练 习 十 二

1. **rate-determining step** The slowest step in a chemical reaction that involves a number of steps. In such reactions, there is often a single step that is appreciably slower than the other steps, and the rate of this determines the overall rate of the reaction.

2. **reversible process** Any process in which the variables that define the state of the system can be made to change in such a way that they pass through the same values in the reverse order when the process is reversed. It is also a condition of a reversible process that any exchanges of energy, work, or matter with the surroundings should be reversed in direction and order when the process is reversed. Any process that does not comply with these conditions when it is reversed is said to be an irreversible process. All natural processes are irreversible, although some processes can be made to approach closely to a reversible process.

3. The effect of temperature on rate is expressed in the rate constant, whose magnitude change with temperature. The rate constant, and hence the rate of reaction, increases rapidly with temperature, approximately doubling for each 10℃ rise in temperature. Why does temperature, or for that matter even concentration, affect reaction rates? One appealing explanation is provided by the collision model of chemical kinetics.

4. The central idea of the collision model is that molecules must collide to react. The greater the number of collisions occurring per second, the greater the reaction rate. This idea allows us to understand the effect of concentration on rate: as the concentration of reactant molecules increases, the number of collisions increases, leading to an increase in reaction rate. The collision model also allows us to understand the effect of temperature: We know from the kinetic-molecular theory of gases that increasing the temperature increases molecular velocities. As molecules move faster, they collide harder (with more energy) and more frequently, increasing reaction rates. However, the matter is not entirely this simple. For most reactions, only a small fraction of collisions actually lead to reaction.

5. A balanced equation for a chemical reaction indicates the substances that are present at the start of the reaction and those produced at the end. However, it provides no information about how the reaction occurs. The process by which a reaction occurs is called the reaction mechanism, at the most sophisticated level, a reaction mechanism will describe in great detail the order in which bonds are broken and formed and the changes in relative positions of the atoms in the course of the reaction.

6. All chemical reactions are accompanied by some heat effects so that the temperature will tend to change, a serious result in view of the sensitivity of most reaction rates to temperature. Factors of equipment size, controllability, and possibly unfavorable product distribution of complex reactions often necessitate provision of means of heat transfer to keep the temperature within bounds. In practical operation of nonflow(batch) or tubular flow reactors, truly isothermal condition are not feasible even if they were desirable.

7. The partial oxidation of a liquid hydrocarbon with air is studied in the laboratory, under atmospheric pressure at e temperature of 350K. The reaction is allowed to proceed to a degree of conversion of 98%. The selectivity is then 85%, so that the yield is 83%. It is found that at higher temperature and pressure the reaction rate increases, but the selectivity is lower. However, it turns out that this is a case of consecutive reactions, so that the selectivity is higher at lower degrees of conversion. It was found by additional experiments that the optimum conditions for a technical process are 10 atmospheres, 450K and a degree of conversion of only 20%. The selectivity appears to be 95% then. These conditions deviate considerably from those in the original laboratory experiments. For the further development one has to study the reaction under these new conditions.

8. The chemical reactor as a separator. It is worth while to consider whether the entire manufacturing process can be optimized by combining a chemical reactor with a separation of products. In a two-phase system, one or several of the reaction products can be transferred from the reaction phase to the other phase, and thus be removed from the reaction mixture. This may facilitate further separations, and may also save the reaction product from further chemical attack and consequently improve the selectivity of the process. It may be especially attractive for reversible reactions. The best known examples are reactions in the liquid phase combined with evaporation of the main product, and reactions where the main product is precipitated from a liquid reaction mixture.