

**Rate Processes**  
**Prof. Mintu Halder**  
**IITKGP-Chemistry**

**Q1. Why does the rate of most chemical reactions increase with rise of temperature?**

A1. According to simple collision theory, increase of temperature will increase the fraction of molecules having energy greater than a critical amount required for the reaction to occur. Also using simple Arrhenius equation one can predict that increase of temperature will increase the rate constant of chemical reaction.

**Q2. Distinguish between the order and the molecularity of a chemical reaction.**

Order: It is sum of the concentration terms on which the rate of reaction actually depends or it is the sum of the exponents of the concentrations in the rate law equation. It need not be a whole number i.e. it can be fractional as well as zero. It can be determined experimentally only and cannot be calculated. It is for the overall reaction and no separate steps are written to obtain it.

Molecularity: It is the number of atoms, ions or molecules that must collide with one another simultaneously so as to result into a chemical reaction. It is always a whole number. It can be calculated by simply adding the molecules of the slowest step. The overall molecularity of a complex reaction has no significance. It is only slowest step whose molecularity has significance for the overall reaction.

**Q3. Define the term activation energy as it is used in chemical kinetics.**

A3. In chemical science, *activation energy* is a term introduced in 1889 by the Swedish scientist Svante Arrhenius that is defined as the energy that must be overcome in order for a chemical reaction to occur. Activation energy may also be defined as the minimum energy required to start a chemical reaction. The activation energy of a reaction is usually denoted by  $E_a$ , and given in units of kJ/ mol.

**Q4. All molecular collisions may not lead to chemical reaction-why?**

A4. Reactants may not have required activation energy, or reactants may not collide with correct orientation required for the reaction to occur.

**Q5. How will you identify a zero order reaction?**

A5. You can distinguish from the plot of concentration vs time. A zero order kinetics will have a linear plot with a negative slope.

**Q6. What is meant by absolute reaction rate theory?**

A6. Rates of the reactions are studied by studying activated complexes which is at the saddle point of the potential energy surface. The activated complexes are in quasi-equilibrium with the reactant molecules. The activated complexes may convert into products.

**Q7. What is meant by pseudo-first order reaction?**

A7. If the concentration of one of the reactants remains virtually constant (if it is in large excess compared to the other reactants), its concentration can be treated as a constant and can be grouped with the rate constant, to give a pseudo constant. If R is the reactant whose concentration is constant, then  $\text{rate} = k.[R].[M]$ , becomes  $\text{rate} = k'.[M]$ . The second-order rate equation has now been reduced, by this, to *pseudo-first-order* rate equation. Thus the treatment to obtain the integrated rate law becomes much simpler.

**Q8. What are necessary for successful collisions to occur in case of, say, gas-phase reactions?**

A8. Favourable collision geometry and kinetic energy sufficient to overcome the barrier.

**Q9. What is catalysis?**

A9. Catalysis is the change (generally increase) in rate reaction due to the participation of another chemical agent called catalyst. Unlike other reagents catalysts participate in the chemical reaction, but is not consumed and remains unaltered after reaction and can be reused. Actually catalysts provide an alternate path demanding lower activation energy.

**Q10. What is heterogeneous catalysis?**

A10. Heterogeneous catalysts act in a different phase than the reactants. For example, finely divided iron acts as catalyst for the Haber synthesis of  $\text{NH}_3$ .

**Q11. What is homogeneous catalysis?**

A11. For homogeneous catalysts the catalyst and the reactants are in same phase. For example, acid catalyzed esterification.

**Q12. What are enzymes?**

A12. Enzymes are biocatalysts act in various bioreactions inside the cell. These enzymes are biomolecules and typically proteins. These catalysts are very specific.

**Q13. What are the characteristics of enzyme catalysis?**

A13. Enzyme activity is very much dependent on temperature, pressure, pH, concentration of substrate, inhibitors. It has optimum pH and temperature for maximum action.

**Q14. What is photochemical reaction?**

A14. Any reaction where photon is an integral part (photons may act like reactants) for its occurrence is called a photochemical reaction. For example, photosynthesis.

**Q15. What are the characteristics of elementary reactions?**

A15. Elementary reactions are generally unimolecular or bimolecular, and ter molecular processes are rare. Order of reaction is related to stoichiometric coefficient. These processes can be reversible.

**Q16. What is meant by rate determining step?**

A16. Rate determining elementary step is the slowest step (bottle-neck) in the overall process.

**Q17. What is monitored in voltammetry?**

A17. The current is monitored as the potential of the electrode is changed.

**Q18. What is the typical use of cyclic voltammetry?**

A18. To find out the redox potential of electroactive substance and explore the kinetics of the process.

**Q19. What is corrosion?**

A19. It is the destructive electrochemical attack on metals/ materials. As for example, rusting of iron.

**Q20. What spin-states are possible for a radical pair?**

A20. Singlet and triplet radical pair.

**Q21. Do you expect magnetic field effect on chemical reaction?**

A21. Yes, if the reaction proceeds *via* radical pairs we may expect magnetic field effect.

**Q22. Name to techniques for studying fast reactions?**

A22. Stopped flow method and flash photolysis.

**Q23. Give one example of diffusion controlled?**

A23. Reaction between  $\text{H}^+$  and  $\text{OH}^-$  to produce water.

**Q24. What are the common mechanisms of solvent exchange reactions?**

A24. Dissociative and associative mechanisms.

**Q25. How will you identify an associative mechanism?**

A25. A negative value of  $\Delta V^\ddagger$  implies a contraction to form the transition state, *i.e.* an associative mechanism.

**Q26. What are the different techniques in ultrafast spectroscopy?**

A26. Transient absorption, fluorescence upconversion to probe transients.

**Q27. Name a process which can be in ultrafast time-domain, which is in femtosecond.**

A27. Dynamics of solvation of a photo generated transient dipole.

**Q28. Can you probe transition state?**

A28. Yes, by using femtosecond spectroscopy you can probe, for example study of NaI decomposition using ultrafast lasers.

**Q29. What is the aim of molecular reaction dynamics studies?**

A29. Chemical reaction dynamics study aims to understand chemistry in detail by probing chemical reactions at a level of single reactive collisions between molecules.

**Q30. What is the advantage of molecular reaction dynamics over traditional kinetics study?**

A30. In a typical kinetics study the rate constant determined is highly averaged quantity, the combined outcome of large number of individual collisions between reactant molecules.

In reaction dynamics, it is possible to control the speeds, quantum states, and even orientation of the colliding molecules to measure the effect of these variables. The study gives us insight into the basic physics underlying chemical reactivity.

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