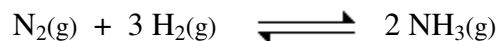


Illustration of the Le Chatelier-Braun Principle

As noted in Callen; "... consider a system that is taken out of equilibrium by some imposed perturbation. The perturbation directly induces a process that, by the Le Chatelier principle, reduces the perturbation. But various other internal processes are simultaneously but indirectly induced. The content of the Le Chatelier-Braun principle is that these indirectly induced processes also tend to reduce the applied perturbation. "

As an example, consider the chemical equilibrium between Nitrogen, Hydrogen and Ammonia:



We will perturb the established equilibrium by adding N_2 at constant total Pressure. According to the Le Chatelier Principle, the system will respond by reducing the Partial Pressure of Nitrogen P_{N_2} . This can be done both directly and indirectly. In one case, the equilibrium will shift right and in the other it will shift left.

We will define:

Stoichiometric Coefficients

$$v_{\text{N}_2}, v_{\text{H}_2}, v_{\text{NH}_3}$$

Reaction Advancement

$$\xi$$

Initial Number of Moles

$$n_{\text{N}_2}^0, n_{\text{H}_2}^0, n_{\text{NH}_3}^0$$

We want to know the direction the reaction will shift ($d\xi$) as the partial pressure of Nitrogen tries to decrease ($dP_{\text{N}_2} < 0$); keeping in mind that the total Pressure (P) must remain constant. In order to answer this question we need to determine the sign of:

$$\left(\frac{\partial P_{\text{N}_2}}{\partial \xi} \right)_P$$

We can write the Partial Pressure of Nitrogen as:

$$\begin{aligned} P_{\text{N}_2} &= x_{\text{N}_2} P \\ &= \frac{n_{\text{N}_2}}{n} P \end{aligned}$$

$$\begin{aligned}
&= \frac{(n_{N_2}^0 + v_{N_2}\xi)}{n} P \\
&= \frac{(n_{N_2}^0 + v_{N_2}\xi)}{\sum n_i} P \\
&= \frac{(n_{N_2}^0 + v_{N_2}\xi)}{((n_{N_2}^0 + v_{N_2}\xi) + (n_{H_2}^0 + v_{H_2}\xi) + (n_{NH_3}^0 + v_{NH_3}\xi))} P
\end{aligned}$$

So, the desired derivative is:

$$\begin{aligned}
\left(\frac{\partial P_{N_2}}{\partial \xi}\right)_P &= \frac{(v_{N_2})}{((n_{N_2}^0 + v_{N_2}\xi) + (n_{H_2}^0 + v_{H_2}\xi) + (n_{NH_3}^0 + v_{NH_3}\xi))} P \\
&\quad - \frac{(n_{N_2}^0 + v_{N_2}\xi)(v_{N_2} + v_{H_2} + v_{NH_3})}{((n_{N_2}^0 + v_{N_2}\xi) + (n_{H_2}^0 + v_{H_2}\xi) + (n_{NH_3}^0 + v_{NH_3}\xi))^2} P \\
&= \frac{(v_{N_2})}{(\sum n_i)} P - \frac{(n_{N_2}^0 + v_{N_2}\xi)(v_{N_2} + v_{H_2} + v_{NH_3})}{(\sum n_i)^2} P \\
&= \frac{(v_{N_2})}{(\sum n_i)} P - \frac{(n_{N_2}^0 + v_{N_2}\xi)(\sum v_i)}{(\sum n_i)^2} P \\
&= \frac{(v_{N_2})}{(\sum n_i)} P - \frac{(n_{N_2}) (\sum v_i)}{(\sum n_i)^2} P \\
&= \frac{(v_{N_2})(\sum n_i)}{(\sum n_i)^2} P - \frac{(n_{N_2})(\sum v_i)}{(\sum n_i)^2} P \\
&= \frac{P}{(\sum n_i)^2} \{v_{N_2}(\sum n_i) - n_{N_2}(\sum v_i)\}
\end{aligned}$$

This last form of the derivative is most useful. For our case:

$$\begin{aligned}
v_{N_2} &= -1 \\
\sum v_i &= -1 - 3 + 2 = -2
\end{aligned}$$

So,

$$\begin{aligned}
\left(\frac{\partial P_{N_2}}{\partial \xi}\right)_P &= \frac{P}{(\sum n_i)^2} \{-1(\sum n_i) + 2n_{N_2}\} \\
&= \frac{P}{(\sum n_i)} \{-1 + 2x_{N_2}\}
\end{aligned}$$

We know the sign of P and $(\sum n_i)$:

$$P > 0$$

$$(\sum n_i) > 0$$

Thus, the sign of our derivative will depend on the term in brackets { }. Based on this, two cases are important.

Case 1

$$x_{N_2} < 1/2$$

In this case, we have:

$$\{-1 + 2x_{N_2}\} < 0$$

So,

$$\left(\frac{\partial P_{N_2}}{\partial \xi}\right)_P < 0$$

Since the system is trying to reduce the partial pressure ($dP_{N_2} < 0$), we have:

$$d\xi > 0$$

Thus, the reaction shifts Right!

In other word, the system will reduce the partial pressure of Nitrogen by advancing the reaction forward and removing some of the Nitrogen.

Case 2

$$x_{N_2} > 1/2$$

In this case, we have:

$$\{-1 + 2x_{N_2}\} > 0$$

So,

$$\left(\frac{\partial P_{N_2}}{\partial \xi}\right)_P > 0$$

Again, since the system is trying to reduce the partial pressure ($dP_{N_2} < 0$), we now have:

$$d\xi < 0$$

Thus, the reaction shifts Left!

In other word, the system will reduce the partial pressure of Nitrogen by advancing the reaction in the reverse direction and making a greater number of moles of gas overall.