
IV. Chemical Equilibria

A. The equilibrium state.

Until now, the reactions have been shown to go 100% to products:

\[ \text{reactants} \rightarrow \text{products} \]

and we have only considered forward reaction rates. What happens when we include the reverse reaction rate? In a reaction equation, the presence of a forward and reverse reaction is represented by a double arrow:

\[ \text{reactants} \rightleftharpoons \text{products} \]

Ex. Mr. Reactant and Ms. Product game. Each participant is given a box with a number of balls - the amounts of reactant and product. Rules: during the music, count the # of balls in your box. Mr. Reactant pulls out ½ of his balls and puts them in Ms. Product’s box. Ms. Product pulls out ¼ of her balls and puts them in Mr. Reactant’s box. At the end of each musical interlude, the # of balls in each box will be counted and recorded. There will be 2 games, the first with all the balls in Mr. Reactant’s box, the second with all the balls in Ms. Product’s box.

After several interludes, the # of balls in each box reach a steady state - the rate of the forward reaction equals the rate of the reverse reaction.

Concept of dynamic equilibrium: A system containing two opposing processes will reach a steady state (equilibrium) at which the rates of the opposing processes will balance.

Ex. Evaporation/condensation of a liquid in a closed container \( \rightarrow \) equilibrium vapor pressure

In a chemical equilibrium, the rates of the forward reaction and reverse reaction match; there is no further change in the concentrations of reactants and products.

In the demonstration, forward rate = ½[reactant]; reverse rate = ¼[product]. At equilibrium:

\[ \frac{1}{2}[\text{reactant}] = \frac{1}{4}[\text{product}] \]

Rearrange: \[ \frac{[\text{product}]}{[\text{reactant}]} = \frac{1}{2}\times\frac{1}{4} = 2 \]

The ratio of product to reactant at equilibrium is equal to a constant. That constant is independent of the starting point of the reaction.
**Law of mass action:** for any reaction: \( aA + bB + \ldots \rightleftharpoons cC + dD + \ldots \)

The reaction quotient defined by the expression: \( \frac{[C]^c[D]^d[\ldots]}{[A]^a[B]^b[\ldots]} \)

is equal to the equilibrium constant (\( K_c \)) when all the concentrations are equilibrium concentrations. The equation coefficients become the exponents.

Ex. \( N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} \)

What about units? In fact, \( K_c \) is unitless. \([A]\) actually means the ratio of the concentration in M to the concentration of the standard state. The standard state concentrations are (a) that of the pure solid, (b) that of a pure liquid, (c) 1 atm for a pure gas, and (d) 1 M for any solute in a solution. Hence, for solutions, \([A] = \) molar conc. of the solute. For gases, we use \( P_A = \) the partial vapor pressure in atm.

**B. Properties of equilibrium constants.**

1. **Manipulations of reactions and \( K_c \).** These manipulations follow from the definition of \( K_c \).

   (a) If a reaction is multiplied by a constant \( (z) \), then the new \( K_c' = (K_c)^z \)

   Ex. Given that \( K_c = 4.0 \) for \( 2HI \rightleftharpoons H_2 + I_2 \), what is \( K_c' \) for \( HI \rightleftharpoons \frac{1}{2} H_2 + \frac{1}{2}I_2 \)?

   \( K_c' = (4.0)^{\frac{1}{2}} = 2.0 \)

   (b) If a reaction is inverted (turned around), then the new \( K_c' = \frac{1}{K_c} \)

   Ex. What is \( K_c' \) for \( H_2 + I_2 \rightleftharpoons 2HI \)? \( K_c' = \frac{1}{4.0} = 0.25 \)

   (c) If two reactions are added, then the new \( K_c' = K_{c1} \cdot K_{c2} \)

   Ex. Given \( H_2O + CH_4 = CO + 3H_2 \quad K_{c1} = 250 \)

   \( CO + H_2O = CO_2 + H_2 \quad K_{c2} = 0.040 \)

   what is \( K_c' \) for: \( CH_4 + 2H_2O = CO_2 + 4H_2 \)\? \( K_c' = (250)(0.040) = 1.0 \)

2. **\( K_p \) and gas phase reactions.**

For gas phase reactions, it is convenient to use gas partial pressures in units of atm instead of molar concentrations. Use \( K_p \) to indicate the use of gas partial pressures. \( K_p \) is also unitless.

Ex. For \( CO(g) + H_2O(g) = CO_2(g) + H_2(g) \quad K_p = \frac{P_{CO_2}P_{H2}}{P_{CO}P_{H2O}} \)
The relation between \( K_p \) and \( K_c \) can be derived by combining the Ideal Gas Law (\( \text{PerVert} = \text{neuRoTic} \)) with the expression for \( K_p \). In general,

\[
K_p = K_c (RT)^{\Delta n}, \text{ where } \Delta n = \text{ the change in the # of moles of gas (products - reactants)}
\]

where \( R = 0.08206 \text{ L·atm/mol·K} \), and \( T \) is in Kelvin.

Ex. For \( \text{H}_2\text{O}(g) + \text{CH}_4(g) = \text{CO}(g) + 3\text{H}_2(g) \), an equilibrium mixture at 700 K contains 0.31 atm of \( \text{H}_2\text{O} \), 0.70 atm of \( \text{CH}_4 \), 0.12 atm of \( \text{CO} \), and 0.38 atm of \( \text{H}_2 \). Calculate \( K_p \) and \( K_c \).

\[
K_p = \frac{\text{P}_{\text{CO}} \cdot \text{P}_{\text{H}_2}^3}{\text{P}_{\text{H}_2\text{O}} \cdot \text{P}_{\text{CH}_4}} = \frac{(0.12)(0.38)^3}{(0.31)(0.70)} = 0.030
\]

\[
K_p = K_c (RT)^\Delta n = K_c / (RT)^2 \text{; hence, } K_c = K_p / (RT)^2 = 0.030 / ((0.08206)(700))^2 = 9.2 \times 10^{-6}
\]

3. Heterogeneous equilibria.

Heterogeneous equilibria have more than one phase present in the reaction. We have discussed how to write equilibria expressions for solutions (use \( K_c \)) and gases (use \( K_p \)). What about:

\[
\text{CaCO}_3(s) = \text{CaO}(s) + \text{CO}_2(g) ?
\]

Recall that in equilibria expressions, \([A]\) actually means the ratio of the concentration in M to the concentration of the standard state. The standard state concentrations are (a) that of the pure solid, (b) that of a pure liquid. Hence, \([A]\) for a pure solid or a pure liquid is 1 by definition. Consequently, terms for pure solids and pure liquids do NOT appear in equilibria expressions. For \( \text{CaCO}_3(s) = \text{CaO}(s) + \text{CO}_2(g) \), \( K_c = [\text{CO}_2] \), and \( K_p = \text{P}_{\text{CO}_2} \).

Ex. An example of a solubility equilibrium is: \( \text{AgCl}(s) = \text{Ag}^+ + \text{Cl}^- \). \( K_c = [\text{Ag}^+][\text{Cl}^-] \) (AgCl does not appear because it is a pure solid).

Ex. An aqueous equilibrium for ammonia is: \( \text{NH}_3(aq) + \text{H}_2\text{O}(l) = \text{NH}_4^+ + \text{OH}^- \). \( K_c = ([\text{NH}_4^+][\text{OH}^-])/[\text{NH}_3] \). (\( \text{H}_2\text{O} \) does not appear because, as the solvent, it is nearly a pure liquid)