

Chemical Kinetics — NEET Chemistry PYQ (2005-2021)

Class 12 Chemistry · 39 real NEET & AIPMT questions, year-tagged · answers checked by RankUp

NEET 2021

1. The slope of Arrhenius Plot ($\ln k$ v/s $1/T$) of first order reaction is $-5 \times 10^3 \text{ K}$. The value of E_a of the reaction is. Choose the correct option for your answer. [Given $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$]

- (A) 41.5 kJ mol^{-1}
- (B) 83.0 kJ mol^{-1}
- (C) 166 kJ mol^{-1}
- (D) -83 kJ mol^{-1}

NEET 2020 · Q109

2. An increase in the concentration of the reactants of a reaction leads to change in :

- (A) activation energy
- (B) heat of reaction
- (C) threshold energy
- (D) collision frequency

NEET 2020 · Q132

3. The rate constant for a first order reaction is $4.606 \times 10^{-3} \text{ s}^{-1}$. The time required to reduce 2.0 g of the reactant to 0.2 g is :

- (A) 100 s
- (B) 200 s
- (C) 500 s
- (D) 1000 s

NEET 2019 · Q63

4. If the rate constant for a first order reaction is k , the time (t) required for the completion of 99% of the reaction is given by:

- (A) $t = 0.693/k$
- (B) $t = 6.909/k$
- (C) $t = 4.606/k$
- (D) $t = 2.303/k$

NEET 2019 · Q67

5. For the chemical reaction $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ the correct option is:

- (A) $-(1/3) d[\text{H}_2]/dt = -(1/2) d[\text{NH}_3]/dt$
- (B) $-d[\text{N}_2]/dt = 2 d[\text{NH}_3]/dt$
- (C) $-d[\text{N}_2]/dt = (1/2) d[\text{NH}_3]/dt$
- (D) $3 d[\text{H}_2]/dt = 2 d[\text{NH}_3]/dt$

NEET 2018 · Q79

6. The correct difference between first- and second-order reactions is that

- (A) a first-order reaction can be catalyzed; a second-order reaction cannot be catalyzed
- (B) the half-life of a first-order reaction does not depend on $[\text{A}]_0$; the half-life of a second-order reaction does depend on $[\text{A}]_0$
- (C) the rate of a first-order reaction does not depend on reactant concentrations; the rate of a second-order reaction does depend on reactant concentrations
- (D) the rate of a first-order reaction does depend on reactant concentrations; the rate of a second-order reaction does not depend on reactant concentrations

NEET 2018 · Q84

7. When initial concentration of the reactant is doubled, the half-life period of a zero order reaction

- (A) is tripled
- (B) is doubled
- (C) is halved
- (D) remains unchanged

NEET 2017 · Q40

8. Mechanism of a hypothetical reaction $X_2 + Y_2 \rightarrow 2XY$ is given below: (i) $X_2 \rightarrow X + X$ (fast) (ii) $X + Y_2 \rightleftharpoons XY + Y$ (slow) (iii) $X + Y \rightarrow XY$ (fast). The overall order of the reaction will be:

- (A) 1
- (B) 2
- (C) 0
- (D) 1.5

NEET 2017 (Gujarati paper) · Q8

9. For the reaction, $XA + YB \rightarrow ZC$, if $-d[A]/dt = -d[B]/dt = 1.5 d[C]/dt$, then the correct statement among the following is:

- (A) The value of $X = Y = Z = 3$
- (B) The value of $X = Y = 3$
- (C) The value of $X = 2$
- (D) The value of $Y = 2$

NEET 2017 (Gujarati paper) · Q29

10. Consider the reaction between chlorine and nitric oxide $Cl_2(g) + 2NO(g) \rightarrow 2NOCl(g)$. On doubling the concentration of both reactants, the rate of the reaction increases by a factor of 8. However, if only the concentration of Cl_2 is doubled, the rate increases by a factor of 2. The order of this reaction with respect to NO is:

- (A) 0
- (B) 1
- (C) 2
- (D) 3

NEET 2016 Phase 2 · Q48

11. The decomposition of phosphine (PH_3) on tungsten at low pressure is a first-order reaction. It is because the

- (A) rate is proportional to the surface coverage
- (B) rate is inversely proportional to the surface coverage
- (C) rate is independent of the surface coverage
- (D) rate of decomposition is very slow

NEET 2016 Phase 1 · Q49

12. The rate of a first-order reaction is $0.04 \text{ mol l}^{-1} \text{ s}^{-1}$ at 10 seconds and $0.03 \text{ mol l}^{-1} \text{ s}^{-1}$ at 20 seconds after initiation of the reaction. The half-life period of the reaction is:

- (A) 24.1 s
- (B) 34.1 s
- (C) 44.1 s
- (D) 54.1 s

NEET 2016 Phase 1 · Q76

13. The addition of a catalyst during a chemical reaction alters which of the following quantities?

- (A) Entropy
- (B) Internal energy
- (C) Enthalpy
- (D) Activation energy

AIPMT 2015

14. The activation energy of a reaction can be determined from the slope of which of the following graphs?

- (A) $T/\ln K$ vs. $1/T$
- (B) $\ln K$ vs. T
- (C) $\ln K/T$ vs. T
- (D) $\ln K$ vs. $1/T$

AIPMT 2015

15. When initial concentration of a reactant is doubled in a reaction, its half-life period is not affected. The order of the reaction is:

- (A) More than zero but less than first
- (B) Zero
- (C) First
- (D) Second

NEET 2013

16. What is the activation energy for a reaction if its rate doubles when the temperature is raised from 20°C to 35°C ? ($R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$)

- (A) 342 kJ mol^{-1}
- (B) 269 kJ mol^{-1}
- (C) 34.7 kJ mol^{-1}
- (D) 15.1 kJ mol^{-1}

NEET 2013

17. A reaction having equal energies of activation for forward and reverse reactions has

- (A) $\Delta S = 0$
- (B) $\Delta G = 0$
- (C) $\Delta H = 0$
- (D) $\Delta H = \Delta G = \Delta S = 0$

AIPMT 2012 Prelims

18. In a reaction, $A + B \rightarrow \text{Product}$, rate is doubled when the concentration of B is doubled, and rate increases by a factor of 8 when the concentrations of both the reactants (A and B) are doubled. Rate law for the reaction can be written as

- (A) $\text{Rate} = k[A]^2[B]$
- (B) $\text{Rate} = k[A][B]^2$
- (C) $\text{Rate} = k[A]^2[B]^2$
- (D) $\text{Rate} = k[A][B]$

AIPMT 2012 Prelims

19. In a zero-order reaction for every 10° rise of temperature, the rate is doubled. If the temperature is increased from 10°C to 100°C , the rate of the reaction will become:

- (A) 128 times
- (B) 256 times
- (C) 512 times
- (D) 64 times

AIPMT 2011 Mains

20. The unit of rate constant for a zero order reaction is

- (A) $\text{L}^2 \text{ mol}^{-2} \text{ s}^{-1}$
- (B) s^{-1}
- (C) $\text{mol L}^{-1} \text{ s}^{-1}$
- (D) $\text{L mol}^{-1} \text{ s}^{-1}$

AIPMT 2011 Mains

21. The rate of the reaction $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$ can be written in three ways:

$$-\text{d}[\text{N}_2\text{O}_5]/\text{dt} = k[\text{N}_2\text{O}_5]$$

$$\text{d}[\text{NO}_2]/\text{dt} = k'[\text{N}_2\text{O}_5]$$

$$\text{d}[\text{O}_2]/\text{dt} = k''[\text{N}_2\text{O}_5]$$

The relationship between k and k' and between k and k'' are

- (A) $k' = 2k$; $k'' = 2k$
- (B) $k' = k$; $k'' = k$
- (C) $k' = 2k$; $k'' = k$
- (D) $k' = 2k$; $k'' = k/2$

AIPMT 2011 Mains

22. The half life of a substance in a certain enzyme-catalysed reaction is 138 s. The time required for the concentration of the substance to fall from 1.28 mg L^{-1} to 0.04 mg L^{-1} is

- (A) 690 s
- (B) 276 s
- (C) 414 s
- (D) 552 s

AIPMT 2011 Prelims

23. Which one of the following statements for the order of a reaction is incorrect?

- (A) Order of reaction is always whole number
- (B) Order can be determined only experimentally
- (C) Order is not influenced by stoichiometric coefficient of the reactants
- (D) Order of reaction is sum of power to the concentration terms of reactants to express the rate of reaction

AIPMT 2010 Mains · Q110

24. The rate of the reaction $2\text{NO} + \text{Cl}_2 \rightarrow 2\text{NOCl}$ is given by the rate equation $\text{rate} = k[\text{NO}]^2[\text{Cl}_2]$. The value of the rate constant can be increased by

- (A) Increasing the temperature
- (B) Increasing the concentration of NO
- (C) Increasing the concentration of the Cl_2
- (D) Doing all of these

AIPMT 2010 Prelims · Q58

25. For the reaction $\text{N}_2\text{O}_5(\text{g}) \rightarrow 2\text{NO}_2(\text{g}) + (1/2)\text{O}_2(\text{g})$ the value of rate of disappearance of N_2O_5 is given as $6.25 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$. The rate of formation of NO_2 and O_2 is given respectively as:

- (A) $1.25 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$ and $6.25 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$
- (B) $6.25 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$ and $6.25 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$
- (C) $1.25 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$ and $3.125 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$
- (D) $6.25 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$ and $3.125 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$

AIPMT 2010 Prelims · Q60

26. During the kinetic study of the reaction $2\text{A} + \text{B} \rightarrow \text{C} + \text{D}$, following results were obtained:

Run I: $[\text{A}] = 0.1$, $[\text{B}] = 0.1$, rate = 6.0×10^{-3}

Run II: $[\text{A}] = 0.3$, $[\text{B}] = 0.2$, rate = 7.2×10^{-2}

Run III: $[\text{A}] = 0.3$, $[\text{B}] = 0.4$, rate = 2.88×10^{-1}

Run IV: $[\text{A}] = 0.4$, $[\text{B}] = 0.1$, rate = 2.40×10^{-2}

($[\text{A}]$, $[\text{B}]$ in mol L^{-1} ; initial rate of formation of D in $\text{mol L}^{-1} \text{ min}^{-1}$)

Based on the above data which one of the following is correct?

- (A) rate = $k[\text{A}][\text{B}]^2$
- (B) rate = $k[\text{A}]^2[\text{B}]$
- (C) rate = $k[\text{A}][\text{B}]$
- (D) rate = $k[\text{A}]^2[\text{B}]^2$

27. For the reaction $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$, if $d[\text{NH}_3]/dt = 2 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$, the value of $-d[\text{H}_2]/dt$ would be :

- (A) $4 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$
- (B) $6 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$
- (C) $1 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$
- (D) $3 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$

28. In the reaction $\text{BrO}_3^-(\text{aq}) + 5\text{Br}^-(\text{aq}) + 6\text{H}^+(\text{aq}) \rightarrow 3\text{Br}_2(\text{l}) + 3\text{H}_2\text{O}(\text{l})$, the rate of appearance of bromine (Br_2) is related to rate of disappearance of bromide ions as following:

- (A) $d[\text{Br}_2]/dt = -(5/3) d[\text{Br}^-]/dt$
- (B) $d[\text{Br}_2]/dt = (5/3) d[\text{Br}^-]/dt$
- (C) $d[\text{Br}_2]/dt = (3/5) d[\text{Br}^-]/dt$
- (D) $d[\text{Br}_2]/dt = -(3/5) d[\text{Br}^-]/dt$

29. Half life period of a first-order reaction is 1386 seconds. The specific rate constant of the reaction is:

- (A) $0.5 \times 10^{-2} \text{ s}^{-1}$
- (B) $0.5 \times 10^{-3} \text{ s}^{-1}$
- (C) $5.0 \times 10^{-2} \text{ s}^{-1}$
- (D) $5.0 \times 10^{-3} \text{ s}^{-1}$

30. For the reaction $\text{A} + \text{B} \rightarrow \text{products}$, it is observed that:

- (a) on doubling the initial concentration of A only, the rate of reaction is also doubled and
- (b) on doubling the initial concentrations of both A and B, there is a change by a factor of 8 in the rate of the reaction.

The rate of this reaction is given by:

- (A) rate = $k[\text{A}][\text{B}]^2$
- (B) rate = $k[\text{A}]^2[\text{B}]^2$
- (C) rate = $k[\text{A}][\text{B}]$
- (D) rate = $k[\text{A}]^2[\text{B}]$

31. The bromination of acetone that occurs in acid solution is represented by this equation



These kinetic data were obtained for given reaction concentrations.

Initial concentrations (M) $[\text{CH}_3\text{COCH}_3]$, $[\text{Br}_2]$, $[\text{H}^+] \rightarrow$ initial rate of disappearance of Br_2 (M s^{-1}):

0.30, 0.05, 0.05 $\rightarrow 5.7 \times 10^{-5}$

0.30, 0.10, 0.05 $\rightarrow 5.7 \times 10^{-5}$

0.30, 0.10, 0.10 $\rightarrow 1.2 \times 10^{-4}$

0.40, 0.05, 0.20 $\rightarrow 3.1 \times 10^{-4}$

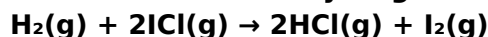
Based on these data, the rate equation is

- (A) Rate = $k[\text{CH}_3\text{COCH}_3][\text{Br}_2][\text{H}^+]$
- (B) Rate = $k[\text{CH}_3\text{COCH}_3][\text{H}^+]$
- (C) Rate = $k[\text{CH}_3\text{COCH}_3][\text{Br}_2]$
- (D) Rate = $k[\text{CH}_3\text{COCH}_3][\text{Br}_2][\text{H}^+]^2$

32. The rate constants k_1 and k_2 for two different reactions are $10^{16} \cdot e^{(-2000/T)}$ and $10^{15} \cdot e^{(-1000/T)}$ respectively. The temperature at which $k_1 = k_2$ is

- (A) $(1000/2.303)$ K
- (B) 1000 K
- (C) $(2000/2.303)$ K
- (D) 2000 K

33. The reaction of hydrogen and iodine monochloride is given as:



The reaction is of first order with respect to $\text{H}_2(\text{g})$ and $\text{ICl}(\text{g})$, following mechanisms were proposed.

Mechanism A: $\text{H}_2(\text{g}) + 2\text{ICl}(\text{g}) \rightarrow 2\text{HCl}(\text{g}) + \text{I}_2(\text{g})$

Mechanism B: $\text{H}_2(\text{g}) + \text{ICl}(\text{g}) \rightarrow \text{HI}(\text{g})$; slow

$\text{HI}(\text{g}) + \text{ICl}(\text{g}) \rightarrow \text{HCl}(\text{g}) + \text{I}_2(\text{g})$; fast

Which of the above mechanism(s) can be consistent with the given information about the reaction?

- (A) A and B both
- (B) neither A nor B
- (C) A only
- (D) B only

34. In a first-order reaction $\text{A} \rightarrow \text{B}$, if k is rate constant and initial concentration of the reactant A is 0.5 M, then the half-life is

- (A) $\log 2/k$
- (B) $\log 2/(k\sqrt{0.5})$
- (C) $\ln 2/k$
- (D) $0.693/(0.5k)$

35. If 60% of a first order reaction was completed in 60 minutes, 50% of the same reaction would be completed in approximately ($\log 4 = 0.60$, $\log 5 = 0.69$)

- (A) 45 minutes
- (B) 60 minutes
- (C) 40 minutes
- (D) 50 minutes

36. For the reaction $2\text{A} + \text{B} \rightarrow 3\text{C} + \text{D}$ which of the following does not express the reaction rate ?

- (A) $-d[\text{C}]/3dt$
- (B) $-d[\text{B}]/dt$
- (C) $d[\text{D}]/dt$
- (D) $-d[\text{A}]/2dt$

37. Consider the reaction $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$. The equality relationship between $d[\text{NH}_3]/dt$ and $-d[\text{H}_2]/dt$ is :

- (A) $d[\text{NH}_3]/dt = -(1/3) d[\text{H}_2]/dt$
- (B) $d[\text{NH}_3]/dt = -(2/3) d[\text{H}_2]/dt$
- (C) $d[\text{NH}_3]/dt = -(3/2) d[\text{H}_2]/dt$
- (D) $d[\text{NH}_3]/dt = -d[\text{H}_2]/dt$

38. For a first order reaction $A \rightarrow B$, the reaction rate at reactant concentration of 0.01 M is found to be $2.0 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}$. The half life period of the reaction is :

- (A) 227 s
- (B) 327 s
- (C) 527 s
- (D) 347 s

39. The rate of reaction between two reactants A and B decreases by a factor of 4, if the concentration of reactant B is doubled. The order of this reaction with respect to reactant B is :

- (A) -1
- (B) -2
- (C) 1
- (D) 2

Answer key and explanations

1. Answer: (A) 41.5 kJ mol^{-1}

$\ln k = \ln A - E_a/(RT)$, so the slope of $\ln k$ vs $1/T$ is $-E_a/R$. $E_a = 5 \times 10^3 \times 8.314 = 41,570 \text{ J mol}^{-1} \approx 41.5 \text{ kJ mol}^{-1}$. E_a is positive since the slope is negative, and 83 kJ is double the correct value.

2. Answer: (D) collision frequency

More reactant molecules per unit volume means more collisions per second, so the collision frequency rises and the rate increases. Activation energy, threshold energy and heat of reaction are properties of the reaction itself and do not depend on concentration.

3. Answer: (C) 500 s

$t = (2.303/k) \log([R]_0/[R]) = (2.303/4.606 \times 10^{-3}) \times \log(2.0/0.2) = 500 \times 1 = 500 \text{ s}$. Leaving out the 2.303 conversion factor would give about 217 s, near the 200 s trap.

4. Answer: (C) $t = 4.606/k$

$t = (2.303/k) \log([A]_0/[A]) = (2.303/k) \log(100/1) = 4.606/k$. $0.693/k$ is only the half-life, and $2.303/k$ corresponds to 90% completion.

5. Answer: (C) $-d[N_2]/dt = (1/2) d[NH_3]/dt$

Rate = $-d[N_2]/dt = -(1/3)d[H_2]/dt = +(1/2)d[NH_3]/dt$. The relation with a negative sign on the NH_3 term is wrong because NH_3 is a product whose concentration increases.

6. Answer: (B) the half-life of a first-order reaction does not depend on $[A]_0$; the half-life of a second-order reaction does depend on $[A]_0$

For first order $t_{1/2} = 0.693/k$, independent of $[A]_0$, while for second order $t_{1/2} = 1/(k[A]_0)$. Rates of both orders depend on concentration, and either type can be catalysed.

7. Answer: (B) is doubled

For a zero-order reaction $t_{1/2} = [A]_0/2k$, directly proportional to initial concentration, so doubling $[A]_0$ doubles $t_{1/2}$. A half-life independent of concentration is the first-order case.

8. Answer: (D) 1.5

The slow step gives rate = $k[X][Y_2]$. X comes from the fast pre-equilibrium $X_2 \rightleftharpoons 2X$, so $[X] = \sqrt{(K[X_2])}$ and rate = $k'[X_2]^{1/2}[Y_2]$. The overall order is $1/2 + 1 = 1.5$; taking the slow step's molecularity of 2 as the order ignores that X is an intermediate.

9. Answer: (B) The value of $X = Y = 3$

Rate = $-(1/X)d[A]/dt = -(1/Y)d[B]/dt = (1/Z)d[C]/dt$. Equal rates of loss of A and B give $X = Y$, and $-d[A]/dt = 1.5 d[C]/dt$ gives $X = 1.5Z$, so the smallest whole numbers are $X = Y = 3$ and $Z = 2$. Z cannot also be 3, because then the rates would be equal, not in the ratio 1.5.

10. Answer: (C) 2

Let rate = $k[Cl_2]^x[NO]^y$. Doubling Cl_2 alone doubles the rate, so $x = 1$. Doubling both gives $2^1 \times 2^y = 8$, so $2^y = 4$ and $y = 2$. The overall order is 3, which is the trap.

11. Answer: (A) rate is proportional to the surface coverage

At low pressure only a small part of the metal surface is covered, and the coverage is proportional to the pressure of PH_3 . The rate depends on the coverage, so it is proportional to pressure: first order. At high pressure the surface is saturated and the rate becomes independent of coverage (zero order).

12. Answer: (A) 24.1 s

For first order, rate $\propto$ concentration, so $0.04/0.03 = e^{(k \times 10)}$ and $k = \ln(4/3)/10 = 0.2877/10 \approx 0.0288 \text{ s}^{-1}$. $t_{1/2} = 0.693/0.0288 \approx 24.1 \text{ s}$. Using the 20 s mark as the time interval instead of the 10 s gap gives a much smaller k and longer half-lives.

13. Answer: (D) Activation energy

A catalyst provides an alternative pathway with a lower activation energy, which speeds up the reaction. Entropy, internal energy and enthalpy are state functions that depend only on the initial and final states, so a catalyst cannot change them.

14. Answer: (D) $\ln K$ vs. $1/T$

From the Arrhenius equation $\ln k = \ln A - E_a/RT$, a plot of $\ln k$ against $1/T$ is a straight line of slope $-E_a/R$, from which E_a is found. $\ln k$ against T is curved.

15. Answer: (C) First

$t_{1/2} \propto [A]_0^{(1-n)}$. It is independent of the initial concentration only when $n = 1$, as in $t_{1/2} = 0.693/k$. For zero order $t_{1/2}$ doubles when $[A]_0$ doubles.

16. Answer: (C) 34.7 kJ mol⁻¹

$\log(k_2/k_1) = (E_a/2.303R)(T_2 - T_1)/(T_1 T_2)$ with $T_1 = 293 \text{ K}$, $T_2 = 308 \text{ K}$. $E_a = 2.303 \times 8.314 \times 0.3010 \times (293 \times 308)/15 = 5.763 \times 6016 \approx 3.47 \times 10^4 \text{ J mol}^{-1} = 34.7 \text{ kJ mol}^{-1}$.

17. Answer: (C) $\Delta H = 0$

$\Delta H = E_a(\text{forward}) - E_a(\text{reverse})$. If the two activation energies are equal, $\Delta H = 0$. ΔG and ΔS need not be zero, since they also depend on entropy changes.

18. Answer: (A) Rate = $k[A]^2[B]$

Let rate = $k[A]^x[B]^y$. Doubling $[B]$ doubles the rate, so $y = 1$. Doubling both gives $2^{(x+1)} = 8$, so $x = 2$. Rate = $k[A]^2[B]$. $k[A][B]^2$ would also give 8 for doubling both, but it would quadruple, not double, the rate on doubling $[B]$.

19. Answer: (C) 512 times

From 10°C to 100°C is a 90° rise, i.e. nine 10° steps. Rate becomes $2^9 = 512$ times. $256 (2^8)$ comes from miscounting the steps. The zero order of the reaction does not affect the temperature factor.

20. Answer: (C) mol L⁻¹ s⁻¹

For a zero-order reaction rate = $k[A]^0 = k$, so k has the units of rate, mol L⁻¹ s⁻¹. s⁻¹ is the first-order unit and L mol⁻¹ s⁻¹ is the second-order unit.

21. Answer: (D) $k' = 2k$; $k'' = k/2$

Rate = $-\frac{1}{2} d[\text{N}_2\text{O}_5]/dt = \frac{1}{4} d[\text{NO}_2]/dt = d[\text{O}_2]/dt$. So $d[\text{NO}_2]/dt = 2 \times (-d[\text{N}_2\text{O}_5]/dt)$, giving $k' = 2k$, and $d[\text{O}_2]/dt = \frac{1}{2} \times (-d[\text{N}_2\text{O}_5]/dt)$, giving $k'' = k/2$. Setting all three constants equal ignores the stoichiometric coefficients.

22. Answer: (A) 690 s

A constant half-life means first-order kinetics. $1.28/0.04 = 32 = 2^5$, so five half-lives are needed: $5 \times 138 = 690 \text{ s}$. 552 s corresponds to only four half-lives.

23. Answer: (A) Order of reaction is always whole number

Order is an experimental quantity and can be zero, fractional or even negative, so the claim that it is always a whole number is incorrect. It is determined experimentally, does not have to follow stoichiometric coefficients, and equals the sum of the powers of concentration terms in the rate law.

24. Answer: (A) Increasing the temperature

The rate constant depends on temperature (Arrhenius, $k = A e^{(-E_a/RT)}$), not on concentrations. Raising concentrations of NO or Cl₂ raises the rate but leaves k unchanged.

25. Answer: (C) $1.25 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$ and $3.125 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$

Rate = $-d[\text{N}_2\text{O}_5]/dt = \frac{1}{2} d[\text{NO}_2]/dt = 2 d[\text{O}_2]/dt$. So $d[\text{NO}_2]/dt = 2 \times 6.25 \times 10^{-3} = 1.25 \times 10^{-2}$ and $d[\text{O}_2]/dt = 6.25 \times 10^{-3}/2 = 3.125 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$.

26. Answer: (A) rate = $k[A][B]^2$

Runs II and III: $[A]$ fixed, $[B]$ doubled, rate $\times 4$, so order in $B = 2$. Runs I and IV: $[B]$ fixed, $[A] \times 4$, rate $\times 4$, so order in $A = 1$. Rate = $k[A][B]^2$; check: Run II/Run I = $(3 \times 4) = 12 = 7.2 \times 10^{-2}/6.0 \times 10^{-3}$.

27. Answer: (D) $3 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$

Rate = $-(1/3)d[\text{H}_2]/dt = (1/2)d[\text{NH}_3]/dt$. So $-d[\text{H}_2]/dt = (3/2) \times 2 \times 10^{-4} = 3 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$. Multiplying by 3 alone gives 6×10^{-4} .

28. Answer: (D) $d[\text{Br}_2]/dt = -(3/5) d[\text{Br}^-]/dt$

Rate = $(1/3)d[\text{Br}_2]/dt = -(1/5)d[\text{Br}^-]/dt$, so $d[\text{Br}_2]/dt = -(3/5)d[\text{Br}^-]/dt$. The minus sign is needed because $[\text{Br}^-]$ decreases while $[\text{Br}_2]$ increases, and $5/3$ inverts the stoichiometric ratio.

29. Answer: (B) $0.5 \times 10^{-3} \text{ s}^{-1}$

For a first-order reaction $k = 0.693/t_{1/2} = 0.693/1386 = 5.0 \times 10^{-4} \text{ s}^{-1} = 0.5 \times 10^{-3} \text{ s}^{-1}$. $5.0 \times 10^{-3} \text{ s}^{-1}$ is ten times too large.

30. Answer: (A) rate = $k[A][B]^2$

Doubling [A] alone doubles the rate, so the order in A is 1. Doubling both raises the rate 8 times: $2^1 \times 2^n = 8$, so $n = 2$ for B. Rate = $k[A][B]^2$.

31. Answer: (B) Rate = $k[\text{CH}_3\text{COCH}_3][\text{H}^+]$

Runs 1 and 2: doubling $[\text{Br}_2]$ leaves the rate unchanged, so the reaction is zero order in Br_2 . Runs 2 and 3: doubling $[\text{H}^+]$ doubles the rate, so it is first order in H^+ . Run 4 checks acetone: $5.7 \times 10^{-5} \times (0.40/0.30) \times (0.20/0.05) \approx 3.0 \times 10^{-4}$, matching 3.1×10^{-4} , so it is first order in acetone. Rate = $k[\text{CH}_3\text{COCH}_3][\text{H}^+]$; any form containing $[\text{Br}_2]$ contradicts runs 1 and 2.

32. Answer: (A) (1000/2.303) K

Setting $10^{16}e^{-(2000/T)} = 10^{15}e^{-(1000/T)}$ gives $10 = e^{(1000/T)}$, so $1000/T = \ln 10 = 2.303$ and $T = 1000/2.303 \text{ K} \approx 434 \text{ K}$. 1000 K would come from wrongly taking $\ln 10$ as 1.

33. Answer: (D) B only

The observed rate law is rate = $k[\text{H}_2][\text{ICl}]$. Mechanism A, as a single step, would be second order in ICl . In mechanism B the slow step $\text{H}_2 + \text{ICl}$ gives exactly rate = $k[\text{H}_2][\text{ICl}]$, so only B is consistent.

34. Answer: (C) $\ln 2/k$

For a first-order reaction $t_{1/2} = \ln 2/k = 0.693/k$, independent of the initial concentration. $\log 2/k$ uses the base-10 log, and $0.693/(0.5k)$ wrongly brings in the 0.5 M concentration.

35. Answer: (A) 45 minutes

$k = (2.303/60) \log(100/40) = (2.303/60)(0.69 - 0.30) \approx 0.0150 \text{ min}^{-1}$. $t_{1/2} = 0.693/0.0150 \approx 46 \text{ min}$, closest to 45 minutes. 50 minutes assumes a linear (zero-order) fall.

36. Answer: (A) $-d[C]/3dt$

Rate = $-\frac{1}{2} d[A]/dt = -d[B]/dt = +\frac{1}{3} d[C]/dt = +d[D]/dt$. Since C is a product its concentration rises, so $-d[C]/3dt$ is negative and cannot represent the rate. The other three expressions are correct.

37. Answer: (B) $d[\text{NH}_3]/dt = -(2/3) d[\text{H}_2]/dt$

Rate = $-\frac{1}{3} d[\text{H}_2]/dt = \frac{1}{2} d[\text{NH}_3]/dt$. Therefore $d[\text{NH}_3]/dt = -(2/3) d[\text{H}_2]/dt$: two moles of NH_3 form for every three moles of H_2 used. The ratio 3/2 inverts the stoichiometry.

38. Answer: (D) 347 s

For first order, rate = $k[A]$, so $k = 2 \times 10^{-5}/0.01 = 2 \times 10^{-3} \text{ s}^{-1}$. $t_{1/2} = 0.693/k = 346.5 \approx 347 \text{ s}$.

39. Answer: (B) -2

rate $\propto [B]^n$. Doubling [B] makes the rate one quarter: $2^n = 1/4$, so $n = -2$. Order +2 would make the rate four times larger.

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