8.3 Equilibrium positions and rates of reaction in S205

Section 8 showed that if a reaction is to occur at a particular temperature, two conditions must be fulfilled: its equilibrium constant must be sufficiently large, and its rate sufficiently great. We finish by pointing out how this crucial distinction between the equilibrium constant and the rate reveals itself in Figure 8.2. The figure shows two different pathways by which the reactants can change into the products, but both routes begin at the *same* reactant energy level, and finish at the *same* product energy level. Regardless of reaction pathway, the energy difference between reactants and products is the same. As you will see in Book 4, it is an energy difference between reactants and products that determines the equilibrium constant of a reaction, and therefore the equilibrium position. The fact that both pathways have the same energy difference, and therefore the same equilibrium constant, shows that the equilibrium constant in a reaction is quite unaffected by *how* reactants change into products. With equilibrium constants, the nature and energies of the initial and final states are everything; what happens in between is immaterial.

After Book 4, the emphasis shifts to the rate of reaction. Here, the reaction pathway is crucial. In Figure 8.2, both routes start with the same reactants, and end with the same products, but the intervening stages along each pathway are very different. Such sequences of intervening stages are called **reaction mechanisms**, and the mechanism in the presence of a catalyst delivers a smaller energy barrier and a faster rate than the one that pertains when the catalyst is absent. With rates of reaction, therefore, the mechanism is crucial. In Book 5, we shall look at rates and reaction mechanisms in detail.

8.4 Summary of Section 8

1 The equilibrium constant of a reaction is fixed at any particular temperature. It depends only on the natures of the initial reactants and the final products; what happens as reactants change into products has no effect on the equilibrium constant or position of equilibrium.

2 The rate of a chemical reaction is affected both by the temperature and by the pathway (reaction mechanism) through which reactants change into products. This pathway can sometimes be altered, for example by the introduction of a catalyst.

3 The catalyst causes a change in the reaction mechanism which leads to a lowering of the energy barrier and to a greater rate of reaction.

QUESTION 8.1

The combination of sulfur dioxide with oxygen, and the decomposition of steam into hydrogen and oxygen are both reactions of great potential practical value. These reactions, and their equilibrium constants at 427 °C (700 K) are as follows:

$$2SO_2(g) + O_2(g) = 2SO_3(g); \qquad K = 10^6\ \text{mol}^{-1}\ \text{litre}$$

$$2H_2O(g) = 2H_2(g) + O_2(g); \qquad K = 10^{-33}\ \text{mol litre}^{-1}$$

Write down expressions for the equilibrium constants of the two reactions. When the two reactions are attempted at 700 K, neither seems to occur. Which of the two might be persuaded to occur at this temperature, and what form might your 'persuasion' take?