

Sub : chemistry

Grade : 11

Unit – 4 (CHEMICAL KINETICS)

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4.1 rate of reaction

4.2 theories of reaction rate

4.3 rate of equation (laws)

4.4 reaction mechanism

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Part one

4.1 rate of reaction

Rate of reaction(rxn) :- is change in concentration (conc) of reactant & product over agiven period of time.

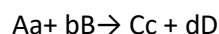
- During rxn conc of reactants dec rease while conc of prouct increase.

Rate of rxn(r) = - $\Delta[\text{reactants}]/\Delta\text{time} = \Delta[\text{product}]/\Delta\text{time}$

- ❖ The negative sign indicates final concentration of reactant is less than the intial concentration.

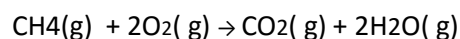
NB unit of rate of rxn is $\text{MOL}^{-1}\text{L}^{-1}\text{S}$

Given hypothetical rxn represented by balanced equation :



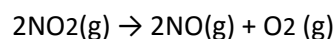
Rate of rxn= $-\Delta[A]/a\Delta t = -\Delta[B]/b\Delta t = \Delta[C]/c\Delta t = \Delta[D]/d\Delta t$

Worked example 1:- express the rate of the ff rxn interms of reactant & product ?



Solution rate = $-\Delta[\text{CH}_4]/\Delta t = -\Delta[\text{O}_2]/2\Delta t = \Delta[\text{CO}_2]/\Delta t = \Delta[\text{H}_2\text{O}]/\Delta t$

Worked example :- 2 write the valid rxn rate for the given rxn?



Rate = $-\Delta[\text{NO}_2]/2\Delta t = \Delta[\text{NO}]/2\Delta t = \Delta[\text{O}_2]/\Delta t$

Factors affecting rate of reactants

1 cocntration of reactants

- ❖ As conctratation of reactants increase rate of rxn also increase
- ❖ For gaseous reactants increasing pressure will increase rate of rxn

2 nature of reactants

- ❖ The more reactive the reactant the fster the rate of rxn

3 surface area of reactants

- ❖ As surface area of solid increase rate of rxn increase

Homogeneous rxn:- rxn occur b/n the same phase .

Heterogeneous rxn :- rxn b/n two d/t phase

4 Temperature of reactants

- ❖ Increasing temp increase average kinetic energy
- ❖ Increasing temp increase the rate of rxn

5 catalyst

- ❖ Catalyst is subs that speed up a given chemical rxn by lowering its activation energy (EA).
- ❖ Catalyst speed up a rxn rate with out consuming in the rxn
- ❖ They doesn't alter position of equilibrium

NB positive catalyst, speed up(increase) rate of rxn by lowering activation energy.

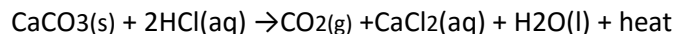
Negative catalyst slow down(decrease) rate of rxn by increasing activation energy.

Questions from entrance exam from this topic 1 & 2

1 In a rxn $A + B \rightarrow \text{product}$, the rate law is doubled when the concn of B is doubled & the rate increased by factor of 8 when the conc of both reactants A & B are doubled, the rate for the rxn can be written as:- (2006 E.C)

- | | |
|----------------|------------------|
| A) $K[A][B]$ | C) $K[A]^2[B]$ |
| B) $K[A][B]^2$ | D) $K[A]^2[B]^2$ |

2 consider rxn below in w/h the effect of conc & temp simultaneous cause an increase in the rate at w/h product are formed ? (2007 E.C)



- | | |
|--|---|
| A) Decrease $[\text{HCl}]$ & decrease temp | c) increase $[\text{HCl}]$ & decrease temp |
| B) Increase $[\text{HCl}]$ & increase temp | D) grind up the CaCO_3 & decrease temp |

3 if we increase the conc of reactants, what happen to collision b/n particles? (2008 E.C)

- | | |
|------------------------------|---|
| A) There are more collision | C) there are same number of collision, but they have less energy |
| B) There are fewer collision | D) there are same number of collision, but they have more energy. |

4 the rate law of the over all rxn $A + B \rightarrow C$ is rate = $k[A]^2$ then w/h of the effect will not increase rate of rxn? (2008 E.C)

- | | |
|-----------------------|-------------------------|
| A) Increase conc of A | C) increase temp of rxn |
| B) Increase conc of B | D) adding catalyst |

5 rate of rxn increase with increasing conc of reactants this is b/c... (2009 E.C)

- A) Avg kinetic energy of molecule increase
- B) Frequency of molecular collision increase
- C) Order of rxn increase
- D) Activation energy increase

6 w/h of the ff increase the rate of rxn at which solid dissolve in liquid ? (2010 EC)

- A) Supersaturating the solution
- B) Grinding solution in to smaller piece
- C) Lowering temp
- D) Placing solution in opaque material

7 ΔH corresponds to process (2010 E.C)

- | | |
|---------------------------|---------------------------|
| A) Positive , endothermic | C) negative , endothermic |
| B) Positive , exothermic | D) Zero, exothermic |

8 the minimum energy required for effective collision is called (2011 E.C)

- | | |
|---------------------|----------------------|
| A) Potential energy | C) free energy |
| B) Kinetic energy | D) activation energy |

9 what does it mean by $\Delta H =$ negative for the given process ? (2011 E.C)

- A) The process is endothermic
- B) The process is adiabatic
- C) The process is exothermic
- D) The process is isothermic

4.2 theories of reaction rate

States that “ for a rxn to occur collision of particle must occur”.

- The rate of rxn is directly proportional to number of collision per second.
- According to collision theory , the more the collision the faster the rate of rxn , however not all collisions b/n reacting species result in reaction .

Collision can be classified into two based on formation of product :-

- ✓ Ineffective collision :- doesn't result in formation of desired product.
- ✓ Effective collision:- results in formation of desired product

- Postulates of collision theory states that for a reaction to occur:-

- ➔ The particles must collide
- ➔ The particles of reacting species must have proper orientation
- ➔ The particles must collide with energy greater than or equal to activation energy

What is activation energy (EA)?

Is the minimum energy required for a reaction to occur during collision of reacting species .

- Increasing concentration of reacting species results in higher number of collision per unit time, and rate of rxn increase .

Transition state(activated complex) theory

According to this theory, collision b/n reacting species results in a short lived, high energy state species in the formation of activated complex.

Activated complex:- is short lived high energy state species that is temporary formed by collision of reactants before formation of product.

- According to transition state theory, the rate of rxn depend on the rate at which the reactants can climb top of barrier & form activated complex.

The difference b/n endothermic & exothermic rxn

Endothermic rxn

- 1 Absorb heat
- 2 $\Delta H > 0$
- 3 Products have higher energy than reactants

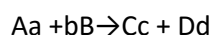
exothermic r

- release heat
- $\Delta H < 0$
- products have lower energy than reactants

4.3 rate of equations(law)

Rate law(equations) :- is an equation w/h link rxn rate with concentration or pressure with certain parameter .

Consider this hypothetical rxn



$$\text{Rate} = k[A]^x [B]^y$$

[A] = concentration of reactant A

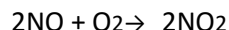
[B] = concentration of reactant B

X = order of rxn for reactant A

Y = order of rxn for reactant B

- ❖ order of rxn can be zero , positive or negative.
- ❖ Order of rxn is not the same as stoichiometric coefficient for balanced equation .

Worked Example :- determine the order of rxn with respect to each reactant & product from the given rate law ?



Solution

Steps 1 :- first we write rate law by the formula given above

$$\text{Rate} = k [\text{NO}]^2 [\text{O}_2]$$

Step 2:- the order of rxn with respect to [NO] is = 2

The order of rxn with respect to [O₂] = 1

Step 3:- the overall order is the sum of the two orders so 2 + 1 = 3

So the overall order is 3

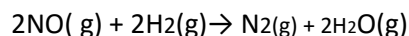
Determination of rate law

For the given rxn $A + bB \rightarrow Cc + dD$

$$\text{Initial rate law} = k[A]^x [B]^y$$

- X is determined by varying conc of A while keeping constant conc of B
- Y is determined by varying conc of B while keeping constant conc of A

Example:- the initial rate of & conc are measured for the given rxn



[NO] , M	[H ₂] , M	Initial rate mol/L/S
0.0005	0.0005	0.000025
0.0005	0.0010	0.000050
0.0010	0.0010	0.00020

What is rate equation for the rxn?

Soln :- rate = $k[\text{NO}]^x[\text{H}_2]^y$

x is determined by 2nd & 3rd data while y is determined by 1st & 2nd dat

$$\text{Rate 2/ rate 3} = k[\text{NO}]^x [\text{H}_2]^y / k[\text{NO}]^x [\text{H}_2]^y =$$

$$0.000050/0.00020 = k(0.0005)^x(0.0010)^y / k(0.0010)^x(0.0010)^y = 1/4 = (1/2)^x = (1/2)^2 \Rightarrow x = 2$$

$$\text{Rate 1/ rate 2} = k[\text{NO}]^1 [\text{H}_2]^1 / k[\text{NO}]^2 [\text{H}_2]^2 =$$

$$0.000025/0.000050 = (0.0005)^x(0.0005)^y / (0.0005)^x(0.0010)^y = 1/2 = (1/2)^y \Rightarrow y = 1$$

So the rate of rxn is rate = $k[\text{NO}]^2[\text{H}_2]$

Questions from entrance exam from this topic

1 kinetic data below are for the rxn : $\text{A} + \text{B} \rightarrow \text{C}$ from this data the order of rxn with respect to A & B?
(2006 E.C)

[A]	[B]	Initial rate
0.1	0.1	1×10^{-5}
0.1	0.2	4×10^{-5}
0.2	0.1	1×10^{-5}

- A) order of A = 1 & order B = 0
- B) order of A = 0 & order of B = 2
- C) order of A = 0 & order of B = 4
- D) Order of A = 1 & order of B = 2

2 given rxn $2\text{NOCl (g)} \rightarrow 2\text{NO(g)} + \text{Cl}_2$ the ff data obtained

[NOCl]	Initial rate
3×10^{-16}	5.98×10^{-4}
2×10^{-16}	2.66×10^{-4}
1×10^{-16}	6.64×10^{-5}
4×10^{-16}	1.06×10^{-3}

Then what is the rate law for the above decomposition? (2008 E.C)

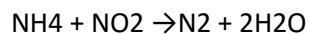
A) $K[\text{NOCl}]$

B) $K[\text{NOCl}]$

C) $K[\text{NOCl}][\text{NO}]$

D) $K[\text{NOCl}][\text{Cl}]$

3 given the ff rxn



Experiment	$[\text{NH}_4] \text{ (M)}$	$[\text{NO}_2] \text{ (M)}$	Rate (M/S)
1	0.01	0.02	0.02
2	0.15	0.02	0.03
3	0.010	0.01	0.005

What will be the rate law for the given rxn? (2009 E.C)

A) $K[\text{NH}_4] [\text{NO}_2]$

B) $K[\text{NH}_4]^2 [\text{NO}_2]$

C) $K[\text{NH}_4]^2 [\text{NO}_2]^2$

D) $K [\text{NH}_4] [\text{NO}_2]^2$

4 for the rxn $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$, the rate of disappearance of H_2 is 0.01 mol/min . what is the rate appearance of NH_3 ? (2011 E.C)

A) 0.01 Mmol/min

B) 0.02 mol/min

C) 0.002 mol/min

D) 0.007 mol/min