

CHEMICAL KINETICS NUMERICALS

1) Write the differential rate equations for the following reactions, assuming them to be elementary reactions.



$$\text{Sol}^2: \text{a) Rate} = -\frac{d[A]}{dt} = -\frac{1}{2} \frac{d[B]}{dt} = -\frac{1}{3} \frac{d[C]}{dt}$$

$$\text{b) rate} = -\frac{d[A]}{dt} = -\frac{1}{3} \frac{d[B]}{dt}$$

$$= \frac{1}{2} \frac{d[C]}{dt} = \frac{1}{1} \frac{d[D]}{dt} = \frac{1}{2} \frac{d[E]}{dt}$$

2) The rate of the reaction



is doubled when the Cl_2 concentration is doubled, but increases by a factor of 8 when the concentrations of both the reactants are doubled.

Determine the overall order of the reaction and the order w.r.t. NO & Cl_2 .

$$\text{Sol}^2: \text{Rate} = k [\text{NO}]^a [\text{Cl}_2]^b$$

If orders $a=0$ and $b=1 \Rightarrow n=k[\text{Cl}_2]$, which does not satisfy the conditions.

If $a=1$ & $b=1 \Rightarrow r = k_2[\text{NO}][\text{Cl}_2]$

which again does not satisfy the conditions.

If $a=0$, $b=2 \Rightarrow r = k_2[\text{Cl}_2]^2$

→ Also not acceptable.

If $a=1$, $b=2 \Rightarrow r = k_2[\text{NO}][\text{Cl}_2]^2$

(condition 1 met but not 2)

∴ If $a=2$, $b=1 \Rightarrow \text{rate} = k_2[\text{NO}]^2[\text{Cl}_2]$

In this case, both conditions are met.

∴ Overall order = $2+1 = 3$

Order wrt NO = 2

Order wrt $\text{Cl}_2 = 1$

3) At 1100K, the following data were obtained



	$[\text{NO}]/\text{mol L}^{-1}$	$[\text{H}_2]/\text{mol L}^{-1}$	Rate ($\text{mol L}^{-1}\text{s}^{-1}$)
a)	5×10^{-3}	2.5×10^{-3}	3×10^{-5}
b)	15×10^{-3}	2.5×10^{-3}	9×10^{-5}
c)	15×10^{-3}	10×10^{-3}	36×10^{-5}

Calculate 1) order wrt NO, H_2 , & overall order

2) rate constant

Also, 3) write the complete rate expression

4) what is the rate if $[\text{NO}] = [\text{H}_2]$
 $= 8 \times 10^{-3} \text{ mol L}^{-1}$?

Sol²: 1) Rate = $k[\text{NO}]^a [\text{H}_2]^b$

From a) & b); $(\text{rate})_a = k [5 \times 10^{-3}]^a [2.5 \times 10^{-3}]^b - a$

$(\text{rate})_b = k [15 \times 10^{-3}]^a [2.5 \times 10^{-3}]^b - b$

Dividing a by b;

$$\frac{r_a}{r_b} = \left(\frac{1}{3}\right)^a = \frac{3 \times 10^{-5}}{9 \times 10^{-5}}$$

$$\Rightarrow \left(\frac{1}{3}\right)^a = \frac{1}{3} \Rightarrow \boxed{a=1}$$

Thus, order wrt NO is 1.

Similarly, on treating b) & c) in the same manner, we get;

$$\frac{r_b}{r_c} = \frac{9 \times 10^{-5}}{36 \times 10^{-5}} = \frac{[2.5 \times 10^{-3}]^b}{[10 \times 10^{-3}]^b}$$

$$\Rightarrow \frac{1}{4} = \left(\frac{1}{4}\right)^b \Rightarrow \boxed{b=1}$$

Thus, order wrt H₂ is 1.

\therefore Overall order = $1+1 = \underline{\underline{2}}$ (i.e.,
second
order
rxn)

2) RATE CONSTANT; $k = \frac{\text{rate}}{[\text{NO}][\text{H}_2]}$

$$= \frac{3 \times 10^{-5} (\text{mol L}^{-1} \text{s}^{-1})}{[5 \times 10^{-3}] [2.5 \times 10^{-3}] (\text{mol L}^{-1})^2}$$

$$k = 30 \text{ L mol}^{-1} \text{s}^{-1}$$

12.5

$$\therefore k = 2.4 \text{ L mol}^{-1} \text{s}^{-1}$$

3) COMPLETE RATE EXPRESSION: $r = k[\text{NO}][\text{H}_2]$

4) If $[\text{NO}] = [\text{H}_2] = 8 \times 10^{-3} \text{ mol L}^{-1}$,

$$\text{rate} = k[\text{NO}][\text{H}_2]$$

$$= (2.4 \text{ L mol}^{-1} \text{s}^{-1}) (8 \times 10^{-3})^2 (\text{mol L}^{-1})^2$$

$$= 1.536 \times 10^{-4} \text{ mol L}^{-1} \text{s}^{-1}$$

4) SIMILAR QUESTION AS 3)

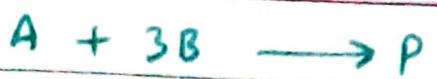
Consider the following data for



	$[\text{A}]/\text{mol L}^{-1}$	$[\text{B}]/\text{mol L}^{-1}$	Rate/ $\text{mol L}^{-1} \text{s}^{-1}$
a)	6×10^{-3}	1×10^{-3}	0.012
b)	6×10^{-3}	2×10^{-3}	0.024
c)	2×10^{-3}	1.5×10^{-3}	0.002
d)	4×10^{-3}	1.5×10^{-3}	0.008

Calculate 1) Order wrt A, B, and overall order
2) Rate constant

5) For the second-order reaction

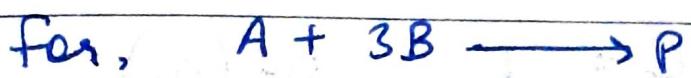


the differential rate equation is

$$\frac{dx}{dt} = k_2(a-x)(b-3x).$$

Integrate this rate equation. a & b are initial concentrations of A & B , and x is pdt. concenⁿ.

Sol²:



At time 't' $(a-x)$ $(b-3x)$ \propto

$$\therefore \frac{dx}{dt} = k_2(a-x)(b-3x)$$

$$\Rightarrow \int \frac{dx}{(a-x)(b-3x)} = k_2 dt$$

Resolving into partial fractions,

$$\frac{1}{(a-x)(b-3x)} = \frac{1}{(3a-b)} \left[\frac{3}{(b-3x)} - \frac{1}{(a-x)} \right]$$

Thus,
$$\int \frac{dx}{(a-x)(b-3x)} = \frac{1}{(3a-b)} \left\{ \int \frac{3 dx}{(b-3x)} - \int \frac{dx}{(a-x)} \right\}$$

$$= k_2 t + C$$

$$\Rightarrow \frac{1}{(3a-b)} \left[-\ln(b-3x) + \ln(a-x) \right] = k_2 t + C$$

$$\Rightarrow \frac{1}{(3a-b)} \frac{\ln \frac{(a-x)}{(b-3x)}}{} = k_2 t + C$$

At $t=0, x=0$, we have,

$$C = \frac{1}{(3a-b)} \ln \left(\frac{a}{b} \right)$$

$$\Rightarrow \frac{1}{(3a-b)} \frac{\ln \frac{(a-x)}{(b-3x)}}{} = k_2 t + \frac{1}{(3a-b)} \ln \left(\frac{a}{b} \right)$$

or, $\frac{1}{(3a-b)} \left[\ln \frac{(a-x)}{(b-3x)} - \ln \left(\frac{a}{b} \right) \right] = k_2 t$

or,
$$\boxed{\frac{1}{(3a-b)} \ln \left[\frac{b(a-x)}{a(b-3x)} \right] = k_2 t}$$

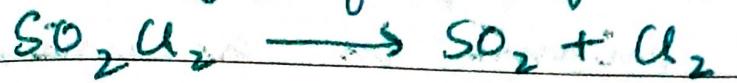
Integrated Rate Equation

(6) SIMILARLY, for the 3rd order reaction
 $2A + B \rightarrow P$

the differential rate equation is,
 $\frac{dx}{dt} = R_3 (a-2x)^2 (b-x).$

Integrate the rate equation.

7) The half-life of the gaseous reaction:



which obeys first-order kinetics, is 8 min. How long will it take for the concentration of SO_2Cl_2 to be reduced to 1% of its initial value?

Sol²:

$$k_1 = \frac{0.693}{t_{1/2}} = \frac{0.693}{8 \text{ min}} = 0.087 \text{ min}^{-1}$$

$$\text{Also, } t_{1/2} = \frac{1}{k_1} \ln \left(\frac{a}{a-x} \right)$$

$$= \frac{1}{0.087 \text{ min}^{-1}} \ln \left(\frac{100}{1} \right) = \underline{\underline{52.93 \text{ min}}}$$

8) A 1st order reaction is 25% completed in 30 min. Determine the $t_{1/2}$.

9) Deduce the rate constant and $t_{1/2}$ for the n^{th} order reaction.



10) If 1% decomposition occurs in the first minute in a unimolecular reaction, calculate how much would remain undecomposed at the completion of the first hour.

Solⁿ: For a unimolecular reaction;

$$k = \frac{2.303}{t} \log \left(\frac{a}{a-x} \right)$$

here,

$$a = 100 ; (a-x) = 100-1 = 99$$

$$t = 1 \text{ min}$$

$$\therefore k = \frac{2.303}{1 \text{ min}} \log \left(\frac{100}{99} \right)$$

$$= 0.01 \text{ min}^{-1}$$

When, $t = 60 \text{ min}$,

$$k = \frac{2.303}{60 \text{ min}} \log \frac{100}{(a-x)}$$

$$\Rightarrow (0.01 \text{ min}^{-1}) = \frac{2.303}{60 \text{ min}} \log \frac{100}{(a-x)}$$

$$\Rightarrow \frac{60 \times 0.01}{2.303} = \log 100 - \log (a-x)$$

$$\Rightarrow 0.2605 = 2 - \log (a-x)$$

$$\Rightarrow 1.7395 = \log (a-x)$$

$$\Rightarrow (\text{antilog}) 1.7395 = (a-x) = 54.89$$

Thus, 54.89% is the undecomposed reactant.

ii) The values of Arrhenius factor and E_a are $4 \times 10^{13} \text{ s}^{-1}$ and 98.6 kJ mol^{-1} for a 1st order reaction. Calculate the temperature at which its half-life is 10 min.

$$\text{Sol}^2: \text{For 1}^{\text{st}} \text{ order rxn; } k = \frac{0.693}{t_{1/2}} = \frac{0.693}{600 \text{ s}} \\ = 1.155 \times 10^{-3} \text{ s}^{-1}$$

$$\text{Also, } k = A e^{-E_a/RT}$$

Taking log,

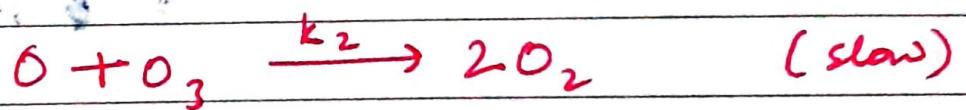
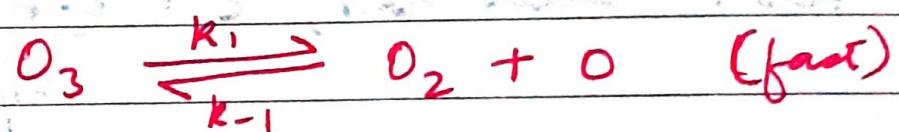
$$\ln k = \ln A - \frac{E_a}{RT}$$

$$\Rightarrow \ln k - \ln A = - \frac{E_a}{RT}$$

$$\Rightarrow 2.303 \log \left(\frac{k}{A} \right) = - \frac{E_a}{RT} \quad \cancel{\Rightarrow}$$

$$\begin{aligned}
 a) T &= \frac{E_a}{2.303 R \log \left(\frac{A}{k} \right)} \\
 &= \frac{(98600 \text{ J mol}^{-1})}{(2.303)(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \log \left(\frac{4 \times 10^{-3}}{1.155 \times 10^{-3}} \right)} \\
 &= \frac{98600}{2.303 \times 8.314 \times 16.539} \text{ K} = 311.35 \text{ K}
 \end{aligned}$$

(2) For the gaseous decomposition of ozone, the following steps take place:



Determine the rate law, employing SSA.

$$\begin{aligned}
 \text{Sol: } \frac{d[O]}{dt} &= k_1 [O_3] - k_{-1} [O_2][O] \\
 &\quad - k_2 [O][O_3]
 \end{aligned}$$

$$\text{Applying SSA, } \frac{d[O]}{dt} = 0$$

$$\Rightarrow k_1 [O_3] - k_{-1} [O_2][O] - k_2 [O][O_3] = 0$$

$$\Rightarrow [O] = -k_1 [O_3]$$

$$k_1 [O_2] + k_2 [O_3]$$

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The rate of the reaction; $\frac{d[O_2]}{dt} = 2k_2 [O][O_3]$ — (2)

Substituting (1) in (2);

$$\Rightarrow \frac{d[O_2]}{dt} = 2k_2 [O_3] \times \frac{k_1 [O_3]}{k_1 [O_2] + k_2 [O_3]}$$

$$\boxed{\text{rate} = \frac{2k_1 k_2 [O_3]^2}{k_1 [O_2] + k_2 [O_3]}} = \cancel{2k_1 [O_3]^2}$$

(3) The rate constant of a 2nd order rxn is $5.7 \times 10^{-5} \text{ L mol}^{-1} \text{ s}^{-1}$ at 25°C, and $1.64 \times 10^{-4} \text{ L mol}^{-1} \text{ s}^{-1}$ at 40°C. Calculate i) the Ea value
ii) the Arrhenius factor A

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

$$\text{i) } E_a = \frac{R(T_1 T_2)}{(T_2 - T_1)} \ln \left(\frac{k_2}{k_1} \right)$$

$$\Rightarrow E_a = \left(8.314 \frac{\text{J K}^{-1} \text{mol}^{-1}}{\text{J mol}^{-1}} \right) \left(\frac{313 \times 298}{15} \right) K \times 2.303 \log \left(\frac{1.64 \times 10^{-4}}{5.7 \times 10^{-5}} \right)$$

$$= (119062 \text{ J mol}^{-1}) \times \log (2.8772)$$

$$= 119062 \times 0.4590 \text{ J mol}^{-1}$$

$$E_a = 54.65 \text{ kJ mol}^{-1}$$

Q14) Can the activation energy be zero or negative?

Sol²: If $E_a = 0$; $k = A e^{-E_a/RT}$

$$k = A$$

i.e., every collision between molecules leads to the chemical reaction, which

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does not happen in reality. \therefore It is not true
and thus, E_a cannot have zero value.

$$\text{If } E_a = -\infty; k = A e^{+\frac{E_a}{RT}} \\ = A e^x \quad (x = \frac{E_a}{RT})$$

$$e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \dots$$

$$= 1 + x \quad (\text{neglecting higher powers of } x) \\ = 1 + \frac{E_a}{RT}$$

$$\therefore k = A \left(1 + \frac{E_a}{RT} \right)$$

i.e., $\boxed{R > A}$

This is an absurd result also, as the
rate of the reaction cannot exceed the
number of colliding molecules.
Thus, E_a cannot be negative.

15) The optical rotations of sucrose in 0.5 M HCl at 35°C at various time intervals are given below. Show that the reaction is of 1st order

time (min)	0	10	20	30	40	∞
rotation (degrees)	+32.4	+28.8	+25.5	+22.4	+19.6	-11.1

Sol²: For the above reaction to be 1st order, it should follow the equation:

$$k_1 = \frac{1}{t} \ln \frac{\alpha_0 - \alpha_\infty}{\alpha_t - \alpha_\infty}$$

where, α_0 , α_t , and α_{∞} represent the optical rotations at the beginning, at time t , and at the completion of rxn, resp.

$$\begin{aligned} \text{Here, } \alpha &= \alpha_0 - \alpha_{\infty} \\ &= 32.4 - (-11.1) \\ &= 43.5 \end{aligned}$$

The value of k at different times is:

Time (min)	α_t (°)	$\alpha_t - \alpha_{\infty}$	$k_1 = \frac{1}{t} \ln \frac{\alpha_0 - \alpha_{\infty}}{\alpha_t - \alpha_{\infty}}$ (min ⁻¹)
10	+28.8	39.9	$\frac{1}{10} \ln \frac{43.5}{39.9} = 0.0008625$
20	+25.5	36.6	$\frac{1}{20} \ln \frac{43.5}{36.6} = 0.0008625$
30	+22.4	33.5	$\frac{1}{30} \ln \frac{43.5}{33.5} = 0.008694$
40	+19.6	30.7	$\frac{1}{40} \ln \frac{43.5}{30.7} = 0.008717$

Since k_1 is nearly constant, hence, the given reaction follows 1st order kinetics.

ANSWERS

4)

1) Order wrt A = 2

2) $k = 3.3 \times 10^5 \text{ L mol}^{-2} \text{s}^{-1}$

Order wrt B = 1

Overall order = 3

6)

$$k_3 t = \frac{1}{(2b-a)^2} \left[\ln \frac{b(a-2x)}{a(b-x)} + \frac{(2b-a)(2x)}{a(a-2x)} \right]$$

8) $t_{1/2} = 72.9 \text{ min.}$

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9) $k = \frac{1}{t(n-1)} \left[\frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}} \right]$

$$t_{1/2} = \frac{1}{k(n-1)} \left[\frac{2^{n-1} - 1}{a^{n-1}} \right]$$