CHEM 331
Physical Chemistry

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:

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

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_{N2}. 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

$\nu_{N2}, \nu_{H2}, \nu_{NH3}$

Reaction Advancement

ξ

Initial Number of Moles

$n_{N2}^{o}, n_{H2}^{o}, n_{NH3}^{o}$

We want to know the direction the reaction will shift ($d\xi$) as the partial pressure of Nitrogen tries to decrease ($dP_{N2} < 0$); keeping in mind that the total Pressure (P) must remain constant. In order to answer this question we need to determine the sign of:

$$\left(\frac{\partial P_{N2}}{\partial \xi}\right)_P$$

We can write the Partial Pressure of Nitrogen as:

$$P_{N2} = x_{N2}\,P$$

$$= \frac{n_{N2}}{n}\,P$$

$$= \frac{(n^o_{N2} + \nu_{N2}\xi)}{n} \text{ P}$$

$$= \frac{(n^o_{N2} + \nu_{N2}\xi)}{\sum n_i} \text{ P}$$

$$= \frac{(n^o_{N2} + \nu_{N2}\xi)}{((n^o_{N2} + \nu_{N2}\xi) + (n^o_{H2} + \nu_{H2}\xi) + (n^o_{NH3} + \nu_{NH3}\xi))} \text{ P}$$

So, the desired derivative is:

$$\left(\frac{\partial P_{N2}}{\partial \xi}\right)_P = \frac{(\nu_{N2})}{((n^o_{N2} + \nu_{N2}\xi) + (n^o_{H2} + \nu_{H2}\xi) + (n^o_{NH3} + \nu_{NH3}\xi))} \text{ P}$$

$$- \frac{(n^o_{N2} + \nu_{N2}\xi)\,(\nu_{N2} + \nu_{H2} + \nu_{NH3})}{((n^o_{N2} + \nu_{N2}\xi) + (n^o_{H2} + \nu_{H2}\xi) + (n^o_{NH3} + \nu_{NH3}\xi))^2} \text{ P}$$

$$= \frac{(\nu_{N2})}{(\sum n_i)} \text{ P} - \frac{(n^o_{N2} + \nu_{N2}\xi)\,(\nu_{N2} + \nu_{H2} + \nu_{NH3})}{(\sum n_i)^2} \text{ P}$$

$$= \frac{(\nu_{N2})}{(\sum n_i)} \text{ P} - \frac{(n^o_{N2} + \nu_{N2}\xi)\,(\sum \nu_i)}{(\sum n_i)^2} \text{ P}$$

$$= \frac{(\nu_{N2})}{(\sum n_i)} \text{ P} - \frac{(n_{N2})\,(\sum \nu_i)}{(\sum n_i)^2} \text{ P}$$

$$= \frac{(\nu_{N2})\,(\sum n_i)}{(\sum n_i)^2} \text{ P} - \frac{(n_{N2})\,(\sum \nu_i)}{(\sum n_i)^2} \text{ P}$$

$$= \frac{P}{(\sum n_i)^2} \{\nu_{N2}(\sum n_i) - n_{N2}(\sum \nu_i)\}$$

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

$$\nu_{N2} = -1$$

$$\sum \nu_i = -1 - 3 + 2 = -2$$

So,

$$\left(\frac{\partial P_{N2}}{\partial \xi}\right)_P = \frac{P}{(\sum n_i)^2} \{-1(\sum n_i) + 2n_{N2}\}$$

$$= \frac{P}{(\sum n_i)} \{-1 + 2x_{N2}\}$$

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

$x_{N2} < ½$

In this case, we have:

$$\{-1 + 2x_{N2}\} < 0$$

So,

$$\left(\frac{\partial P_{N2}}{\partial \xi}\right)_P < 0$$

Since the system is trying to reduce the partial pressure ($dP_{N2} < 0$), 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

$x_{N2} > ½$

In this case, we have:

$$\{-1 + 2x_{N2}\} > 0$$

So,

$$\left(\frac{\partial P_{N2}}{\partial \xi}\right)_P > 0$$

Again, since the system is trying to reduce the partial pressure ($dP_{N2} < 0$), 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.