

CHE201 – PHYSICAL CHEMISTRY

FINAL TERM MOST IMPORTANT QUESTIONS

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Q-1 Write elementary steps for the reaction mechanism.

Elementary Steps for Reaction Mechanism

A mechanism for a reaction is a collection of elementary processes (also called elementary steps or elementary reactions) that explains how the overall reaction proceeds.

Elementary Processes or Steps:

An elementary process is also called an elementary step or elementary reaction.

It expresses how molecules or ions actually react with each other.

The equation in an elementary step represents the reaction at the molecular level, not the overall reaction.

Based on numbers of molecules involved in the elementary step, there are three kinds of elementary steps:

- Unimolecular step (or process),
- Bimolecular step,
- Trimolecular step.

An elementary step is proposed to give the reaction rate expression.

1. The rate of an elementary step is always written according to the proposed equation.
2. This practice is very different from the derivation of rate laws for an overall reaction.

Q-2 Explain mechanism of stopped flow method.

- These are by far the most common means of studying fast solution phase reactions over time intervals of down to a fraction of a millisecond.
- The use of reasonably simple devices is now practical even in student laboratory experiments.
- These techniques make it possible to follow not only changes in the concentrations of reactants and products, but also the buildup and decay of reaction intermediates.

- The basic stopped flow apparatus consists of two or more coupled syringes that rapidly inject the reactants into a small mixing chamber and then through an observation cell that can be coupled to instruments that measure absorption, fluorescence, light scattering, or other optical or electrical properties of the solution.

- As the solution flows through the cell, it empties into a stopping syringe that, when filled, strikes a backstop that abruptly stops the flow.

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- The volume that the stopping syringe can accept is adjusted so that the mixture in the cell has just become uniform and has reached a steady state; at this point, recording of the cell measurement begins and its change is followed.
- Of course, there are many reactions that cannot be followed by changes in light absorption or other physical properties that are conveniently monitored.
- In such cases, it is often practical to quench (stop) the reaction after a desired interval by adding an appropriate quenching agent.
- For example, an enzyme catalyzed reaction can be stopped by adding an acid, base, or salt solution that denatures (destroys the activity of) the protein enzyme.
- Once the reaction has been stopped, the mixture is withdrawn and analyzed in an appropriate manner.
- The quenched flow technique works something like the stopped flow method described above, with a slightly altered plumbing arrangement.
- The reactants A and B are mixed and fed directly through the diverter valve to the measuring cell, which is not shown in this diagram.
- After a set interval that can vary from a few milliseconds to 200 sec or more, the controller activates the quenching syringe and diverter valve, flooding the cell with the quenching solution.

Q-3 Define syrup, saline and seltzer.

- A solution of water and sugar is called syrup.
- A sterilized specific concentration (0.15 molar) of sodium chloride in water is called saline.
- A solution of carbon dioxide in water is called seltzer.

Q-4 What are azeotropes?

- An azeotrope is a mixture that exhibits the same concentration in the vapor phase and the liquid phase.
- This is in contrast to ideal solutions with one component typically more volatile than the other; this is the reason we use distillation to separate materials.
- If the mixture forms an azeotrope, the vapor and the liquid concentrations are the same, which preventing separation via this approach.
- Azeotropes are a mixture of at least two different liquids.
- Their mixture can either have a higher boiling point than either of the components or they can have a lower boiling point.

Q-5 What are limitations of thermodynamics?

- Thermodynamics is a powerful approach toward understanding chemical reactions, but only provides part of the picture.
- Thermodynamics only points the way
- Thermodynamics says nothing about how long it takes to get there
- The stoichiometric equation for the reaction says nothing about its mechanism.

Q-6 Write methods for the measurement of the rate of reaction.

These are the methods for the measurement of the reaction rate:

- | | |
|--|-----------------------|
| 1. Continuous Flow | 4. Relaxation methods |
| 2. Methods for measuring concentration | 5. Spectrophotometry |
| 3. Rate vs Concentration Proportionalities | 6. Stopped Flow |

Q-7 Name types of specific latent heat.

There are two types of specific latent heat: vaporization and fusion.

The specific latent heat of vaporization:

The specific latent heat of vaporization is defined as the quantity of heat energy that is necessary to raise one unit of weight (pounds or grams) with no change of temperature in the surroundings. Like the name implies, this specific latent heat quantifies the transfer of energy when a substance's state changes from liquid to gas or from gas to liquid.

Specific Latent heat of fusion:

The specific heat of fusion is the quantity of heat that is necessary to raise one unit of weight without any change in temperature. This specific latent heat quantifies the transfer of energy when a substance's state changes from a solid to a liquid or from a liquid to a solid.

Q-8 Name factors that affect the rate of reaction.

Factors That Affect Reaction Rates:

- Although a balanced chemical equation for a reaction describes the quantitative relationships between the amounts of reactants present and the amounts of products that can be formed, it gives us no information about whether or how fast a given reaction will occur.
- This information is obtained by studying the chemical kinetics of a reaction, which depend on various factors:
 - Reactant concentrations
 - Temperature
 - Physical states and surface areas of reactants
 - Solvent and catalyst properties if either are present.
- By studying the kinetics of a reaction, chemists gain insights into how to control reaction conditions to achieve a desired outcome.

Q-9 Write examples of nearly reversible reactions.

Some examples of nearly reversible processes are: Frictionless relative motion, Expansion and compression of spring, Frictionless adiabatic expansion or compression of fluid, polytrophic expansion or compression of fluid, Isothermal expansion or compression, Electrolysis.

Q-10 Write effects of enzyme on activation energy.

Effects of Enzymes on Activation Energy:

- However, if a catalyst is added to the reaction, the activation energy is lowered because a lower energy transition state is formed.
- Enzymes can be thought of as biological catalysts that lower activation energy.
- Enzymes are proteins or RNA molecules that provide alternate reaction pathways with lower activation energies than the original pathways
- Enzymes affect the rate of the reaction in both the forward and reverse directions; the reaction proceeds faster because less energy is required for molecules to react when they collide.
- Thus, the rate constant (k) increases.
- A catalyst helps lower the activation energy barrier, increasing the reaction rate.
- In the case of a biological reaction, when an enzyme (a form of catalyst) binds to a substrate, the activation energy necessary to overcome the barrier is lowered, increasing the rate of the reaction for both the forward and reverse reaction.

Q-11 Explain how viscosity is measured by Ostwald's viscometer.

An Ostwald Viscometer consists of two reservoir bulbs and a capillary tube. The viscometer is filled with liquid until the liquid reaches the mark A with the aid of a pipette to accurately measure out the volume of needed liquid. The viscometer is then put into a water bath which equilibrates the temperature of the test liquid. As noted before, the equilibration is important to maintain a constant temperature as to not affect the viscosity otherwise. The liquid is then drawn through the side 2 of the U-tube by use of suction and lastly, the flow is time between marks C and B. The viscosity is calculated with equation: $\eta = Kt$ Where, K is the value of a liquid with known viscosity and density such as water. Once the value of K is known, the viscosity can be determined by measuring the amount of time the test liquid flows between the two graduated marks.

Q-12 Write Maxwell distribution peak.

1. The peaks are not symmetrical.
2. There are more molecules at higher speed than at lower speeds.
3. When the temperature increases, the peak shifts to the right.

Q-13 Write down properties of colloids.

1. A suspended mixture of particles of this type is called a colloid, or colloidal suspension, or colloidal dispersion.
2. For colloids or temporary suspensions the phrase dispersed material or the word dispersants describes the material in suspension, analogous to the solute of a solution.
3. The phrase dispersing medium is used for the material of similar function to a solvent in solutions.
4. Foams are liquids or solids with a gas dispersed into them.
5. Emulsions are liquids or solids with liquids dispersed through them.

6. Aerosols are colloids with a gas as the dispersing medium and either a solid or liquid dispersant.
7. Fine dust or smoke in the air are good examples of colloidal solid in a gas.
8. Fog and mist are examples of colloidal liquid in a gas.
9. Liquid dispersion media with solid or liquid dispersants are the most often considered.
10. Homogenized whole milk is a good example of a liquid dispersed into a liquid.
11. The cream does not break down into molecular sized materials to spread through the milk, but collects in small micelles of oily material and proteins with the more ionic or hydrophilic portions on the outside of the globule and the more fatty, or oily, or non-polar, or hydrophobic portions inside the ball-shaped little particle.
12. Blood carries liquid lipids (fats) in small bundles called lipoproteins with specific proteins making a small package with the fat.
13. Proteins are in a size range to be considered in colloidal suspension in water.
14. Broth or the independent proteins of blood or the casein (an unattached protein) in milk are colloidal. There are many proteins in the cellular fluids of living things that are in colloidal suspension.

Q-14 What is mechanism of stopped flow technique?

1. This technique involves two reactants held in separate reservoirs that are prevented from freely flowing by syringe pumps.
2. The reaction is initiated by depressing the reactant syringes, and thus releasing the reactants into the connecting "mixing chamber" where the solutions are mixed.
3. The reaction is monitored by observing the change in absorbance of the reaction solution as a function of time.
4. As the reaction progresses it fills the "stop syringe" which then expands until it hits a block at the point when the reaction has reached a continuous flow rate, thereby stopping the flow and the reaction, and thus allowing the researcher to calculate the exact initial rate of reaction.
5. The Stopped Flow technique works because within milliseconds of combining the two reactants the absorbance can be read.
6. In addition, the stop syringe assures for a steady rate of flow past the spectrophotometer so that reactants are being added to solution and forming products at a consistent rate.

Q-15 Which characteristics can be monitored for measurement of the rate of reaction?

Any physical characteristic related to the quantity or concentration of a product or reactant can be monitored. Some of the characteristics to be monitored are: change in pressure, change in color (spectroscopic measurement), temperature for exothermic or endothermic reaction, and presence of certain key substance.

Q-17 What is the effect of phase and surface area on the rate of reaction?

Phase and Surface Area Effects:

- When two reactants are in the same fluid phase, their particles collide more frequently than when one or both reactants are solids (or when they are in different fluids that do not mix).
- If the reactants are uniformly dispersed in a single homogeneous solution, then the number of collisions per unit time depends on concentration and temperature, as we have just seen.
- If the reaction is heterogeneous, however, the reactants are in two different phases, and collisions between the reactants can occur only at interfaces between phases.
- The number of collisions between reactants per unit time is substantially reduced relative to the homogeneous case, and, hence, so is the reaction rate.
- The reaction rate of a heterogeneous reaction depends on the surface area of the more condensed phase • Automobile engines use surface area effects to increase reaction rates.
- Gasoline is injected into each cylinder, where it combusts on ignition by a spark from the spark plug.
- The gasoline is injected in the form of microscopic droplets because in that form it has a much larger surface area and can burn much more rapidly than if it were fed into the cylinder as a stream.
- Similarly, a pile of finely divided flour burns slowly (or not at all), but spraying finely divided flour into a flame produces a vigorous reaction.

Q-18 What is the effect of pressure and temperature on heat capacity?

Effect of Temperature on Heat Capacity:

Specific heat or Heat Capacity is a measure of the ability of the substance to absorb heat. The heat goes first into increasing the kinetic energies of the molecules. Molecules can also store energy in vibrations and rotations. At low temperatures, collisions do not provide enough energy to get out of the ground states for rotation or vibration. As the substance heats up, the average kinetic energy of the molecules increases. The collisions impart enough energy to allow rotation to occur. Rotation then contributes to the internal energy and raises the specific heat.

Effect of Pressure on Heat Capacity:

Conventional thermodynamic expression predicts that the heat capacity decreases with increasing pressure. In model calculations, heat capacity increases with pressure, decreases, or remains insensitive to pressure, depending on the model applied.

Q-19 Explain if Carbon Dioxide is polar or non-polar.

A molecule that contains polar bonds might not have any overall polarity, depending upon its shape. The simple definition of whether a complex molecule is polar or not depends upon whether its overall centers of positive and negative charges overlap. A good example of a nonpolar molecule that contains polar bonds is carbon dioxide. This is a linear molecule and the C=O bonds are, in fact, polar. The central carbon will have a net positive charge and the two outer oxygens a net negative charge. However, since the molecule is linear, these two bond

dipoles cancel each other out (i.e. the vector addition of the dipoles equals zero) and the overall molecule has a zero dipole moment ($\mu=0$).

Q-20 How ice floats on water?

Water is one of the few substances whose solid state can float on its liquid state. Water continues to become denser until it reaches 4°C. After it reaches 4°C, it becomes LESS dense. When freezing, molecules within water begin to move around more slowly, making it easier for them to form hydrogen bonds and eventually arrange themselves into an open crystalline, hexagonal structure. Because of this open structure as the water molecules are being held further apart, the volume of water increases about 9%. So molecules are more tightly packed in water's liquid state than its solid state.

Q-21 Describe the process of fractional distillation.

Process of Fractional Distillation:

1. Heat mixture containing 2 or more substances (e.g., water and ethanol solution).
2. The mixture will begin to boil, vaporizing some substances (e.g., ethanol will start to boil at 78.4 °C (351.6 K) and water at 100 °C (212 °F)). □ Vapor goes through the fractional distillation column (long glass tube).
3. Vapor rises to the top and begins to cool down on its way into the second column. Condensers in commercial processes are the mechanics that cool down the vapor.
4. Condensation (vapor to liquid) phase takes place as the vapor is cooled to liquid and finally the substance is transferred into a container on the other end of the second distillation column.

Q-22 What are applications of kinetic energy?

Kinetic energy, as defined in classical mechanics, is the energy an object possesses due to its motion. In physical chemistry, kinetic energy plays a fundamental role in understanding various processes and phenomena. Here are some applications of kinetic energy in physical chemistry:

1. **Reaction Rates:** Kinetic energy is directly related to the speeds of molecules or particles involved in chemical reactions. The Arrhenius equation, which describes the relationship between reaction rates and temperature, incorporates kinetic energy through the Boltzmann factor. Higher kinetic energy (higher temperature) leads to increased molecular motion, resulting in higher reaction rates.
2. **Collision Theory:** In collision theory, the kinetic energy of colliding particles determines whether a collision is effective in producing a chemical reaction. For a reaction to occur, particles must possess sufficient kinetic energy to overcome the activation energy barrier.

3. **Gas Laws:** The behavior of gases is governed by their kinetic energy. The ideal gas law ($PV = nRT$) relates pressure, volume, amount of substance, and temperature. Kinetic theory of gases explains this relationship by considering the kinetic energy and motion of gas molecules.

4. **Dissociation and Activation:** In physical chemistry, reactions involving the breaking of bonds often require a minimum amount of kinetic energy, known as activation energy. This energy enables molecules to overcome the potential energy barrier and dissociate into products.

5. **Catalysis:** Kinetic energy is crucial in catalytic processes. Catalysts provide an alternative reaction pathway with lower activation energy, allowing molecules to achieve the required kinetic energy more easily and thus increasing reaction rates.

6. **Rate Laws:** Kinetic energy affects the order of reactions and the form of rate laws. The rate of a reaction often depends on the concentration of reactants raised to certain powers, influenced by how often molecules with sufficient kinetic energy collide.

7. **Transition State Theory:** This theory involves the concept of a transition state, where reactants are in a temporary, unstable state with higher energy. The kinetic energy of molecules is vital in determining the likelihood of reaching and passing through the transition state to form products.

8. **Thermodynamics and Equilibrium:** Kinetic energy affects the distribution of molecules among energy levels in a system. In chemical equilibrium, the Boltzmann distribution of energy states is related to temperature and influences the equilibrium constant.

Q-23 Explain Henry's law.

HENRY'S LAW

Henry's law is one of the gas laws formulated by William Henry in 1803 and states: "At a constant temperature, the amount of a given gas that dissolves in a given type and volume of liquid is directly proportional to the partial pressure of that gas in equilibrium with that liquid." An equivalent way of stating the law is that the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas above the liquid: $C = kP_{\text{gas}}$ Where, C is the solubility of a gas at a fixed temperature in a particular solvent (in units of M or mL gas/L). k is Henry's law constant (often in units of M/atm).

Applications of Henry's law:

- Henry's law only works if the molecules are at equilibrium.
- Henry's law does not work for gases at high pressures (e.g., N_2 (g) at high pressure becomes very soluble and harmful when in the blood supply).
- Henry's law does not work if there is a chemical reaction between the solute and solvent (e.g., $HCl(g)$ reacts with water by a dissociation reaction to generate H_3O^+ and Cl^- ions).

Q-24 Define mass percent, volume percent and mass/volume percent.

Mass Percent:

The mass percent is used to express the concentration of a solution when the mass of a solute and the mass of a solution is given as:

$$\text{Mass percent} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 100$$

Volume percent:

The volume percent is used to express the concentration of a solution when the volume of a solute and the volume of a solution is given as:

$$\text{Volume percent} = \frac{\text{Volume of solute}}{\text{Volume of solution}} \times 100$$

Mass/Volume Percent:

Since the density of dilute aqueous solutions are close to 1 g/mL, if the volume of a solution is measured in mL (as per definition), then this will approximate the mass of the solution in grams {making a true relative unit (m/m)}.

$$\text{Mass/Volume percent} = \frac{\text{Mass of solute (g)}}{\text{Mass of solution (mL)}} \times 100$$

Q-25 What is precipitation?

Precipitation:

- Precipitation is the process of a compound coming out of solution. It is the opposite of dissolution or solvation.
- In dissolution, the solute particles separate from each other and are surrounded by solvent molecules.
- In precipitation, the solute particles find each other and form a solid together. This solid is called the precipitate or sometimes abbreviated "ppt".

Q-26 What are effects of Le Chatelier's principle?

Le Chatelier's principle is a fundamental concept in chemistry that predicts the behavior of chemical systems when they are subjected to changes in temperature, pressure, concentration, or other external conditions. The principle states that if a system at equilibrium is disturbed by an external change, the system will adjust itself to counteract that change and re-establish a new equilibrium. This principle is widely used to understand and predict how reactions respond to changes in their conditions. Here are some effects of Le Chatelier's principle:

1. **Change in Concentration:** If the concentration of reactants or products is changed, the system will shift its position to counteract the change. For example, if more reactants are added, the equilibrium will shift towards the formation of products, and vice versa.

2. **Change in Pressure (for gases):** If the pressure is increased, the equilibrium will shift in the direction that reduces the number of moles of gas. If the pressure is decreased, the equilibrium will shift in the direction that increases the number of moles of gas.
3. **Change in Temperature:** Changes in temperature affect the equilibrium position differently for exothermic and endothermic reactions. An increase in temperature will favor the endothermic reaction (absorbing heat), and a decrease in temperature will favor the exothermic reaction (releasing heat).
4. **Change in Volume (for gases):** Changes in volume can be related to changes in pressure. If the volume of the container is decreased, the pressure will increase, and the equilibrium will shift to the side with fewer moles of gas. If the volume is increased, the pressure will decrease, and the equilibrium will shift to the side with more moles of gas.
5. **Catalysts:** Catalysts are substances that speed up the rate of a reaction without being consumed in the process. They don't affect the position of the equilibrium. However, they can help the system reach equilibrium faster by accelerating the forward and reverse reactions equally.
6. **Solubility Equilibria:** Le Chatelier's principle can also be applied to solubility equilibria. If a common ion is added to a solution, the solubility of a slightly soluble salt will decrease. This is because the system will shift towards the direction that counteracts the increase in ion concentration.