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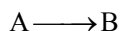
Chemical Kinetics

CHEMICAL KINETICS

Chemical kinetics is the branch of chemistry which deals with the study of rates of reactions, the factors which influence them and the mechanism by which the reactions take place.

REACTION RATE

The rate of a reaction tells us to what speed the reaction occurs. Let us consider a simple reaction



The concentration of the reactant A decreases and that of B increases as time passes. The rate of reaction is defined as the change in concentration of any of reactant or products per unit time. For the given reaction the rate of reaction may be equal to the rate of disappearance of A which is equal to the rate of appearance of B.

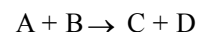
Factors affecting the reaction rate

1. Greater are the concentrations of the reactants, faster is the reaction. As the concentration of the reactants decrease, the rate of reaction also decreases.
2. A catalyst generally increases the speed of a reaction without itself being consumed in the reaction. In case of reversible reactions, a catalyst helps to attain the equilibrium quickly without disturbing the state of equilibrium.
3. Some reactions do not occur in the dark but take place in presence of light. Such type of reaction is called photochemical reaction.
4. For a reaction involving a solid reactant or catalyst, the smaller is the particle size i.e., greater is the surface area, faster is the reaction.
5. The rate of reaction increases with increase of temperature. In most of the cases, the rate of reaction becomes nearly double for 10 K rise of temperature. In some cases reaction do not take place at room temperature but take place at higher temperature.

LAW OF MASS ACTION AND RATE CONSTANT

The rate at which a substance reacts is directly

proportional to its active mass and the rate at which a reaction proceeds is proportional to the product of the active masses of the reacting substances.



Concentration of the reactants A and B decreases with time and that of the products C and D increases with time.

RATE LAWS

At a fixed temperature, the rate of a given reaction depends on concentrations of reactants. The exact relation between concentration and rate is determined by measuring the reaction rate with different initial reactant concentrations. By a study of numerous reactions it is shown that the rate of a reaction is directly proportional to the reactant concentrations, each concentration being raised to some power. Thus, for a substance A, undergoing reaction,

$$\text{rate} \propto [A]^n$$

$$\text{or rate} = k[A]^n$$

For a reaction, $2A + B \longrightarrow \text{products}$

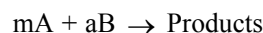
The reaction rate with respect to A or B is determined by varying the concentration of one reactant keeping that of the other constant. Thus the rate of reaction may be expressed as

$$\text{rate} = k[A]^m [B]^n$$

An expression which shows how the reaction rate is related to concentrations is called the rate law or rate equation.

ORDER OF A REACTION

The dependence of reaction rates on concentration may be expressed in terms of order of reaction. The order of reaction is defined as "sum of the powers of the concentration terms in the rate law." Thus if rate of the reaction,



is given by the equation,

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

then the power m is the order of the reaction with respect to reactant A and the power n is the order of the reaction with respect to the reactant B. Their sum (m + n) is called the overall order of reaction.

ZERO ORDER REACTION

A reactant whose concentration does not affect the reaction rate is not included in the rate law. In effect, the concentration of such a reactant has the power 0. Thus $[A] = 1$.

A zero order reaction is one whose rate is independent of concentration.

MOLECULARITY OF A REACTION

The number of atoms, ions or molecules that must collide with one simultaneously so as to result into a chemical reaction is called the molecularity of the reaction (whereas sum of the powers to which the concentration are raised in the rate law is known as the order of reaction).

HALF-LIFE OF A REACTION

Reaction rates can also be expressed in terms of half-life or half-life period. It is defined as the time required for the concentration of a reactant to decrease to half its initial value. In other words, half-life is the time required for one-half of the reaction to be completed. It is represented by the symbol $t_{1/2}$ or $t_{0.5}$. The half-life of a reaction can be calculated by using the integrated rate equation for its order.

Calculation of half-life of a First order reaction:

The integrated rate equation for a first order reaction can be stated as

$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$$

where $[A]_0$ is initial concentration and $[A]$ is concentration at any time t .

Half-life, $t_{1/2}$, is time when initial concentration reduces to half, i.e.

$$[A] = \frac{1}{2}[A]_0$$

$$k = \frac{2.303}{t_{1/2}} \log \frac{[A]_0}{1/2[A]_0} = \frac{2.303}{t_{1/2}} \log 2$$

$$\text{or } t_{1/2} = \frac{2.303}{k} \log 2 = \frac{2.303}{k} \times 0.3010 = \frac{0.693}{k}$$

It is clear from this relation that:

- half-life for a first order reaction is independent of the initial concentration.
- it is inversely proportional to k , the rate-constant.

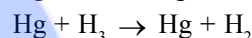
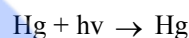
PHOTOCHEMICAL REACTIONS

Photochemical reactions are the reactions which

take place in the presence of light. The absorption of light by the reactant molecules increases their energy. This facilitates the reactant molecules to acquire the activation energy for the reaction, e.g. reaction between H_2 and Cl_2 to produce HCl . Photochemistry plays an important role in our daily life. Photosynthesis and vision are two well known examples. Light is used in synthesis of many organic compounds. Photography is based on the principles of photochemistry. Fading of bright coloured cloths when exposed to sunlight is also due to photochemical reaction.

PHOTOSENSITIZATION

Sometimes molecules that absorb light transfers its extra energy to another molecule which undergoes reaction. It is known as photosensitization, e.g., hydrogen molecule do not dissociate when exposed to ultraviolet rays. But when H_2 gas is mixed with mercury vapours and then exposed to ultraviolet rays, these dissociate to give H atoms as shown below



Quantum yield or Quantum efficiency of a photochemical reaction

$$\phi = \frac{\text{Number of molecules reacting in a given time}}{\text{Number of quanta of light absorbed in the same time}}$$

COLLISION THEORY

A reaction takes place because the reacting molecules collide with each other. However the rate of reaction depends not on the total number of collisions per second per unit volume (collision frequency) but on the fraction of molecules having energy greater than threshold energy, i.e., on the number of effective collisions (resulting into chemical reaction). Hence,

$$\text{Rate} = \frac{dx}{dt} = Z \times f$$

where Z = collision frequency and

f = fraction of molecules with energy greater than threshold value which is given by

$$f = e^{-E/RT}$$

As a rate constant (k), we write $k = Z e^{-E/RT}$. Again, rate not only depends upon the energy factor but also on the orientation factor. Hence the equation is modified to $k = P Z e^{-E/RT}$ where P is called steric factor.

- is diluted by an equal volume of water would be
- a) 4 times b) 2 times
c) 0.5 times d) 0.25 times
13. For the decomposition of HI at 600 K
 $2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$
 the following data were obtained
- | [HI]
(mol. L ⁻¹) | B Rate of decomposition of HI
(mol. L ⁻¹ s ⁻¹) |
|---------------------------------|--|
| 0.10 | 2.75×10^{-8} |
| 0.20 | 11.00×10^{-8} |
| 0.30 | 24.75×10^{-8} |
- The order of the reaction is
- a) 1(b) 2
c) 0 d) 1.5
14. The activation energy for the reaction
 $2\text{HI}(\text{g}) \sim \text{H}_2(\text{g}) + \text{I}_2(\text{g})$ is 209.5 kJ mol⁻¹ at 581 K.
 The fraction of molecules of reactants having energy equal to or greater than activation energy would be
- a) 1.462×10^{24} b) 1.462×10^{-19}
c) 1.462×10^{28} d) 1.462×10^{34}
15. Which of the following best explains how catalysts increase the rate of a chemical reaction?
- a) They reduce the amount of product
b) They increase the amount of the product
c) They reduce the amount of reactants
d) They reduce the activation energy for the reaction
16. For a third order reaction, $3\text{X} \rightarrow \text{Y} + \text{Z}$, the initial rate is $5 \times 10^{-2} \text{ mol L}^{-1} \text{ S}^{-1}$, when the conc. of X is 0.1 mol L⁻¹. The value of rate constant for the reaction is
- a) $5 \times 10^{-2} \text{ L}^2 \text{ mol}^{-2} \text{ g}^{-1}$
b) $5 \times 10^{-3} \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$
c) $5 \times 10^{-4} \text{ L}^2 \text{ mol}^{-2} \text{ S}^{-1}$
d) $50 \text{ L}^2 \text{ mol}^{-2} \text{ S}^{-1}$
17. $2\text{FeCl}_3 + \text{SnCl}_2 \rightarrow 2\text{FeCl}_2 + \text{SnCl}_4$. The reaction is an example of
- a) second order reaction
b) third order reaction
c) first order reaction
d) none of these
18. The hydrolysis of ethyl acetate,
 $\text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O}$
 $\xrightarrow{\text{H}^+} \text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH}$
 is reaction of
- a) pseudo first order
- b) second order
c) third order
d) zero order
19. Which one of the following statements is wrong in case of enzyme catalysis?
- a) Enzymes work best at an optimum temperature
b) Enzymes work at optimum pH value
c) Enzymes are highly specific for substrates
d) An enzyme raises activation energy
20. Which is not true of first order reaction?
- a) Half-life time is independent of initial concentration of reactants
b) Unit for first order reaction is sec-1
c) log C us Time plot is a straight line
d) Rate increases with decrease in concentration of reactants
21. When the concentration of a solution changes from 0.2 to 0.4, then what will be the rate and equilibrium constant, if reaction is of first order and rate constant is $k = 1 \times 10^{-6}$?
- a) 2×10^{-7} ; 1×10^{-6}
b) 1×10^{-7} ; 1×10^6
c) 4×10^{-7} ; 1×10^{-6}
d) 2×10^{-3} ; 1×10^{-3}
22. The rate constant for a reaction, $2\text{A} \rightarrow \text{B} + \text{C}$, is $1.0 \times 10^{-2} \text{ mol L}^{-1} \text{ S}^{-1}$. The rate of the reaction when concentration of A is 2.0 mol L⁻¹, would be
- a) $1.0 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$
b) $2.0 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$
c) $4.0 \times 10^{-2} \text{ mol L}^{-1} \text{ S}^{-1}$
d) $8.0 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$
23. Which of the following statements is false?
- a) fast reactions have low activation energy
b) activation energy of a reaction depends on the chemical nature of reactants and products.
c) with increase in temperature the rate of reaction decreases in case of exothermic reactions.
d) a catalyst increases the rate of reaction by decreasing the activation energy of the reaction.
24. The reaction N_2O_5 (in CCl_4) $\longrightarrow 2\text{NO}_2 + \frac{1}{2}\text{O}_2(\text{g})$ is offirst order in N_2O_5 with rate constant $6.2 \times 10^{-4} \text{ s}^{-1}$. What is the value of rate of reaction when $\text{N}_2\text{O}_5 = 1.25 \text{ mol L}^{-1}$?
- a) $7.75 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$
b) $6.35 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$

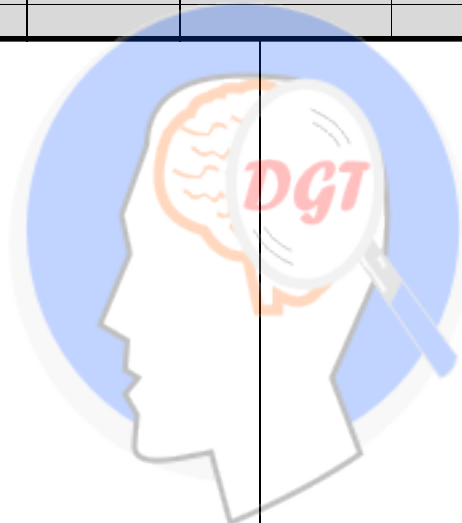
- c) $5.15 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}$
 d) none of these
25. For the reaction $A \rightarrow B$, the rate law expression is $\text{rate} = k[A]$. Which of the following statements is incorrect ?
 a) the reaction follows first order kinetics
 b) the $t_{1/2}$ of reaction depends on initial concentration of reactants
 c) K is constant for the reaction at a constant temperature
 d) the rate law provides a simple way of predicting the concentration of the reactants and products at any time after the start of the reaction.
26. If α is the dissociation constant, then the number of moles for the following reaction is :
 $2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$
 a) $2 - \alpha$ b) $1 - \alpha$
 c) 1 d) 2
27. The rate law expressions for the four reactions are given below. In which case, the per cent increase in the rate of reaction would be maximum when concentration of A is doubled?
 a) $r = k[A]$ b) $r = k[A]^0$
 c) $r = k[A]^2$ d) $r = k[A]^{3/2}$
28. Which of the following statements is not true?
 a) A reaction having fractional order must be a complex reaction
 b) Order of the reaction is determined from experimental data
 c) Molecularity of a reaction may be equal to three
 d) Order of a reaction does not tell us anything about mechanism of the reaction.
29. The rate of a gaseous reaction is given by the expression $k[A][B]$. If the volume of the reaction vessel is suddenly reduced to 1/4th of the original volume, the reaction rate relating to the original rate would be
 a) $\frac{1}{10}$ b) $\frac{1}{8}$
 c) 8 d) 16
30. In a catalytic conversion of N_2 to NH_3 by Haber's process, the rate of reaction expressed as change in the concentration of ammonia per second is $40 \times 10^{-13} \text{ mol}^{-1} \text{ s}^{-1}$. If there are no side reactions, then rate of the reaction as expressed in terms of hydrogen is
 a) $60 \times 10^{-3} \text{ mol}^{-1} \text{ s}^{-1}$ b) $20 \times 10^{-3} \text{ mol}^{-1} \text{ s}^{-1}$
 c) $30 \times 10^{-3} \text{ mol}^{-1} \text{ s}^{-1}$
 d) $10 \times 10^{-3} \text{ mol}^{-1} \text{ s}^{-1}$
31. In the titration between oxalic acid and acidified potassium permanganate, the manganous salt formed catalyses the reaction. The manganous salt is
 a) a promoter b) a positive catalyst
 c) an autocatalyst d) none of these
32. For the reaction, $2A + B \rightarrow C + D$, the rate of reaction increases eight times when concentrations of both A and B are doubled the rate of reaction increases four times when initial concentration of only B is doubled. The rate expression for the reaction is
 a) $r = k[A]^2 [B]$
 b) $r = k [A] [B]^2$
 c) $r = k [A] [B]$
 d) $r = k [A]^2 [B]^2$
33. For producing the effective collisions, the colliding molecules must possess
 a) a certain minimum amount of energy
 b) energy equal to or greater than threshold energy
 c) proper geometry
 d) threshold energy and proper orientation.
34. The chemical reaction $2\text{O}_3 \rightarrow 3\text{O}_2$ proceeds as follows
 $\text{O}_3 \rightarrow \text{O}_2 + \text{O}$ (fast)
 $\text{O} + \text{O}_3 \rightarrow 2\text{O}_2$ (slow)
 The rate law expression should be
 a) $r = k [\text{O}_2] [\text{O}_3]$
 b) $r = k [\text{O}_3]^2$
 c) $r = k [\text{O}_3]^2 [\text{O}_2]^{-1}$
 d) none of these
35. The activation energy of reaction I is 80 kJ mol^{-1} and that of reaction II is 60 kJ mol^{-1} . Which of the following statements is correct ?
 a) The rate of reaction II is greater than that of I
 b) The rate constant of reaction II is greater than that of I
 c) The order of reaction I is greater than that of II
 d) The molecularity of reaction II is less than that of I.
36. $A + B \rightarrow C$, choose the rate equation for the above reaction with the help of given data

Experiment	[A]	[B]	Initial rate
1	0.012	0.035	0.10
2	0.024	0.070	0.80
3	0.024	0.035	0.10
4	0.012	0.070	0.80

- a) Rate = $k[B]^2$
 b) Rate = $k[B]^4$
 c) Rate = $k[A][B]^3$
 d) Rate = $k[A]^2[B]^2$
37. The catalyst remains unchanged at the end of the reaction as regards
 a) quantity
 b) chemical composition
 c) quality and chemical composition
 d) quantity and chemical composition
38. Which of the following statements is not correct?
 a) Molecularity of a reaction cannot be fractional
 b) Molecularity of a reaction cannot be more than three.
 c) Molecularity of a reaction can be obtained from balance chemical equation.
 d) Molecularity of a reaction may or may not be equal to the order of the reaction.
39. For the chemical reaction $A + 2B \rightarrow \text{Product}$, the rate of the reaction is given by
 a) $\frac{1}{2} \frac{d[A]}{dt}$ b) $\frac{d[B]}{dt}$
 c) $\frac{d[A]}{dt} = \frac{d[B]}{dt}$ d) $\frac{d[A]}{dt} = \frac{1}{2} \frac{d[B]}{dt}$
40. For the chemical reaction the $\frac{d[A]}{dt} = k[A]^2$, the units for rate constant is
 a) time
 b) minute^{-1}
 c) $\text{sec}^{-1} \text{ mol}^{-1} \text{ litre}^+1$
 d) $\text{minuter}^{-1} \text{ mol}^{-1} \text{ litre}^{-1}$
41. In which of the following case, does reaction go nearest to completion ?
 a) $k = 10^{-2}$ b) $k = 1$ c) $k = 10$ d) $k = 10^3$
42. In a reversible reaction a catalyst in substance which
 a) reduces the time required for reaction equilibrium state in the reaction
 b) increases the rate of forward reaction
 c) decreases the rate of reverse reaction
 d) Changes entropy of the reaction
43. Which of the following relations in correct ?
 a) $k = \frac{A E_a}{RT}$
 b) $\ln k - \ln A = \frac{E_a}{RT}$
 c) $\ln A - \ln k = \frac{E_a}{RT}$
 d) $\ln A - \ln k = \frac{E_a}{RT}$
44. In a reversible reaction $A + B \rightleftharpoons AB$, which one of the following statement is correct ?
 a) The combination reaction will be endothermic and the dissociation reaction will be exothermic
 b) The combination reaction will be exothermic and the dissociation reaction will be endothermic
 c) Both the reactions will be exothermic
 d) Neither of the reactions will be endothermic
45. A plot of the Concentration of A versus Time found for the reaction A products, is a straight line. The order of the reaction is
 a) zero b) one
 c) two d) 0.5
46. The decomposition of A follows second order kinetics. The initial rate of decomposition when $[A]_0 = 0.50 \text{ M}$ is
 a) the same as the initial rate for any value of $[A]_0 = 0.50 \text{ M}$ is
 b) half of that found when $(A)_0 = 1.00 \text{ M}$
 c) five times the rate found when $(A)_0 = 0.10 \text{ M}$
 d) four times the rate found when $(A)_0 = 0.25 \text{ M}$

Answer Key

Q.No.	Ans	Q.No.	Ans	Q.No.	Ans
1.	c)	2.	d)	3.	d)
4.	a)	5.	b)	6.	c)
7.	d)	8.	d)	9.	d)
10.	b)	11.	a)	12.	d)
13.	b)	14.	b)	15.	d)
16.	d)	17.	b)	18.	a)
19.	d)	20.	d)	21.	c)
22.	a)	23.	c)	24.	a)
25.	b)	26.	d)	27.	c)
28.	d)	29.	d)	30.	a)
31.	c)	32.	b)	33.	d)
34.	c)	35.	b)	36.	a)
37.	d)	38.	c)	39.	d)
40.	c)	41.	d)	42.	a)
43.	c)	44.	b)	45.	a)
46.	d)				





EXPLANATIONS

3. (a) can be measured by noting the change in colour, (b) by noting change in pressure, (c) by noting rotation of the plane polarised light and (d) by noting change in pH value.

$$4. (i) -\frac{\Delta[I^-]}{\Delta t} = (-) \frac{\Delta[I^-]_f - [I^-]_i}{\Delta t}$$

$$= -\frac{(0.46 - 0.50) \text{ mol L}^{-1}}{(10 - 0) \text{ min}}$$

$$= \frac{0.04 \text{ mol L}^{-1}}{10 \text{ min}}$$

$$(ii) +\frac{\Delta[I_2]}{\Delta t} = -\frac{1}{2} \frac{\Delta[I^-]}{\Delta t} = 0.004 \text{ mol L}^{-1} \text{ min}^{-1}$$

$$= \frac{(0.004) \text{ mol L}^{-1} \text{ min}^{-1}}{2} = 0.002 \text{ mol L}^{-1} \text{ min}^{-1}$$

This is because 2 moles of I^- produces 1 mole of I_2 .

5. $2N_2O_5 \rightarrow 4NO_2 + O_2$, this reaction is of first order and the rate expression for this reaction

$$\frac{dx}{dt} = k [N_2O_5]$$

$$\text{or } [N_2O_5] = \frac{dx}{dt} \times \frac{1}{k}$$

$$= \frac{1.02 \times 10^{-4}}{3.4 \times 10^{-5}} = 3.$$

6. Rate = $k[X]$

$$k = \frac{\text{Rate}}{[X]} = \frac{7.5 \times 10^{-4}}{0.5}$$

$$= 1.5 \times 10^{-3} \text{ s}^{-1}.$$

8. Given, $r = Ka^\alpha$... (i)
 $2r = K(4a)^\alpha$... (ii)

Dividing equation (ii) by equation (i), we get

$$4^\alpha = 2, \quad \text{or } 2^{2\alpha} = 2$$

$$\text{or } 2\alpha = 1 \quad \text{or } \alpha = \frac{1}{2}$$

10. The overall rate = $1 + \frac{1}{2} = \frac{3}{2}$

For unit use the formula,

$$\left(\frac{\text{mol}}{\text{litre}}\right)^{1-n} \text{ s}^{-1} = \left(\frac{\text{mol}}{\text{litre}}\right)^{1-3/2} \text{ s}^{-1}$$

$$= \text{mol}^{-1/2} \text{ L}^{1/2} \text{ s}^{-1}$$

11. On increasing the pressure, boiling point increases and the beans are cooked earlier in pressure cooker.

12. rate = $k [CH_3COOH] [C_2H_5OH]$

When each con. is reduced to half, the rate of

reaction would become $\frac{1}{4}$ times.

13. As the rate of the reaction is increasing four times when concentration of HI is doubled, then order of the reaction is 2.

14. Fraction of molecules with energy equal to or greater than activation energy = $e^{-E_a/RT}$

$$= e^{\frac{2095 \times 1000 \text{ J mol}^{-1}}{33143 \text{ J mol}^{-1} \text{ K}^{-1} \times 581 \text{ K}}} = e^{-13.369} = 1.462 \times 10^{-19}$$

15. We know that higher the energy barrier, slower is the rate of the reaction. When a catalyst is added, a new reaction path with lower energy barrier is provided.

16. rate = $k[X]^3$,

$$k = \frac{\text{rate}}{[X]^3}$$

$$= \frac{5 \times 10^{-2}}{(0.1)^3}$$

$$= 50 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$$

17. Greater the order of the reaction, more is the percent increase in the rate of the reaction for a given increase in concentration.

19. Enzyme or any other of catalyst does not raise the activation energy.

21. Rate equation of first order reaction is $\text{Rate} = k[A]$
 $= 1 \times 10^{-6} \times 0.4$
 $= 4 \times 10^{-7}$

Hence the equilibrium constant is independent of the concentration of reactants and is a characteristic constant for a given reaction.

22. By observing the dimension of k , we come to know that the given reaction is a zero order reaction.

For a zero order reaction, $\text{Rate} = \text{Rate constant}$
 $= 1.0 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$

24. $\text{Rate} = k[\text{N}_2\text{O}_5] = 6.2 \times 10^{-4} \text{ s} \times 1.25 \text{ mol L}^{-1}$
 $= 7.75 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$

25. The half life period of a first order reaction is independent of concentration.

26. $2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$

2	0	0	Initial state
$2 - 2\alpha$	α	α	Equilibrium state

Hence, the number of total moles at equilibrium is

$$2 - 2\alpha + \alpha + \alpha = 2$$

29. $\text{rate} = k[A] \cdot [B]$

When volume is reduced to $\frac{1}{4}$ th of its original volume, pressure increases to four times; then A and B becomes 4A and 4B.

$$\therefore \text{rate} = k \times 4 \times 4 = 16k$$

30. $\text{Rate} = \frac{1}{2} \cdot \frac{d(\text{NH}_3)}{dt} = 40 \times 10^{-3} \text{ mol}^{-1} \text{ s}^{-1}$

So $\frac{d(\text{NH}_3)}{dt} = 20 \times 10^{-3} \text{ mol}^{-1} \text{ s}^{-1}$

and $\frac{d[\text{H}_2]}{dt} = 3 \times 20 \times 10^{-3} \text{ mol}^{-1} \text{ s}^{-1}$
 $= 60 \times 10^{-3} \text{ mol}^{-1} \text{ s}^{-1}$.

34. Rate law for slow reaction : $r = [\text{O}_3][\text{O}] \dots (i)$

For equilibrium, $k = \frac{[\text{O}_2]}{[\text{O}_3]}[\text{O}]$ or $[\text{O}] = k \frac{[\text{O}_3]}{[\text{O}_2]}$

Putting the value of $[\text{O}]$ in equation (i), we get
 $r = k[\text{O}_3]^2 [\text{O}_2]^{-1}$.

35. $K \propto \frac{1}{E_a}$

36. $\text{Rate} = k[\text{B}]^3$. The rate of the given reaction depends on the concentration of B and not A.

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