

## 10.3: Pressure and Composition Dependence of $K_{eq}$

While  $K_{eq}$  is independent of both temperature and number of moles for an ideal gas, the same is not necessarily true for the other equilibrium constants.

*[Math Processing Error]*

For example, it is easy to look at Equation 10.1.13 and determine that  $K_{eq}$  usually depends on  $K_{eq}$ .<sup>1</sup> Using Dalton's Law, Equation 9.4.7, we can also notice that the equilibrium partial pressures of the reactants and products in a gas-phase reaction can be expressed in terms of their equilibrium mole fractions  $K_{eq}$  and the total pressure  $K_{eq}$ . As such, we can use  $K_{eq}$  to demonstrate that the equilibrium mole fractions will change when  $K_{eq}$  changes,<sup>2</sup> as it is demonstrated by the following exercise.

### ? Exercise *[Math Processing Error]*

Calculate the mole fraction change for the dissociation of  $K_{eq}$  when the pressure is increased from  $K_{eq}$  to  $K_{eq}$  at constant  $K_{eq}$ , knowing that  $K_{eq}$  and  $K_{eq}$ , and remembering that both of these values are tabulated at  $K_{eq}$ .

### Answer

Let's consider the reaction:  $K_{eq}$

We can divide the exercise into two parts. In the first one, we will deal with calculating the equilibrium constant at  $K_{eq}$  from the data at  $K_{eq}$ . In the second one, we will calculate the change in mole fraction when the pressure is increased from  $K_{eq}$  to  $K_{eq}$ .

Let's begin the first part by calculating  $K_{eq}$  and  $K_{eq}$  from:  $K_{eq}$  and since  $K_{eq}$  is an element in its most stable form at  $K_{eq}$ , its standard enthalpy and Gibbs free energy of formation are  $K_{eq}$ . Therefore:  $K_{eq}$   $K_{eq}$  Using Equation 10.1.8 to calculate  $K_{eq}$ , we obtain:  $K_{eq}$   $K_{eq}$  We can now use the integrated van 't Hoff equation, Equation 10.2.5, to calculate  $K_{eq}$  at  $K_{eq}$ :  $K_{eq}$  which becomes:  $K_{eq}$  which corresponds to:  $K_{eq}$

Let's now move to the second part of the exercise, where we increase the pressure from  $K_{eq}$  to  $K_{eq}$  at constant  $K_{eq}$ . We start by writing the definition of  $K_{eq}$  and  $K_{eq}$ :  $K_{eq}$  and using Equation 10.1.13:  $K_{eq}$  we can calculate the initial  $K_{eq}$  at  $K_{eq}$ , using:  $K_{eq}$  and calculate the initial concentration of  $K_{eq}$  and  $K_{eq}$  at  $K_{eq}$ , recalling that  $K_{eq}$   $K_{eq}$  Solving the quadratic equation, we obtain one negative answer—which is unphysical—,  $K_{eq}$  and:  $K_{eq}$  At the end of the process,  $K_{eq}$ , and we obtain:  $K_{eq}$  and, using the same technique used before to solve the quadratic equation:  $K_{eq}$  gives:  $K_{eq}$  To summarize, when we increase the pressure from  $K_{eq}$  to  $K_{eq}$  at  $K_{eq}$ , the equilibrium constant in terms of the mole fraction decreases from  $K_{eq}$  to  $K_{eq}$ . This reduction is causing a shift of the equilibrium towards the reactants, with the concentration of  $K_{eq}$  increasing from  $K_{eq}$  to  $K_{eq}$  and the concentration of  $K_{eq}$  decreasing from  $K_{eq}$  to  $K_{eq}$ .

The dependence of  $K_{eq}$  on  $K_{eq}$  highlighted above is another mathematical expression of Le Chatelier's principle, on this occasion, for changes in pressure. The interpretation For a reaction happening in the gas phase is as follows:

- If the total pressure increases, the equilibrium will shift towards the side of the chemical equation that contains the smallest total amount of moles (the equilibrium in exercise  $K_{eq}$  shifts toward the reactant).

1.  $\Delta G^\circ$  becomes independent of  $\Delta n$  in the particular case where  $\Delta n = 0$ , i.e., for reactions where the total number of moles of reactants is the same as the total number of moles of the products.
2. Keep in mind that  $\Delta G^\circ$  will *not* change.
3. Notice how a positive  $\Delta G^\circ$  indicates that the dissociation of  $\text{H}_2\text{O}$  is non-spontaneous at  $25^\circ\text{C}$  and  $1\text{ atm}$ . As such, we should expect a very small value for  $K$ .
4. The results corresponds to  $K$ , an incredible miniscule number, as we should expect given the data of  $\Delta G^\circ$ .
5. Concentration cannot be negative.

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