**Half-lives**

The half-life is the time taken for a given concentration to decrease to half of its value, for example

 if [M] = 12 × 10-3 mole dm-3 at the start of the reaction, then the first half-life is the time taken for [M] to drop to 6×10-3 mole dm-3.



**Sometime** the reaction is monitored by measuring the concentration of product from time to time. If Ct is the concentration of product at any time t and the final concentration of product when the reaction is completed , the is a measure of the initial concentration of reactant and - is a measure of reactant remaining at time t .

Q:- From the following data for the decomposition of N2O5 in CCl4 solution at 480C, show that the reaction is first order

 ( N2O5 🡪 2NO2 + O2)

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| t/min | 10 | 15 | 20 |  |
| Vol. of O2 evolved / ml | 6.3 | 8.95 | 11.4 | 34.75 |

Solution: - For the first order reaction the integrated rate equation is

Y=2.06×10-3 + 0.01976X

R=0.99998

THEN THE REACTION IS FIRST ORDER

 

Q:- Trichloroethanoic acid is readily decarboxylated in aqueous solution

CCl3COOH(aq.) 🡪 CHCl3(aq.) + CO2(g)

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Vol.CO2/ml | 2.25 | 8.3 | 14.89 | 31.14 | 40.04 |
| t/min | 330 | 1200 | 2400 | 7760 |  |

Show the reaction to be first order, and calculate the time taken for the initial concentration of CCl3COOH to fall by 25 per cent.

 For first order reaction =kt

 or

The least square equation is

y=3.694+(-1.94×10-4)x

r=-0.9998

Then the reaction is first order

k=1.94×10-4 min-1

When 25 per cent of the CCl3COOH has reacted, 25 per cent of the final amount of

CO2 will have been formed, i.e. 10.01 ml

ln(40.04-10.01)=ln(40.04)- 1.94×10-4t

t = 1485 min

t/min

Inversion of sucrose:-

Q: - The optical rotation of sucrose in 0.9N HCl at various time intervals is given in the table below

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| t/min | 0 | 7.18 | 18 | 27.1 |  |
| Rotation/degree | +24.09 | +21.4 | +17.7 | +15 | -10.74 |

Show that inversion of sucrose is a first order reaction.

The integral rate equation for first order reaction can be written as follows

 kt =

Time/min

Y=A+BX

=kt

Y = A + BX

Y=8.45×10-4+0.011X

R=0.999996

Then the reaction is first order

**Second order reactions with different initial concentrations**

 A + B 🡪 Product

When [A]o ≠ [B]o then

 Kt =

 a=[A]o b=[B]o

or =

 then = + ……….1

if the (in y axis) plotted against (t) in x axis

 or = + ………2 if

Q: - The table below shows the data for the second order reaction

 R1COOR + OH- 🡪 R1COO- + ROH

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| t/min | 0 | 5 | 17 | 36 | 65 |
| (a-x)/mM | 19.75 | 14.75 | 9.4 | 5.93 | 3.57 |
| (b-x)/mM | 20.85 | 15.85 | 10.5 | 7.03 | 4.67 |

Calculate k.

 then we use eq. 2

Time/min

 Y = 0.0547 + 3.273×10-3 X

 Intercept = 0.0547 =

Slope = (b-a)k = 3.273×10-3

 k = 3.273×10-3 / (20.85-19.75)

 k = 0.00297 mM-1.min-1.

**\*Using integrated rate law for a gaseous reaction**

Q: - A gas reaction (2A 🡪B) is second order in A and goes to completion in a reaction vessel of constant volume and temperature with a half-life of 1h. If the initial pressure of A is 1atm, what are the partial pressure of A and B, and what is the total pressure at 1h, 2h, and at equilibrium?

 2A 🡪 B

 Po zero before reaction

 Po-2x x

PT = PA+PB = Po-2x + x = Po – x ===> x= Po - PT

Then PA= Po-2x = Po – 2(Po- PT) = 2PT – Po -----------1

PB = x = Po - PT ------------2

 For second order reaction

 kt = and =

 k = = 1 atm-1.h-1.

1. At 1h

 1 atm-1.h-1 × 1h =

 PA = 0.5 atm.

In eq.1 PT = = = 0.75 atm.

 PB = 1-0.75 = 0.25 atm.

1. At 2h

 PA = 0.3333 atm.

 PT = 0.6666 atm.

 PB = 0.3333 atm.

1. At (equil.) PA = zero

 Then PT = 0.5 atm. PB = 0.5 atm.

Q: - The gaseous reaction (A2🡪 2A) is first order in A2 , after 751 sec. 64.7% of A2 remains undecomposed. Calculate

1. The half-life
2. The length of time required to decompose 90% of A2.

For first order reaction

 = kt

 or = kt

 k = = 5.798 × 10-4 sec-1.

1. = = 1196 sec.
2. t = = 3971 sec.

Q: - The first order rate constant for the gas phase decomposition of dimethyl ether,

(CH3)2O 🡪 CH4 + H2 + CO

Is 3.2 × 10-4 S-1 at 450oC. The reaction is carried out in a constant volume container , initially only dimethyl ether is present , and the pressure is 0.350 atm. . what is the pressure of the system after 8 min ? assume ideal gas behavior.

PT= Po-x+3x = PO + 2x

 = 3.2 × 10-4 × 8 × 60

 PO-x = 0.3 ==🡺 x = 0.05 atm.

 PT = PO + 2x = 0.35 + 2 \* 0.05 = 0.45 atm.

**Complex reactions: -**

1. Reversible reactions

K1

 A B

k-1

 = -k1[A] + k-1[B] ……………(1)

At equilibrium, there is no net change in the concentration of A with time

Then = 0 ……………..(2)

Eq.1 became

 k1[A] = k-1[B] ====> ………(3)

Where K is the equilibrium constant

We have

Δ[B] = -Δ[A]

So [B]-[B]o = -([A]-[A]o)

Or [B] = [B]o+[A]o-[A] …………..(4)

By substituting eq.4 into eq1

 -k1[A] + k-1[B]o+ k-1[A]o- k-1[A] …………(5)

 At ( t 🡪 ) the system reaches equilibrium , the rates of the forward and reverse reactions having become equal.

At equilibrium (eq.2) = 0 and [A]=[A]eq

Then k-1[B]o+ k-1[A]o = (k1+k-1)[A]eq …………….(6)

By sub. eq 6 into eq 5

 -k1[A] - k-1[A] + (k1+k-1)[A]eq

 = (k1+k-1)[A]eq – (k1+k-1)[A] = (k1+k-1)( [A]eq-[A]) ….(7)

Or = (k1+k-1)dt ………..(8)

By integration eq 8 then

 = (k1+k-1) t ……………….(9)

Or ……..(10)

Or = (k1+k-1) t or = (k1+k-1) t

Note

time

concentration

1. **Consecutive Reactions: -**

A consecutive reaction is one in which the product from the first step becomes the reactant for the second step, and so on.

Ex.

1. CH3COCH3 🡪 CH2=CO + CH4

 CH2=CO 🡪 CO + ½ C2H4

1. 🡪 +

 🡪 +

For a two-step consecutive reaction, we have

K2

K1

 A B C

R1= k1 [A] R2 = k2 [B]

 = - k1 [A] ---------(1) = k2 [B] ----------(3)

Because the decrease in A is first order, we write

 -----------------(4)

By applying the steady state approximation for the intermediate B, that is

Or

In eq. 3 ==🡺

By substituting equation 6 in equation 7

 Note

 =

1. Parallel Reactions (Competing Reactions)

Frequently a species can react in different ways to give a variety of products. For example, in the nitration of bromobenzene, ortho, meta, and para nitrobromobenene are obtained.



 we shall consider the simplest case, that of two parallel irreversible first order reaction

K2

K1

 A B A C

K1

 B

 or A

K2

 C

 HOW?

and HOW?

1. Chain Reaction

For example

 CH3CHO(g) 🡪 CH4 (g) + CO(g)

 Prove that the rate law is R = k [CH3CHO

CH3CHO 🡪 .CH3 + .CHO R=ki[CH3CHO] initiation

CH3CHO + .CH3 🡪 CH3CO. + CH4 R=kp[CH3CHO][.CH3]

Propagation

CH3CO. 🡪 .CH3 + CO R=k’p[CH3CO.]

.CH3 + .CH3 🡪 C2H6 R= kt[.CH3]2 termination

Sol.: -

 kp[CH3CHO][.CH3] ---------(1)

 = ki[CH3CHO] + k’p[CH3CO.] - kp[CH3CHO][.CH3] -2 kt[.CH3]2-------(2)

 = kp[CH3CHO][.CH3] - k’p[CH3CO.] -------(3)

By steady state approximation

 = = 0

Eq 2 + eq 3 = 0

ki[CH3CHO] + k’p[CH3CO.] - kp[CH3CHO][.CH3] -2 kt[.CH3]2 + kp[CH3CHO][.CH3] - k’p[CH3CO.]=0

Then ki[CH3CHO] = 2 kt[.CH3]2 ---------(4)

and [.CH3] = [CH3CHO]1/2 ----------(5)

by substitution equation 5 in eq 1

 = R = kp[CH3CHO] × [CH3CHO]1/2

 If kp × = K

 Then R = K [CH3CHO]3/2

**Reaction Mechanisms**

Many reactions that follow simple rate laws occur through a series of steps, these steps are called elementary reactions because they cannot be broken down further into simpler chemical reactions.

The sequence of elementary reactions that add up to give the overall reaction is called the mechanism of the reaction.

The mechanism of a reaction leads directly to a set of differential equations that completely describe the kinetic behavior of that mechanism.

There are two approximation methods that yield expression for the rate of the overall reaction in terms of concentration of the various reactants and products and the rate constants.

1. Steady state method.

The net change of the concentration of intermediate with the time is zero.

1. Rapid equilibrium method.

The slow step in the mechanism is the rate determining step.

Example

For this reaction ( A + B 🡪 D )

Consider the following mechanism

K1

 A + B C

K2

K3

 C D

Derive the rate law using the steady state approximation to eliminate the concentration of C.

 R = = ---------- (1)

 ---------- (2)

By steady state approximation

 Then = --------- (3)

Then the rate of reaction = R = =

**Reaction Mechanism**

Q:- For this reaction

Br-

H+ + HNO2 + C6H5NH2 C6H5N2+ + 2H2O

The rate law is observed to

 R = -------- (1)

Prove that the rate law is suitable when the proposed mechanism is:-

K1

 H+ + HNO2  H2NO2+ rapid equilibrium

K-1

K2

 H2NO2+ + Br- ONBr + H2O slow

 ONBr + C6H5NH2 C6H5N2+ + H2O + Br-  fast

We can say that the rate of the reaction is

 R = ------- (2)

But the species is an intermediate so

 ( steady state approximation )

 Then = ------------ (3)

 ---------------- (4)

By applying the rate determining step approximation

 k-1 >> k2[Br-]

Then eq.4 becomes

 ------------(5)

By substituting eq.5 in eq.2

R = k2 [Br-] =

If = K

Then R = K

Q: - For this reaction

 H2O2 + 2H+ + 2I- 🡪 I2 + 2H2O

Find the rate law, suppose one mechanism

K1

 H+ + I- HI rapid equilibrium

K-1

 HI + H2O2 H2O + HOI slow

K2

K3

 HOI + I- I2 + OH- fast

K4

 OH- + H+ H2O fast

 Solution:-

 R = k2 [HI] [H2O2] ---------(1)

 ---------(2)

By steady state approximation

 Then [HI] = --------(3)

By substituting eq. 3 in eq. 1

 R = ------------(4)

By applying Rate-Determining step approximation

 k-1 >> k2 [H2O2]

 R = k [H+][I-][H2O2] -------------(5)

Q: - Apply the steady-state approximation and R.D.S.A to the mechanism

K1

 A + B C + D Rapid equilibrium

K2

K-1

 D + E F + B Slow

to obtained the rate law .

 R = -----------(1)

 --------(2)

By applying S.S.A

Then [D] = -----------(3)

By sub eq 3 into eq 1

 R = ------------(4)

By R.D.S.A

 k-1[C] >> k2[E]

Then R = ---------------(5)

Q: - For a reversible first order reaction

K1

 A B

K2

k1= 10-2 s-1 , k-1= 0.0025 s-1 , [A]o = 1 M , and [A]equ.= 0.1 M .

Calculate the concentration of [A] after 30 sec.

 = (k1+k-1) t

 = (0.01+0.0025) 30

[A] = 0.718 mol/L.

Q : For the first order consecutive reaction type

K1

K2

 A B C

After 30 min of the initiation of reaction we found that the concentration of C = 0.259 mol/L.

If k1 = 0.01 min-1 , and k2 = 1min-1 .

Calculate [A]o and concentration of A and B after 30 min.

 0.259 = [A]o ( 1- )

[A]o = 1 mol/L

[B] =

[B] = 7.408 × 10-3 mol/L

 then = 0.7408 mol/L

Q: - Consider the parallel reaction

K1

B

 A

C

K2

In an experiment it was observed that 60% decomposition of A takes place in 20 min. and analysis of product showed that 75% of B and 25 % of C are present . calculate k1 and k2 .

 = = 3

 K1 = 3k2

K2 = 0.01145 min-1.

K1= 0.0344 min-1.

**Rate influencing factors**

The effect of Temperature on Reaction Rate

Reaction rate

Reaction rate

T/Ko

T/Ko

(b)

(a)

Reaction rate

Reaction rate

T/Ko

T/Ko

(c)

(d)

These figures shows four types of temperature dependence for reaction rate constants.

1. Represent normal reactions whose rates increase with increasing temperature.
2. Enzyme catalyzed reaction.
3. Complex mechanism (some exothermic reaction).
4. Chain reaction. Explosive .

The Arrhenius Equation

In 1889 , Arrhenius discovered that the temperature dependence of many reactions could be described by the following equation: -

k = rate constant

A = frequency factor or pre-exponential factor

Ea = Activation energy J/mol or cal/mol

R = gas constant

T = absolute temperature.

The activaton energy is the minimum amount of energy required to initiate the chemical reaction.

(A) represents the frequency of collisions between reactant molecules ( A have the same units of the rate constant ).

 Exp ( -Ea/RT ) resembles the Boltzman distribution law , it represents the fraction of molecular collisions that have energy equal to or greator than the activation energy (Ea)

A high activation energy signifies that the rate onstant depends strongly on temperature.

**Energy**

**Activated state**

**Ea for forward reaction**

**Ea for reverse reaction**

**Reactants**

**Products**

 

**Arrhenius Equation**

Q: - Determine A and Ea from the following data

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| T / oK | 300 | 350 | 400 | 450 | 500 |
| K / l.mol-1.s-1 | 7.9×106 | 3×107 | 7.9×107 | 1.7×108 | 3.2×108 |

|  |  |
| --- | --- |
| 1/T | Ln k |
| 3.33×10-3 | 15.88 |
| 2.86×10-3 | 17.22 |
| 2.50×10-3 | 18.18 |
| 2.22×10-3 | 18.95 |
| 2.00×10-3 | 19.58 |

 By plotting a curve between 1/T and (ln k) we can calculate A and Ea

y=25.11 + (-2767.34x)

r=0.9999

Slope = -2767.34 =

Q: - Determine A and Ea from the following data: -

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| T/ok | 700 | 730 | 760 | 790 | 810 | 840 | 910 | 1000 |
| k/dm3.mol-1.s-1 | 0.011 | 0.035 | 0.105 | 0.343 | 0.789 | 2.17 | 20 | 145 |

Ans.

A = 1.1×1012 l.mol-1.s-1 Ea= 188.32 kJ/mol

Q: - the rate constant of a first order reaction is 4.6×10-4 s-1 at 350oC . If the activation energy is 104 kJ/mol . Calculate the temperature at which its rate constant is 8.8×10-4 s-1.

Sol. 1- ln A = 12.38 ( k1 and Ea and T1 are known )

 T2 = 644.08 oK = 371 oC

 Or 2-

 T2 = 644.08 oK = 371 oC

Q1: - 20% for a particular reaction completed in 12.5min at 300oK, and the same percent completed in 3.2min at 340oK, calculate activation energy if the reaction is first order .

Q2: - The gas-phase reaction between methane (CH4) and diatomic sulpher (S2) is given by the equation

 

At 550oC the rate constant for this reaction is 1.1 l.mol-1.s-1 and at 625oC the rate constant is 6.4 l.mol-1.s-1 .

Calculate Ea for this reaction.

Q3: - Many reactions double their rates with every 10o rise in temperature .Assume that such a reaction takes place at 305oK and 315oK. What must its activation energy be for this statement to hold?

Q4: - Consider the following parallel reactions

B

k1

 A

k2

C

The activation energies are 45.3 kJ/mol for k1 and 69.8 kJ/mol for k2 . If the rate constants are equal at 320 oK , at what temperature will k1/k2 = 2 ?