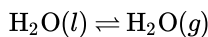


13.5: The Equilibrium Constant in Terms of Pressure

Some equilibria involve physical instead of chemical processes. One example is the equilibrium between liquid and vapor in a closed container. In other sections we stated that the vapor pressure of a liquid was always the same at a given temperature, regardless of how much liquid was present. This can be seen to be a consequence of the equilibrium law if we recognize that the pressure of a gas is related to its concentration through the ideal gas law. Rearranging $PV = nRT$ we obtain

$$P = \frac{n}{V}RT = cRT \quad (13.5.1)$$

since $c = \text{amount of substance/volume} = n/V$. Thus if the vapor pressure is constant at a given temperature, the concentration must be constant also. Equation 13.5.1 also allows us to relate the equilibrium constant to the vapor pressure. In the case of water, for example, the equilibrium reaction and K_c are given by:



$$K_c = [\text{H}_2\text{O}(g)]$$

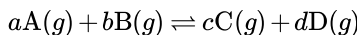
Substituting for the concentration of water vapor from Equation 13.5.1, we obtain

$$K_c = \frac{P_{\text{H}_2\text{O}}}{RT}$$

At 25°C for example, the vapor pressure of water is 17.5 mmHg (2.33 kPa), and so we can calculate

$$\begin{aligned} K_c &= \frac{2.33 \text{ kPa}}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})} \\ &= 9.40 \times 10^{-4} \text{ mol/L} \end{aligned}$$

For some purposes it is actually more useful to express the equilibrium law for gases in terms of partial pressures rather than in terms of concentrations. In the general case:



The **pressure-equilibrium constant** K_p is defined by the relationship:

$$K_p = \frac{p_C^c p_D^d}{p_A^a p_B^b}$$

where p_A is the partial pressure of component A, p_B of component B, and so on. Since $p_A = [A] \times RT$, $p_B = [B] \times RT$, and so on, we can also write as follows:

$$K_p = \frac{p_C^c p_D^d}{p_A^a p_B^b} = \frac{([C] \times RT)^c ([D] \times RT)^d}{([A] \times RT)^a ([B] \times RT)^b} \quad (13.5.2)$$

$$= \frac{[C]^c [D]^d}{[A]^a [B]^b} \times \frac{(RT)^c (RT)^d}{(RT)^a (RT)^b} \quad (13.5.3)$$

$$= K_c \times (RT)^{(c+d-a-b)} \quad (13.5.4)$$

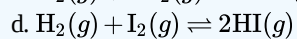
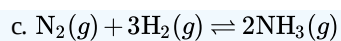
$$= K_c \times (RT)^{\Delta n} \quad (13.5.5)$$

Again Δn is the increase in the number of gaseous molecules represented in the equilibrium equation. If the number of gaseous molecules does not change, $\Delta n = 0$, $K_p = K_c$, and both equilibrium constants are dimensionless quantities.

✓ Example 13.5.1 : SI Units

In what SI units will the equilibrium constant K_c be measured for the following reactions? Also predict for which reactions $K_c = K_p$.

- $2\text{NOBr}(g) \rightleftharpoons 2\text{NO}(g) + \text{Br}_2(g)$
- $\text{H}_2\text{O}(g) + \text{C}(s) \rightleftharpoons \text{CO}(g) + \text{H}_2(g)$



Solution

We apply the rule that the units are given by $(\text{mol dm}^{-3})^{\Delta n}$.

a. Since $\Delta n = 1$, units are moles per cubic decimeter.

b. Since $\Delta n = 1$, units are moles per cubic decimeter (the solid is ignored).

c. Here $\Delta n = -2$ since two gas molecules are produced from four. Accordingly the units are $\text{mol}^{-2} \text{dm}^6$.

d. Since $\Delta n = 0$, K_c is a pure number. In this case also $K_c = K_p$.

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