

Equilibrium Constants

As an example, we will use the reaction $A+B \rightleftharpoons C$

1. Write out an expression for K_p in terms of partial pressures. It is best to include the standard pressure p^\ominus explicitly.

$$K_p = \frac{(p_C/p^\ominus)}{(p_A/p^\ominus)(p_B/p^\ominus)}$$

2. Convert partial pressures to mole fractions e.g. $p_A = x_A p$, where p is the total pressure.

$$K_p = \frac{(x_C p/p^\ominus)}{(x_A p/p^\ominus)(x_B p/p^\ominus)} = \frac{x_C}{x_A x_B} \frac{p}{p^\ominus}$$

3. Define the fraction of one of the reactants that has reacted as α (or any other symbol you like), and work out what the partial pressures are in terms of this quantity and the initial total pressure. You will generally be given enough information in the question to allow you to do this, but it may require a bit of thought to get it right. For example, in this case, if the reactants are initially present at equal pressures and we have a total initial pressure p_0 , the initial pressures of A and B must each be $p_0/2$. The partial pressures of reactants and products at some time t after the reaction has started must then be:

$$p_A = \frac{p_0}{2} (1-\alpha) \quad p_B = \frac{p_0}{2} (1-\alpha) \quad p_C = \frac{p_0}{2} \alpha$$

4. Now work out the total pressure and the mole fractions in terms of p_0 and α .

$$p = p_A + p_B + p_C = \frac{p_0}{2}(1-\alpha + 1-\alpha + \alpha) = \frac{p_0}{2}(2-\alpha)$$

$$x_A = \frac{p_A}{p} = \frac{1-\alpha}{2-\alpha} \quad x_B = \frac{p_B}{p} = \frac{1-\alpha}{2-\alpha} \quad x_C = \frac{p_C}{p} = \frac{\alpha}{2-\alpha}$$

N.B. At some point in most problems you will be given either the total pressure or one of the mole fractions at some point in the reaction, which allows you to determine a numerical value for α .

5. Substitute the mole fractions back into the equilibrium constant.

$$K_p = \left(\frac{\alpha}{2-\alpha} \right) \left(\frac{2-\alpha}{1-\alpha} \right)^2 \frac{p}{p^\ominus} = \frac{\alpha(2-\alpha)}{(1-\alpha)^2} \frac{p}{p^\ominus}$$