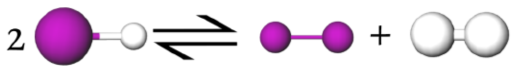
13.12: Effect of Adding a Reactant or Product

If we have a system which is already in equilibrium, addition of an extra amount of one of the reactants or one of the products throws the system out of equilibrium. Either the forward or the reverse reaction will then occur in order to restore equilibrium conditions. We can easily tell which of these two possibilities will happen from Le Chatelier's principle. If we add more of one of the *products*, the system will adjust in order to offset the gain in concentration of this component. The *reverse* reaction will occur to a limited extent so that some of the added product can be consumed. Conversely, if one of the *reactants* is added, the system will adjust by allowing the *forward* reaction to occur to some extent. In either case *some of the added component will be consumed*.

We see this principle in operation in the case of the decomposition of HI at high temperatures:

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$



In Example 1 from Calculating the Extent of a Reaction we saw that if 1 mol HI is heated to 745 K in a 10 L flask, some of the HI will decompose, producing an equilibrium mixture of composition **1** $[HI] = 0.0780\ \text{mol/L}$; $[I_2] = 0.0110\ \text{mol/L}$; $[H_2] = 0.0110\ \text{mol/L}$ This is a genuine equilibrium mixture since it satisfies the equilibrium law

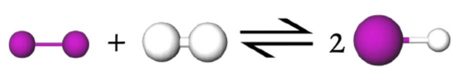
$$K_c = \frac{[H_2][I_2]}{[HI]^2} = \frac{(0.011\ \text{mol L}^{-1})(0.011\ \text{mol L}^{-1})}{(0.078\ \text{mol L}^{-1})^2} = 0.020 = K_c$$

If an extra mole of H_2 is added to this mixture, the concentrations become **2** $[HI] = 0.0780\ \text{mol/L}$; $[I_2] = 0.0110\ \text{mol/L}$; $[H_2] = 0.111\ \text{mol/L}$ The system is no longer in equilibrium (hence the lack of square brackets to denote equilibrium concentrations) as we can easily check from the equilibrium law

$$K_c = \frac{[H_2][I_2]}{[HI]^2} = \frac{(0.011\ \text{mol/L})(0.011\ \text{mol/L})}{(0.078\ \text{mol/L})^2} = 0.020 = K_c$$

The addition of H_2 has increased the concentration of this component. Accordingly, Le Chatelier's principle predicts that the system will achieve a new equilibrium in such a way as to reduce this concentration. The reverse reaction occurs to a limited extent. This not only reduces the concentration of H_2 but the concentration of I_2 as well. At the same time the concentration of HI is increased. The system finally ends up with the concentrations calculated in Example 2 from Calculating the Extent of a Reaction, namely,

$$H_2 + I_2 \rightarrow 2HI$$



3 $[HI] = 0.0963\ \text{mol/L}$;$[I_2] = 0.001\ 82\ \text{mol/L}$; $[H_2] = 0.1018\ \text{mol/L}$ This is again an equilibrium situation since it conforms to the equilibrium law

$$\frac{[H_2][I_2]}{[HI]^2} = \frac{0.1018\ \text{mol L}^{-1} \times 0.001\ 82\ \text{mol L}^{-1}}{(0.0963\ \text{mol L}^{-1})^2} = 0.02 = K_c$$

The way in which this system responds to the addition of H_2 is also illustrated schematically in Figure 1. The actual extent of the change is exaggerated in this figure for diagrammatic effect.

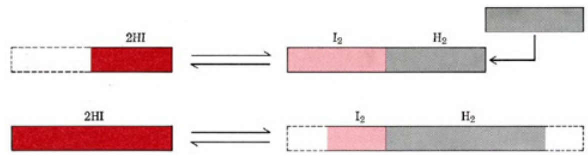
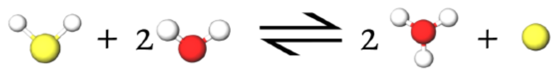


Figure 13.12.1 Le Chatelier's principle: effect of adding a component. At 745 K, HI is partially decomposed into H_2 and I_2: 2HI H_2 + I_2. If extra hydrogen (gray) is added to the equilibrium mixture, the system responds in such a way as to reduce the concentration of H_2. Some I_2 reacts with the H_2, and more HI is formed. The equilibrium is shifted to the left. Note, however, that some of the I_2 has been consumed, and its concentration is smaller than before.

Le Chatelier's principle can also be applied to cases where one of the components is *removed*. In such a case the system responds by *producing more of the component removed*. Consider, for example, the ionization of the weak diprotic acid H_2S:

$$\mathrm{H_2S + 2\,H_2O \rightleftharpoons 2\,H_3O^+ + S^{2-}}$$



Since H_2S is a weak acid, very few S^{2-} ions are produced, but a much larger concentration of S^{2-}ions can be obtained by adding a strong base. The base will consume most of the H_3O^+ ions. As a result, more H_2S will react with H_2O in order to make up the deficiency of H_3O^+, and more S^{2-}ions will also be produced. This trick of removing one of the products in order to increase the concentration of *another product* is often used by chemists, and also by living systems.

Previously, we've investigated the effect of adding/subtracting a product/reactant in mathematical terms. The video below allows you to visually see the changes the equilibrium shifts that occur upon the addition of a reactant or product, courtesy of the North Caroline School of Science and Mathematics.

Example 13.12.1 : Yield

When a mixture of 1 mol N_2 and 3 mol H_2 is brought to equilibrium over a catalyst at 773 K (500°C) and 10 atm (1.01 MPa), the mixture reacts to form NH_3 according to the equation

$\mathrm{N_2}(g) + 3\mathrm{H_2}(g) \rightleftharpoons 2\mathrm{NH_3}(g)$ ΔH_m = – 94.3 kJ The yield of NH_3, however, is quite small; only about 2.5 percent of the reactants are converted. Suggest how this yield could be improved (a) by altering the pressure; (b) by altering the temperature; (c) by removing a component; (d) by finding a better catalyst.

Solution:

a) Increasing the pressure will drive the reaction in the direction of fewer molecules. Since Δn = - 2, the forward reaction will be encouraged, increasing the yield of NH_3. **b)** Increasing the temperature will drive the reaction in an endothermic direction, in this case in the reverse direction. In order to increase the yield, therefore, we need to *lower* the temperature. **c)** Removing the product NH_3 will shift the reaction to the right. This is usually done by cooling the reaction mixture so that $NH_3(l)$ condenses out. Then more $N_2(g)$ and $H_2(g)$ are added, and the reaction mixture is recycled to a condition of sufficiently high temperature that the rate becomes appreciable. **d)** While a better catalyst would speed up the *attainment* of equilibrium, it would not affect the position of equilibrium. It would therefore have no effect on the yield.

Note: As mentioned in Chaps. 3 and 12, NH_3 is an important chemical because of its use in fertilizers. In the design of a Haber-process plant to manufacture ammonia, attempts are made to use as high a pressure and as low a temperature as possible. The pressure is usually of the order of 150 atm (15 MPa), while the temperature is not usually below 750 K. Although a lower temperature would give a higher yield, the reaction would go too slowly to be economical, at least with present-day catalysts. The discoverer of a better catalyst for this reaction would certainly become a millionaire over-night.

Acknowledgements:

Two of the equations in this article were created using help from https://www.latex4technics.com/.