

Chapter 6 — Equilibria

2. Questions for Short Answers

1. How is dynamic equilibrium different from the static equilibrium?

Ans: In a static equilibrium nothing is moving or changing at all; the system is simply at rest and both the forward and the backward processes have stopped. In a dynamic chemical equilibrium the reaction has not ceased at all — the forward and the backward reactions both keep on going, but at exactly the same rate. As many reactant molecules disappear by the forward reaction as are formed again by the reverse reaction, so the concentrations of all the reacting species stay constant and it only appears as if nothing is going on in the reaction vessel. That is why this state is called a dynamic equilibrium and not a static one.

2. How will the following reversible reaction be affected if its temperature is increased? $2\text{H}_2\text{O}(\text{l}) \rightleftharpoons 2\text{H}_2(\text{g}) + \text{O}_2(\text{g})$

Ans: The decomposition of water into hydrogen and oxygen is an endothermic reaction in the forward direction; energy has to be supplied (here by an electric current) to break the strong O—H bonds. When the temperature of such a system at equilibrium is increased, the extra heat supplied is used up by the reaction which absorbs heat. The equilibrium therefore shifts in the forward direction, so more hydrogen and oxygen are formed and the amount of water decreases. Equilibrium is then re-established at new, different concentrations.

3. How can you get the maximum yield in a reversible reaction?

Ans: A reversible reaction never goes to completion on its own, so to get the maximum yield the equilibrium must be pushed towards the products. This can be done by (1) withdrawing one or more of the products from the reaction mixture as soon as it is formed, or letting a gaseous product escape — for example, carbon dioxide escaping in an open container forces CaCO_3 to decompose completely; (2) adding more of one of the reactants, which makes the forward reaction take place until a new equilibrium is reached; (3) choosing the right temperature — for an exothermic forward reaction the temperature should be decreased, and for an endothermic one it should be increased; and (4) choosing the right pressure for gaseous reactions — increasing the pressure drives the reaction to the side having the smaller number of moles of gas, which is why ammonia is formed at high pressure.

4. How can you decrease the time to attain the position of equilibrium in a reversible reaction?

Ans: The time can be decreased by carrying out the reaction in the presence of a suitable catalyst. A catalyst increases the rates of both the forward and the backward reactions of a reversible reaction, so the two rates become equal to each other much sooner. The catalyst therefore decreases the time taken by the reaction to attain the state of equilibrium, although it does not change the position of the equilibrium or the final concentrations. Raising the temperature also makes both reactions faster and shortens the time, which is why the formation and decomposition of ammonia are carried out at about 400 °C in the presence of a catalyst and reach equilibrium within minutes.

5. What is the effect of increasing pressure on the following reaction at equilibrium? $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$

Ans: A change of pressure disturbs the equilibrium of only those gaseous reactions in which the number of moles of the reacting gases is different from the number of moles of the gases being produced. In this reaction one mole of nitrogen and one mole of oxygen, that is 2 moles of gas, produce 2 moles of nitric oxide. Since the number of moles of gas is the same on both sides, increasing the pressure has no effect on this equilibrium; the position of the equilibrium and the concentrations of all the species remain unchanged.

3. Constructed Response Questions

1. Why are some reactions irreversible while others are reversible?

Ans: It depends on whether the products can react with each other again under the same conditions. In an irreversible reaction the products are either removed from the reaction mixture as they are formed — for instance an insoluble solid which settles out, or a gas which escapes — or they are so much more stable than the reactants that they have no tendency to change back. Such a reaction goes to completion and moves in the forward direction only; $\text{NaCl(aq)} + \text{AgNO}_3\text{(aq)} \rightarrow \text{AgCl(s)} + \text{NaNO}_3\text{(aq)}$ is an example, because the AgCl leaves the solution as a precipitate. In a reversible reaction the products stay together in the mixture and, under the same conditions, they react among themselves to give back the reactants, so the reaction moves in both directions and never goes to completion — for example $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$ in a closed container.

2. Why are combustion reactions generally irreversible?

Ans: Combustion is a strongly exothermic reaction in which a large amount of energy is given out as heat and light, and the products formed — mainly carbon dioxide and water — are far more stable and at a much lower energy than the fuel and oxygen from which they were made. To reverse the change, exactly that large amount of energy would have to be put back into the products, and the very stable CO_2 and H_2O bonds would have to be broken. Besides this, the gaseous products escape into the atmosphere as soon as they are formed and are no longer present in the reaction mixture to react back. For both these reasons combustion reactions go to completion in the forward direction only and are generally irreversible.

3. Can you make an irreversible reaction reversible and vice versa?

Ans: Yes, to a large extent this depends on the conditions under which the reaction is carried out, especially on whether the products are allowed to remain in the mixture. The decomposition of limestone shows both cases with the same chemical change: $\text{CaCO}_3\text{(s)} \rightleftharpoons \text{CaO(s)} + \text{CO}_2\text{(g)}$. If it is heated in an open container the carbon dioxide escapes into the atmosphere as soon as it is formed, it cannot react back, and the change becomes practically irreversible and goes to completion. If the very same reaction is carried out in a closed container, the carbon dioxide stays in contact with the calcium oxide and reacts with it to give back calcium carbonate, so the change is clearly reversible. In the same way a reversible reaction is driven to completion, that is made irreversible, by withdrawing a product, and an apparently irreversible reaction can often be made reversible by keeping all the products together in a closed system.

4. How do you know if a reaction is reversible or irreversible?

Ans: A reaction is reversible if, after some time, all the species — the reactants as well as the products — are still simultaneously present in the reaction mixture and their concentrations become constant instead of the reactants being finished. Such a reaction is written with the double half-arrow sign $\rightleftharpoons$, one arrowhead pointing in each direction. Very often it can also be recognised by an observable property which stops changing, or by a change which can be undone: white anhydrous copper sulphate turns blue again when it absorbs moisture, and blue anhydrous cobalt chloride turns purple and then pink again. A reaction is irreversible if it goes to completion — one or all of the reactants are completely used up, nothing is left to react further, and the change cannot be undone under the same conditions. It is written with a single arrow $\rightarrow$.

5. Are the phase changes in water (solid to liquid, liquid to vapour) reversible or irreversible?

Ans: They are reversible. Like chemical changes, physical changes may also be reversible in nature, and the phase changes of water are the clearest everyday example. Ice melts to give liquid water and liquid water freezes to give back ice; liquid water evaporates to give vapour and the vapour condenses to give back liquid water. No new substance is formed in any of these changes and each one can be completely undone simply by reversing the condition, that is by heating or cooling. In a closed container the three states can even reach a dynamic equilibrium with one another, the rate of evaporation becoming equal to the rate of condensation.