

Rate law and Rate constant

- (d) Molecularity of the reaction does not influence the rate of reaction.
- (c) The rate law for an reaction can be given by; $\text{rate} = K(A)(B)^2$,
i.e. the powers are raised which are given as coefficient of reactant.

- (a) $p_0 = 500 \text{ atm}$

$$K = \frac{2.303}{t} \log_{10} \frac{p_0}{p_t}$$

$$3.38 \times 10^{-5} = \frac{2.303}{10 \times 60} \log \frac{500}{p_t}$$

$$\text{or } 0.00880 = \log \frac{500}{p_t} \Rightarrow \frac{500}{p_t} = 1.02 = 490 \text{ atm}$$

- (b) It is a pseudo-unimolecular reaction.

- (a) $A + 2B \rightarrow C + D$

$$\frac{-d[A]}{dt} = 5 \times 10^{-4}$$

$$-\frac{1}{2} \frac{d[B]}{dt} = 2 \times 5 \times 10^{-4} = 1.0 \times 10^{-3} \text{ mol l}^{-1} \text{ s}^{-1}$$

- Assume the rate law: $\text{Rate} = k[A]^m[B]^n$

Step 1: Determine order with respect to [A]

Compare experiments 1 and 3:

$[A]_1 = 0.012 \rightarrow [A]_3 = 0.024$ (doubled)

$[B]$ constant at 0.035

Rate₁ = 0.10, Rate₃ = 0.10

$$\text{Rate}_1 / \text{Rate}_3 = 0.10 / 0.10 = 1$$

$$\frac{[A]_3^m}{[A]_1^m} = \frac{0.024^m}{0.012^m} = 2^m \Rightarrow m = 0$$



Order with respect to A: **0**

Step 2: Determine order with respect to [B]

Compare experiments 1 and 4:

$$[B]_1 = 0.035 \rightarrow [B]_4 = 0.070 (\text{doubled})$$

[A] constant at 0.012

$$\text{Rate}_1 = 0.10, \text{Rate}_4 = 0.80$$

$$\text{Rate}_1 / \text{Rate}_4 = 0.10 / 0.80 = 8$$

$$[B]_1 / [B]_4 = 2 \Rightarrow n = 3$$

Order with respect to B: **3**

Step 3: Rate law

$$\text{Rate} = k[B]^3$$

7. Assume rate law:

$$\text{Rate} = k[A]^m[B_2]^n$$

Step 1: Order with respect to [A]

Compare experiments 2 and 3:

$$[A]^2 = 0.50 \rightarrow [A]^3 = 1.00 (\text{doubled})$$

$[B_2]$ constant at 1.00

$$\text{Rate}_2 = 3.2 \times 10^{-4}, \text{Rate}_3 = 3.2 \times 10^{-4}$$

$$\frac{\text{Rate}_2}{\text{Rate}_3} = 1 \Rightarrow m = 0$$

Order with respect to A: **0**

$$[B_2]^1 = 0.50 \rightarrow [B_2]^2 = 1.00 (\text{doubled})$$



[A] constant at 0.50

$$Rate_1 = 1.6 \times 10^{-4}, Rate_2 = 3.2 \times 10^{-4}$$

$$\frac{Rate_1}{Rate_2} = 2 \Rightarrow 2^n = 2 \Rightarrow n = 1$$

Order with respect to B₂: 1

Step 3: Rate law

$$Rate = k[B_2]$$

8. (c) For following reaction, $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$

When the volume of vessel change into $\frac{1}{3}$ then concentration of reactant become three times.

The rate of reaction for first order reaction \propto concentration. So rate of reaction will increases three times.

9. (b) $2A + B \rightarrow$ Products

According to question : Rate of reaction of 'A' \propto [B] as increase in rate is double when [B] is doubled.

Rate of reaction \propto [A] [B] as increase in rate is 8 times when concentration of both reactant is doubled. It means that order of reaction is 3 and overall rate reaction should be $r = K[A]^2[B]$

10. (b) Let the rate of reaction depends on x^{th} power of [A]. Then

$$r_1 = k[A]^x \text{ and } r_2 = k[2A]^x$$

$$\therefore \frac{r_1}{r_2} = \frac{[A]^x}{[2A]^x} = \frac{1}{4} = \left(\frac{1}{2}\right)^2 \quad (\because r_2 = 4r_1)$$

$\therefore x = 2$. As the reaction rate does not depend upon the concentration of B. Hence, the correct rate law will be $rate = K[A]^2[B]^0$ or $= K[A]^2$



11. (b) **velocity constant (k)** (also called the **rate constant**) '*K*' is characteristic constant of a reaction and depends only on temperature and catalyst. Yes, *k* strongly depends

on temperature (Arrhenius equation: $k = A e^{\left\{-\frac{E_a}{RT}\right\}}$)

Catalyst → lowers activation energy (*E_a*), so *k* increases

12. (d) Unit of *K* for 1st order reaction is $Time^{-1}$.

13. (a) $K = A e^{-\frac{E_a}{RT}}$ by this equation it is clear that rate constant of a reaction depends on temperature

14. (c) $k = \frac{2.303}{t} \log_{10} \frac{a}{a-x}$; $t = 2 \times 10^2$, $a = 800$, $a - x = 50$

$$\begin{aligned} k &= \frac{2.303}{2 \times 10^2} \log_{10} \frac{800}{50} = \frac{2.303}{2 \times 10^2} \log_{10} 16 \\ &= \frac{2.303}{2 \times 10^2} \log_{10} 2^4 = \frac{2.303}{2 \times 10^4} \times 4 \times 0.301 \\ &= 1.38 \times 10^{-2} s^{-1} \end{aligned}$$

15. (d) Rate of reaction is quadrupled on doubling the concentration. Thus $r \propto [A]^2$.

16. (d) *K* is not constant for all the reaction.

17. 1) Units of rate constant for the homogeneous reaction

Reaction: $A + B \rightarrow C$ (elementary, bimolecular)

Rate law (elementary):

$$Rate = k [A][B]$$

Units:

- Rate has units $mol L^{-1} s^{-1}$.





- Concentrations each have units mol L^{-1} , so $[A][B]$ has units $(\text{mol L}^{-1})^2 = \text{mol}^2 \text{L}^{-2}$.
- Therefore k must have units $= (\text{mol L}^{-1} \text{s}^{-1}) / (\text{mol}^2 \text{L}^{-2}) = \text{L mol}^{-1} \text{s}^{-1}$.

Match to options: **(c)** $\text{s}^{-1} \text{litre mole}^{-1}$ (this is the same as $\text{L mol}^{-1} \text{s}^{-1}$).

Answer (part 1): (c)

18. Most stable oxide of nitrogen (based on K values)

Solution:

- The smaller the equilibrium constant (K) for decomposition, the more stable the oxide.
- Comparing values:
 - $\text{NO}_2: K = 6.7 \times 10^{16}$ (smallest)
 - $\text{NO}: K = 2.2 \times 10^{30}$
 - $\text{N}_2\text{O}_5: K = 1.2 \times 10^{34}$
 - $\text{N}_2\text{O}: K = 3.5 \times 10^{33}$
- Therefore, NO_2 is the most stable oxide.

19. (c) Rate determining step is a slow step by which rate of reaction can be determined.

20. (c) It is a second order reaction and the unit of k for second order reaction is $\text{litre mol}^{-1} \text{sec}^{-1}$.

21. (b) For reversible reaction rate constant is also reverse.

22. (a) $\text{Rate} = K(\text{N}_2\text{O}_5) = 6.2 \times 10^{-1} \times 1.25$
 $= 7.75 \times 10^{-1} \text{mol L}^{-1} \text{s}^{-1}$

23. (a) We know that for first order kinetics

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$



$$(a - x) = 0.05 \text{ mol l}^{-1}, 6 = \frac{2.303}{t} \log \frac{0.5}{0.05}$$

$$\text{or } t = \frac{2.303}{6} \log \frac{0.5}{0.05} = \frac{2.303}{6} = 0.384 \text{ min}$$

24. (d) Rate = $K(N_2O_5)$ hence $2.4 \times 10^{-5} = 3.0 \times 10^{-5}(N_2O_5)$
or $(N_2O_5) = 0.8 \text{ mol l}^{-1}$

