I.9 Chemical Kinetics

Civil Services 2016–2026: **29** parts, **305** marks · IFoS 2016–2025: **22** parts, **233** marks

Syllabus. Differential and integral rate equations for zeroth, first, second and fractional order reactions; rate equations involving reverse, parallel, consecutive and chain reactions; branching chain and explosions; effect of temperature and pressure on rate constant. Study of fast reactions by stop-flow and relaxation methods. Collisions and transition state theories.

Marks	2016	2017	2018	2019	2020	2021	2022	2023	2024	2025	2026
CSE	20	25	25	30	40	30	30	30	25	20	30
IFoS	15	15	23	20	38	23	23	23	25	28	

How to use this chapter. Read every question once and mark the ones that repeat. Pick three, write them by hand against the clock (about 7 minutes for 10 marks), then compare with the model answers on vkcscience.com.

2026

CSE 2026 · Q1(h) Activation energy of food spoilage [5 marks]

Everyday experience demonstrates that food will spoil outside in a hot summer day much faster than it would be in a refrigerator. Estimate the activation energy of these decomposition processes by assuming that food will spoil about 40 times faster at a temperature of 30 °C than at a temperature of 8 °C.

CSE 2026 · Q4(b) Rate constants of A ⇌ B + C from a temperature jump; Rate coefficients of two parallel first-order reactions [25 marks]

(i) The equilibrium $A \rightleftharpoons B + C$ at 25 °C is subjected to a sudden temperature increase that slightly increases the concentrations of B and C. The measured relaxation time is 3.0 μs. The equilibrium constant for the system is 2.0×10^{-16} mol dm^{-3} at 25 °C, and the equilibrium concentrations of B and C at 25 °C are both 2.0×10^{-4} mol dm^{-3}. Calculate the rate constants involved in the system.

(ii) A substance B converts simultaneously to the products D and D' by two parallel elementary reactions $D \xleftarrow{k_1} B \xrightarrow{k_2} D'$. The initial concentration of B is $C_{B,0}$ = 0.5 kmol m^{-3}. After 40 minutes, the concentration of B has decreased to 0.05 kmol m^{-3}; in the same time, the product D' with a concentration $C_{D'}$ = 0.1 kmol m^{-3} is formed. Calculate the rate coefficients k_1 and k_2.

2025

CSE 2025 · Q5(a) Activation energy from two rate constants [5 marks]

The gas-phase reaction between methane (CH_4) and diatomic sulphur (S_2) is given by the following reaction:

$$CH_4(g) + 2\,S_2(g) \longrightarrow CS_2(g) + 2\,H_2S(g)$$

At 823 K, the rate constant for this reaction is 1.1×10^{-3} m^3 mol^{-1} S and at 898 K, the rate constant is 6.4×10^{-3} m^3 mol^{-1} S. Calculate the activation energy for this reaction.

[Given: R = 8.3145 J K^{-1} mol^{-1}]

CSE 2025 · Q5(d) Showing that a decomposition is first order [5 marks]

From the following data for the decomposition of ammonium nitrite in aqueous solution, show that the reaction is of the first order.

Time (minutes)	10	15	20	25	∞
Volume of N_2 (cc)	6.25	9.00	11.40	13.65	35.05

CSE 2025 · Q7(d) Second-order rate law with unequal concentrations; units of k [10 marks]

(i) Consider a second-order reaction:

$$A + B \longrightarrow P$$

where the initial concentration of A is 'a' mol dm^{-3} and that of B is 'b' mol dm^{-3}. After time 't', x mol dm^{-3} of A and x mol dm^{-3} of B react to form x mol dm^{-3} of the product, P.

Show that the second-order rate constant for this reaction will be given by $k_2 = \frac{1}{(a-b)t} \ln\left[\frac{b(a-x)}{a(b-x)}\right]$ with the assumption that $a > b$. What will be the unit of k_2? (Consider time in seconds)

(ii) Determine the units of the rate constants for zeroth-order and $\frac{5}{2}$ order reactions. Assume that concentrations are expressed in mol dm^{-3} and time in seconds.

IFoS 2025 · Q5(a) Order from total-pressure measurements [8 marks]

The following gas-phase reaction was studied at 290 °C by observing the change in pressure as a function of time in a constant volume vessel:

$$ClCO_2CCl_3(g) \longrightarrow 2\,COCl_2(g)$$

Determine the order of the reaction and rate constant based on the following data:

Time (s)	*P* (mmHg)
0	15.76
181	18.88
513	22.79
1164	27.08

where *P* is the total pressure.

[Use graph sheets]

IFoS 2025 · Q6(a)(i) Ozone decomposition [10 marks]

(i) The decomposition of ozone, $2\,O_3(g) \longrightarrow 3\,O_2(g)$, occurs by the reaction mechanism

$$M(g) + O_3(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2(g) + O(g) + M(g)$$

$$O(g) + O_3(g) \xrightarrow{k_2} 2\,O_2(g)$$

where *M* is a molecule that can exchange energy with the reacting ozone molecule through a collision but *M* itself does not react. Using this mechanism, derive the rate law expression for $\frac{d[O_3]}{dt}$ assuming that the intermediate, O(g), concentration can be treated by the steady-state approximation. [10]

IFoS 2025 · Q6(b)(i) Arrhenius temperature from half-life [10 marks]

(i) A first-order reaction has an activation energy of 104500 J mol^{-1} and the pre-exponential factor, *A*, in the Arrhenius equation has a value of 5.0×10^{13} s^{-1}. At what temperature will the reaction have a half-life of 1 minute?

[Given: $R = 8.314$ J K^{-1} mol^{-1}] [10]

2024

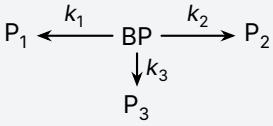
CSE 2024 · Q1(e) Temperature at which the uncatalysed reaction matches catalase at 20 °C [10 marks]

The activation energy for the decomposition of hydrogen peroxide $2\,H_2O_2(aq) \longrightarrow 2\,H_2O(l) + O_2(g)$ is 42 kJ/mol, whereas when the reaction is catalyzed by enzyme catalase, it is 7.0 kJ/mol. Calculate the temperature that would cause the uncatalyzed reaction to proceed as rapidly as the enzyme catalyzed decomposition at 20 °C. Assume the frequency factor A to be the same in both cases.

CSE 2024 · Q4(c) Time of maximum concentration of B in A → B → C; Yield of P_1 from three parallel paths [15 marks]

(i) For the sequential reaction $A \xrightarrow{k_A} B \xrightarrow{k_B} C$, the rate constants are $k_A = 5 \times 10^6\ s^{-1}$ and $k_B = 3 \times 10^6\ s^{-1}$. Determine the time when the concentration of B is at a maximum. *10*

(ii) In acidic condition, benzyl penicillin (BP) undergoes the following reaction:



Imagine while swallowing penicillin, pH of the stomach is ~ 3. At this pH, and temperature 22 °C, the rate constants for the processes are: $k_1 = 7.0 \times 10^{-4}\ s^{-1}$, $k_2 = 4.1 \times 10^{-3}\ s^{-1}$, $k_3 = 5.7 \times 10^{-3}\ s^{-1}$. What is the yield of P_1 formation? *5*

IFoS 2024 · Q2(c) Arrhenius parameters from a logarithmic law [10 marks]

The rate constant for the first-order decomposition of ethylene oxide into CH_4 and CO follows the equation:

$$\log k\ (\text{in } s^{-1}) = 14.34 - (1.25 \times 10^4\ K)/T$$

Calculate:
(i) the activation energy of the reaction.
(ii) the rate constant at 700 K.
(iii) the frequency factor, A.

IFoS 2024 · Q3(a) Thermodynamic transition-state theory [15 marks]

Explain the thermodynamic formulation of the activated complex theory for a simple bimolecular reaction. Draw energy profile diagram for an exothermic and an endothermic reaction.

2023

CSE 2023 · Q5(a) First-order decomposition of AB_2 [10 marks]

The decomposition of AB_2 to AB and B is a first-order reaction with $k = 2.8 \times 10^{-7}\ s^{-1}$ at $T = 1000$ K. The atomic weights of A and B are 12 and 32, respectively.
(i) Find the half-life of this reaction at 1000 °C.
(ii) In how many days will 1 g of AB_2 decompose to the extent that 0.6 g of AB_2 remains?
(iii) How much of 1 g of AB_2 would remain after 35 days?

CSE 2023 · Q8(d) Transition-state theory and the pre-exponential factor [20 marks]

Explain the transition-state theory for reaction rates. How is this theory considered superior to collision theory in providing a much more complete interpretation of the pre-exponential factor A in the Arrhenius equation?

IFoS 2023 · Q5(a) Integration of a reversible first-order reaction [8 marks]

Starting with pure A (of concentration a) in the reversible reaction $A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$, derive the following relation:

$$t = \frac{1}{k_2(K+1)} \ln \frac{k_a}{k_a - (K+1)x}$$

where K is equilibrium constant and other symbols have their usual meanings.

IFoS 2023 · Q6(a) Initial-rate analysis [15 marks]

For a reaction between two gaseous species *A* and *B* at 1000 °C represented as

$$2\,A\,(g) + 2\,B\,(g) \longrightarrow C\,(g) + 2\,D\,(g)$$

the following kinetic data are collected at this temperature:

Sl. No.	$[A]$ (M)	$[B]$ (M)	Initial rate (M/sec)
1.	4×10^{-3}	1.5×10^{-3}	1.2×10^{-5}
2.	8×10^{-3}	1.5×10^{-3}	4.8×10^{-5}
3.	8×10^{-3}	3×10^{-3}	9.6×10^{-5}

Determine—(i) the rate law; (ii) the rate constant; (iii) the rate of the reaction when $[A] = 12.0 \times 10^{-3}$ M and $[B] = 6.0 \times 10^{-3}$ M.

2022

CSE 2022 · Q5(a) Product concentration in a first-order reaction, N_2O_2 → 2NO [10 marks]

The rate Law for the reaction

$$N_2O_2(g) \longrightarrow 2\,NO\,(g)$$

is of first order in the concentration of N_2O_2. Derive an expression for the time-dependent behaviour of the product concentration [NO].

CSE 2022 · Q7(c) Opposing first-order reactions: time to form half the equilibrium amount [10 marks]

The reaction cis-2-butene $\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}$ trans-2-butene is first order in both the direction. At 25 °C, the equilibrium constant is 0.406 and the forward reaction rate constant is 4.21×10^{-4} sec^{-1}. Starting with a sample of pure cis isomer with $[cis]_0 = 0.115$ mol dm^{-3}, how long it will take to form half of equilibrium amount of the trans isomer from cis isomer?

CSE 2022 · Q8(c) Stationary and branching chain reactions; conditions for explosion [10 marks]

Define stationary and non-stationary (branching) chain reaction. Non-stationary chain reactions always lead to explosion under certain conditions. Give a detailed account of these conditions.

IFoS 2022 · Q5(a) Two mechanisms of HI formation [8 marks]

Consider two possible mechanisms for the synthesis of HI. The first is

$$H_2 + I_2 \xrightarrow{k} 2\,HI$$

and the second is

$$I_2 \xrightarrow{k_1} 2\,I \qquad 2\,I \xrightarrow{k_2} I_2 \qquad 2\,I + H_2 \xrightarrow{k_3} 2\,HI.$$

Derive the expressions for the rate of formation of HI for both mechanisms. Under what conditions will both the mechanisms lead to the same type of kinetic equation?

IFoS 2022 · Q8(c) Equilibrium and relaxation of an isomerisation; Zero or negative activation energy [15 marks]

(i) For a hypothetical isomerization that is first order in both directions with $k_f = 17.7$ min^{-1} and $k_r = 32.2$ min^{-1}, find the equilibrium composition if the initial concentration of A is equal to 0.150 mol L^{-1} and the initial concentration of B is equal to zero. Find the half-life and the relaxation time. 10

(ii) Can the activation energy of a reaction be zero or negative? Explain your answer. 5

2021

CSE 2021 · Q5(a) Rate constant and half-life of a zero-order reaction [10 marks]

Derive an equation for rate constant of a zero-order reaction. Show that half-life period of the reaction is proportional to the initial concentration of reactant.

CSE 2021 · Q6(b) Limitations of collision theory; the answer of transition-state theory [20 marks]

What are the limitations of collision theory? How is it explained by transition state theory?

IFoS 2021 · Q5(a) Second-order conversion after 60 minutes [8 marks]

A reactant reacts 30% in 30 min. If the reaction follows a second order kinetics, find the rate constant and remaining concentration of the reactant after 60 min.

IFoS 2021 · Q6(a) Reversible first-order reaction [15 marks]

Derive rate equation for kinetics of a reversible reaction of type, $A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$.

2020

CSE 2020 · Q2(c) Opposing first-order reactions A ⇌ B with $k_1/k_2=2$ [15 marks]

Consider the following opposing reaction :

$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$ (both are elementary)

Depict the plots of concentration of *A* and *B* as a function of time and explain.

Given : $\frac{k_1}{k_2} = 2$

CSE 2020 · Q5(c) Half-life of two parallel first-order reactions [10 marks]

Show that half-life period ($t_{1/2}$) of the following parallel reaction is $\frac{\ln(2)}{k_1 + k_2}$.

$A \xrightarrow{k_1} B$, $A \xrightarrow{k_2} C$ (Both reactions are elementary).

CSE 2020 · Q7(a)(i) A reaction complete in twice its half-life: zero order [7 marks]

A reaction completes in twice the time of its half-life period. What is the order of the reaction? Give reason(s).

CSE 2020 · Q7(a)(ii) First order: $t_{99.9\%} \approx 10\, t_{50\%}$ [8 marks]

Show that for a first order reaction, the time required for 99.9% completion is almost 10 times the time for 50% completion.

IFoS 2020 · Q5(a) Rate law of AB + CD from two straight-line plots [8 marks]

Considering the reaction $AB + CD \rightarrow AC + BD$, determine the rate expression for the following condition :

A plot of $[AB]$ versus time is a straight line whenever $[CD]$ is held very high and nearly constant. A plot of $\frac{1}{[CD]}$ versus time is a straight line.

IFoS 2020 · Q6(a) Successive half-lives of a second-order reaction [15 marks]

The rate constant for a certain second-order reaction is $8{\cdot}00 \times 10^{-5}\ M^{-1}\ min^{-1}$. How long will it take a 1·00 M solution to be reduced to 0·500 M in reactant? How long will it take from that point until the solution is 0·250 M in reactant? Explain why half-life is not used often for second-order reactions.

IFoS 2020 · Q8(c) Collision model of reaction rates; $Ce^{4+} + Hg_2^{2+}$ versus $H_3O^+ + OH^-$ [15 marks]

(i) What is the basis of collision model describing the kinetics of chemical reactions? How is the rate affected by each of the following?

(1) Activation energy
(2) Temperature
(3) Frequency of collisions
(4) Orientation of collisions 10

(ii) Among the following reactions, which one will proceed at a faster rate at room temperature? Justify your answer :

$$2\,Ce^{4+}(aq) + Hg_2^{2+}(aq) \longrightarrow 2\,Ce^{3+}(aq) + 2\,Hg^{2+}(aq)$$
$$H_3O^+(aq) + OH^-(aq) \longrightarrow 2\,H_2O(l)$$

5

2019

CSE 2019 · Q5(d) Linear fall of [A] with time: zero order [10 marks]

For the reaction $A \rightarrow B$ the plot of conc. of A against time (t) was found to be linear with a negative slope. Predict the order of reaction. Justify your answer.

CSE 2019 · Q6(b) Rate constants of $H^+ + OH^-$ ⇌ H_2O from the relaxation time [20 marks]

When a sample of pure water is heated by a pulse of microwave radiation the equilibrium in the water dissociation reaction is shifted. The relaxation time for the re-establishment of equilibrium at 25 °C is 36 microseconds. Calculate k_1 and k_{-1} in $H^+ + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_2O$. Ion product of water at 25 °C is 10^{-14}.

IFoS 2019 · Q6(a) Order from log[A]–time data; second-order $I^- + ClO^-$ [20 marks]

(i) For the reaction of reagent A in solution to give products, the following data were obtained :

t; min	0·0	9·0	12·0	14·0	18·0	20·0	24·0	30·0
log [A]	0·583	0·343	0·257	0·223	0·170	0·133	0·118	0·079

Determine the order of the reaction and calculate the value of the rate constant.

(ii) At 25 °C, the second order rate constant for the reaction

$$I^- + ClO^- \longrightarrow IO^- + Cl^-$$

is $0{\cdot}0606\ M^{-1}s^{-1}$.

If the solution is initially $3{\cdot}50 \times 10^{-3}$ M with respect to each other, what will be the concentration of each species present after 300 s? 10+10=20

2018

CSE 2018 · Q5(a) Half-life of the neutralisation $H^+ + OH^-$ [10 marks]

The rate constant k_1 for the reaction described by $H^+(aq) + OH^-(aq) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_2O(l)$ is 1.4×10^{11} $dm^3.mol^{-1}.s^{-1}$. Calculate the half life of the above reaction if the initial conditions are

(i) $[H^+]_0 = [OH^-]_0 = 0.10$ mol.dm^{-3} (ii) $[H^+]_0 = [OH^-]_0 = 1.0 \times 10^{-7}$ mol.dm^{-3}

CSE 2018 · Q6(a)(i) Effect of temperature on the rate constant [5 marks]

Explain the effect of temperature on rate constant.

CSE 2018 · Q6(a)(ii) Alkaline hydrolysis of ethyl acetate is second order [10 marks]

In the hydrolysis of ethyl acetate using equal concentrations of ester and NaOH, the following results were obtained:

t (minutes)	0	5	15	25	35
HCl (ml)	16.0	10.24	6.13	4.32	3.41

Show that the reaction is of second order.

IFoS 2018 · Q1(e) Activation energy from equal-conversion times [8 marks]

A certain chemical reaction completes 20% in 15 min at 27 °C and in 5 min at 37 °C. Calculate the activation energy (in SI units) of the reaction.

IFoS 2018 · Q3(b) Half-life of a first-order reaction and its temperature dependence [15 marks]

Derive the expression of half-life period ($t_{1/2}$) of a first order chemical reaction from its integrated rate equation. Does this value depend on the temperature of the reaction? Give reason in support of your answer.

2017

CSE 2017 · Q5(a) Arrhenius equation for zero order; high-temperature limit of k [10 marks]

For zero-order reaction, write down the Arrhenius equation, indicating name of the symbols and their units in SI system. What is high temperature limiting value of rate constant?

CSE 2017 · Q6(a)(ii) Activation energy from two equal-conversion times [15 marks]

Define activation energy, E_a of a chemical reaction. A gas-phase reaction completes 25% in 30 min at 27 °C and in 10 min at 37 °C. Determine the E_a in SI unit.

IFoS 2017 · Q1(b) Proving first order from concentration–time data [5 marks]

For the reaction

$$A \rightarrow B + C,$$

the following data were obtained:

t in sec	0	900	1800
conc. of A	50·8	19·7	7·62

Prove that the reaction is of the first order.

IFoS 2017 · Q3(b) Arrhenius equation as a straight line [10 marks]

Consider the Arrhenius equation. Derive the expression relating rate-constant, energy of activation and frequency factor, in the form of a straight line equation.

2016

CSE 2016 · Q2(a)(ii) Theory of absolute reaction rates; how a catalyst works [10 marks]

Discuss the theory of absolute reaction rate. How does a catalyst make reaction faster?

CSE 2016 · Q4(c) Equilibrium constant of A + B ⇌ C from two relaxation times [10 marks]

Find out the equilibrium constant for the reaction A + B $\underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}}$ C assuming the relaxation time (τ) = 2.0 μs and 3.0 μs for
$[A] = [B]$ = 1.0 M and
$[A] = [B]$ = 0.5 M respectively.

IFoS 2016 · Q1(b)(i) Activation energy from rate constants at two temperatures [5 marks]

Assuming that the activation energy and pre-exponential factor are temperature independent, obtain the expression relating the activation energy (E_a) and the rate parameters $k(T_1)$ and $k(T_2)$ for the same reaction at temperatures T_1 and T_2.

IFoS 2016 · Q3(c) Rate constants of C ⇌ D from the relaxation time and K [10 marks]

The 'relaxation time' for a reversible first-order reaction C $\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}$ D is 100 microsecond and the equilibrium constant is 1.0×10^2. Find k_1 and k_{-1}.