = A × e^(-Ea/RT)
Taking log: log k = log A - Ea/(2.303RT)

log A = log k + Ea/(2.303 × R × T)
= log(2.418 × 10^{-5}) + 179900/(2.303 × 8.314 × 546)
= (-4.617) + 179900/(10454)
= -4.617 + 17.22
= 12.60

A = $10^{12.60}$ = 3.98 × 10^{12} s^{-1} ≈ 3.9 × 10^{12} s^{-1}.

Verification: Ea/(RT) = 179900/(8.314×546) = 39.64
A = k × e^(Ea/RT) = 2.418×10^{-5} × $e^{39.64}$ = 2.418×10^{-5} × 1.67×10^{17} = 4.0×10^{12} s^{-1}.

Answer: Pre-exponential factor A = 3.93 × 10^{12} s^{-1}

Q24 Consider a certain reaction A -> Products with k = 2.0 × 10^{-2} s^{-1}. Calculate the concentration of A remaining after 100 s if the initial concentration of A is 1.0 mol L^{-1}.

SOLUTION

k = 2.0 × 10^{-2} s^{-1}. Since k has units s^{-1}, this is a first order reaction.
Given: $[A]_0$ = 1.0 mol L^{-1}, t = 100 s.

For first order: $[A] = [A]_o \times e^{(-kt)}$
$[A] = 1.0 \times e^{(-2.0 \times 10^{-2} \times 100)}$
$[A] = 1.0 \times e^{(-2.0)}$
$[A] = 1.0 \times 0.1353$
$[A] = 0.1353 \text{ mol } L^{-1}$.

Using logarithmic form:
$\log([A]_o/[A]) = kt/2.303 = (2.0 \times 10^{-2} \times 100)/2.303 = 0.8685$
$[A]_o/[A] = 10^{0.8685} = 7.39$
$[A] = 1.0/7.39 = 0.1353 \text{ mol } L^{-1}$.

Answer: [A] remaining after 100 s = $0.1353 \text{ mol } L^{-1}$

Q25 Sucrose decomposes in acid solution into glucose and fructose according to the first order rate law, with t_(1/2) = 3.00 hours. What fraction of sample of sucrose remains after 8 hours?

SOLUTION

Given: t_(1/2) = 3.00 h, t = 8 h.

$k = 0.693/t_{(1/2)} = 0.693/3.00 = 0.231 \text{ h}^{-1}$.

For first order: $[A]/[A]_o = e^{(-kt)} = e^{(-0.231 \times 8)} = e^{(-1.848)}$.

$e^{(-1.848)} = 0.1576$.

Alternatively, using log form:
$\log([A]_o/[A]) = kt/2.303 = (0.231 \times 8)/2.303 = 0.8025$
$[A]_o/[A] = 10^{0.8025} = 6.344$
Fraction remaining = $[A]/[A]_o = 1/6.344 = 0.1576$.

Answer: Fraction of sucrose remaining after 8 hours = 0.1576 (i.e., 15.76%)

Q26 The decomposition of hydrocarbon follows the equation $k = (4.5 \times 10^{11} \text{ s}^{-1}) e^{(-28000K/T)}$. Calculate Ea.

SOLUTION

Comparing with the Arrhenius equation $k = A \times e^{(-Ea/RT)}$:
$-Ea/(RT) = -28000 \text{ K}/T$
$Ea/R = 28000 \text{ K}$
$Ea = 28000 \times R = 28000 \times 8.314 \text{ J mol}^{-1}$

Ea = 2,32,792 J mol^{-1}

Ea = 232.79 kJ mol^{-1} ≈ 232.8 kJ mol^{-1}.

Answer: Ea = 232.79 kJ mol^{-1}

Q27 The rate constant for the first order decomposition of H_2O_2 is given by the following equation: log k = 14.34 - 1.25 × 10^4 K/T. Calculate Ea for this reaction and at what temperature will its half-period be 256 minutes?

SOLUTION

The given equation: log k = 14.34 - 1.25 × 10^4 / T.

Comparing with Arrhenius in log form: log k = log A - Ea/(2.303RT):

Ea/(2.303 × R) = 1.25 × 10^4 K

Ea = 1.25 × 10^4 × 2.303 × 8.314

Ea = 1.25 × 10^4 × 19.147

Ea = 2.393 × 10^5 J mol^{-1} = 239.3 kJ mol^{-1}.

Also: log A = 14.34 => A = 2.19 × 10^{14} s^{-1}.

Temperature for t_(1/2) = 256 min:

k = 0.693/t_(1/2) = 0.693/(256 × 60) = 0.693/15360 = 4.51 × 10^{-5} s^{-1}.

log k = log(4.51 × 10^{-5}) = -4.346.

Substituting in the given equation:

log k = 14.34 - 1.25 × 10^4 / T

-4.346 = 14.34 - 1.25 × 10^4 / T

1.25 × 10^4 / T = 14.34 + 4.346 = 18.686

T = 1.25 × 10^4 / 18.686 = 669 K.

Answer: Ea = 239.3 kJ mol^{-1}; Temperature for t_(1/2) = 256 min: T = 669 K

Q28 The decomposition of A into product has value of k as 4.5 × 10^3 s^{-1} at 10°C and energy of activation 60 kJ mol^{-1}. At what temperature would k be 1.5 × 10^4 s^{-1}?

SOLUTION

Given: k_1 = 4.5 × 10^3 s^{-1} at T_1 = 10°C = 283 K.

k_2 = 1.5 × 10^4 s^{-1}, Ea = 60 kJ mol^{-1} = 60000 J mol^{-1}.

Using the Arrhenius two-temperature equation:

$\log(k_2/k_1) = Ea/(2.303 \times R) \times (1/T_1 - 1/T_2)$

$\log(1.5 \times 10^4 / 4.5 \times 10^3) = (60000/(2.303 \times 8.314)) \times (1/283 - 1/T_2)$
$\log(3.333) = 3133.6 \times (1/283 - 1/T_2)$
$0.5229 = 3133.6 \times (1/283 - 1/T_2)$
$1/283 - 1/T_2 = 0.5229/3133.6 = 1.669 \times 10^{-4}$
$1/T_2 = 1/283 - 1.669 \times 10^{-4} = 3.534 \times 10^{-3} - 1.669 \times 10^{-4} = 3.367 \times 10^{-3}$
$T_2 = 1/(3.367 \times 10^{-3}) = 297$ K = 24°C.

Answer: $T_2 = 297$ K (24°C)

Q29 The time required for 10% completion of a first order reaction at 298 K is equal to that required for its 25% completion at 308 K. If the value of A is 4×10^{10} s^{-1}, calculate k at 318 K and Ea.

SOLUTION

For first order: $t = (2.303/k) \times \log([A]_0/([A]_0 - x))$.

$t(10\% \text{ at } 298K) = (2.303/k_1) \times \log(100/90) = (2.303/k_1) \times \log(10/9)$.
$t(25\% \text{ at } 308K) = (2.303/k_2) \times \log(100/75) = (2.303/k_2) \times \log(4/3)$.

Setting these equal:
$(1/k_1) \times \log(10/9) = (1/k_2) \times \log(4/3)$
$k_2/k_1 = \log(4/3)/\log(10/9) = 0.1249/0.04576 = 2.730$.

Find Ea using the two-temperature equation:
$\log(k_2/k_1) = Ea/(2.303 \times R) \times (T_2 - T_1)/(T_1 \times T_2)$
$\log(2.730) = [Ea/(2.303 \times 8.314)] \times [(308 - 298)/(298 \times 308)]$
$0.4362 = [Ea/19.147] \times [10/91784]$
$0.4362 = Ea \times 5.683 \times 10^{-6}$
$Ea = 0.4362 / (5.683 \times 10^{-6}) = 76752$ J $mol^{-1} \approx 76.8$ kJ mol^{-1}.

k at 318 K: using k = A × e^(-Ea/RT)
log k = log A - Ea/(2.303RT)
$\log k = \log(4 \times 10^{10}) - 76752/(2.303 \times 8.314 \times 318)$
log k = 10.602 - 76752/6090.0
log k = 10.602 - 12.603 = -2.001
$k(318 \text{ K}) = 10^{(-2.001)} = 9.98 \times 10^{-3}$ $s^{-1} \approx 1.0 \times 10^{-2}$ s^{-1}.

Answer: Ea = 76.8 kJ mol^{-1}; k at 318 K = 1.0×10^{-2} s^{-1}

Q30 The rate of a reaction quadruples when the temperature changes from 293 K to 313 K. Calculate the energy of activation of the reaction assuming that it does not change with temperature.

SOLUTION

Given: $k_2/k_1 = 4$, $T_1 = 293$ K, $T_2 = 313$ K.

Using the Arrhenius equation:

$\log(k_2/k_1) = Ea/(2.303 \times R) \times (T_2 - T_1)/(T_1 \times T_2)$

$\log(4) = [Ea/(2.303 \times 8.314)] \times [(313 - 293)/(293 \times 313)]$

$0.6021 = [Ea/19.147] \times [20/91709]$

$0.6021 = Ea \times 1.1406 \times 10^{-5}$

$Ea = 0.6021 / (1.1406 \times 10^{-5})$

$Ea = 52785$ J mol^{-1} ≈ 52.8 kJ mol^{-1}.

Answer: Energy of activation Ea = 52.8 kJ mol^{-1}