Section 13.4
Equilibrium Calculations

Michael Stogsdill

Mott Community College

Learning Objectives

- Identify the changes in concentration or pressure that occur for chemical species in equilibrium systems
- Calculate equilibrium concentrations or pressures and equilibrium constants, using various algebraic approaches

Calculating Equilibrium Constant

- Equilibrium constants are calculated from the equilibrium concentrations of reactants and products.
- If equilibrium concentrations are known, they can simply be substituted into the *K* expression
- If less information is available, you may need to make an ICE table to calculate the equilibrium concentration.

Representing Changes in Concentration

- Representing changes in concentration can be done using an ICE table.

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

	$[NH_3]$	$[N_2]$	$[H_2]$
Initial Concentration	$[NH_3]_i$	$[N_2]_i$	$[H_2]_i$
Change	$-2x$	$+x$	$+3x$
Equilibrium Concentration	$[NH_3]_i - 2x$	$[N_2]_i + x$	$[H_2]_i + 3x$

K_c Calculation Example

- Iodine molecules react reversibly with iodide ions to produce triiodide ions.

$$I_2\ (aq) + I^-\ (aq) \rightleftharpoons I_3{}^-\ (aq)$$

If a solution with the concentrations of I_2 and I^- both equal to 1.000×10^{-3} M before reaction gives an equilibrium concentration of I_2 of 6.61×10^{-4} M, what is the equilibrium constant for the reaction?

K_c Calculation Example

	I_2	$+ \; I^-$	$\rightleftharpoons \; I_3^-$
Initial concentration (*M*)	1.000×10^{-3}	1.000×10^{-3}	0
Change (*M*)	$-x$	$-x$	$+x$
Equilibrium concentration (*M*)	$1.000 \times 10^{-3} - x$	$1.000 \times 10^{-3} - x$	x

- At equilibrium the concentration of I_2 is 6.61×10^{-4} M so

$$1.000 \times 10^{-3}\ \mathrm{M} - x = 6.61 \times 10^{-4}\ \mathrm{M}$$

$$x = 3.39 \times 10^{-4}\ \mathrm{M}$$

K_c Calculation Example

- The ICE table may now be updated with numerical values for all its concentrations

	I_2 +	I^- $\rightleftharpoons$	I_3^-
Initial concentration (*M*)	1.000×10^{-3}	1.000×10^{-3}	0
Change (*M*)	-3.39×10^{-4}	-3.39×10^{-4}	$+3.39 \times 10^{-4}$
Equilibrium concentration (*M*)	6.61×10^{-4}	6.61×10^{-4}	3.39×10^{-4}

K_c Calculation Example

- Finally, substitute the equilibrium concentrations into the K expression and solve

$$K_c = \frac{[I_3{}^-]}{[I_2][I^-]}$$

$$= \frac{3.39\ \times 10^{-4}\ \text{M}}{(6.61\ \times 10^{-4}\ \text{M})(6.61\ \times 10^{-4}\ \text{M})} = 776$$

Missing Equilibrium Concentration Example

Nitrogen oxides are air pollutants produced by the reaction of nitrogen and oxygen at high temperatures. At 2000 °C, the value of the K_c for the reaction, $N_2\ (g) + O_2\ (g) \rightleftharpoons 2NO\ (g)$, is 4.1×10^{-4}. Calculate the equilibrium concentration of NO (*g*) in air at 1 atm pressure and 2000 °C. The equilibrium concentrations of N_2 and O_2 at this pressure and temperature are 0.036 M and 0.0089 M, respectively.

Missing Equilibrium Concentration Example

$$K_c = \frac{[\mathrm{NO}]^2}{[\mathrm{N_2}][\mathrm{O_2}]}$$

$$[\mathrm{NO}]^2 = K_c[\mathrm{N_2}][\mathrm{O_2}]$$

$$[\mathrm{NO}] = \sqrt{K_c[N2][O2]}$$

$$= \sqrt{(4.1 \times 10^{-4})(0.036\ \mathrm{M})(0.0089\ \mathrm{M})} = 3.6\ \times 10^{-4}\ \mathrm{M}$$

Equilibrium Concentrations from Initial Concentrations

- The most challenging type of equilibrium calculation can be one in which equilibrium concentrations are derived from initial concentrations and an equilibrium constant.
- For these calculations, a four-step approach is used
  1) Identify the direction in which the reaction will proceed to reach equilibrium.
  2) Develop an ICE table.
  3) Calculate the concentration changes and, subsequently, the equilibrium concentrations.
  4) Confirm the calculated equilibrium concentrations.

Equilibrium Concentration Example

- Under certain conditions, the equilibrium constant K_c for the decomposition of PCl_5 (*g*) into PCl_3 (*g*) and Cl_2 (*g*) is 0.0211. What are the equilibrium concentrations of PCl_5, PCl_3, and Cl_2 in a mixture that initially contained only PCl_5 at a concentration of 1.00 M?

Step One

- Determine the direction the reaction proceeds.

$$PCl_5\ (g) \rightleftharpoons PCl_3\ (g) + Cl_2\ (g)$$

- Because only the reactant is present initially $Q_c = 0$, which is less than K_c. Therefore the reaction will proceed to the right.

Step Two

- Develop an ICE table.

	PCl_5 $\rightleftharpoons$	PCl_3 +	Cl_2
Initial concentration (*M*)	1.00	0	0
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium concentration (*M*)	$1.00 - x$	x	x

Step Three

- Substituting the equilibrium concentrations into the equilibrium constant equation gives

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

$$= \frac{(x)(x)}{(1.00 - x)} = \frac{x^2}{(1.00 - x)} = 0.0211$$

$$x^2 = 0.0211\,(1.00 - x) = 0.0211 - 0.0211x$$

$$x^2 + 0.0211x - 0.0211 = 0$$

$$x = 0.135 \quad \text{or} \quad -0.156$$

Step Three Continued

- We can now substitute *x* into our concentration expressions.

$$[PCl_5] = 1.00 - x = 1.00 - 0.135 = 0.87\ \mathrm{M}$$

$$[PCl_3] = x = 0.135\ \mathrm{M}$$

$$[Cl_2] = x = 0.135\ \mathrm{M}$$

Step Four

- To check the calculation, substitution the concentrations expression for K_c.

$$K_c = \frac{[\mathrm{PCl_3}][\mathrm{Cl_2}]}{[\mathrm{PCl_5}]} = \frac{(0.135)(0.135)}{0.87} = 0.021$$

Approximations

- When the change in concentration (x) is significantly less than the initial concentration the initial concentration experiences a negligible change.
  - This is a consequence of the small K value
- When these conditions are met, a clever approximation can be used.

Approximation Example

- What are the concentrations at equilibrium of a 0.15 M solution of HCN?

$$HCN(aq) \rightleftharpoons H^+(aq) + CN^-(aq) \qquad K_c = 4.9 \times 10^{-10}$$

	$HCN(aq)$ $\rightleftharpoons$	$H^+(aq)$ +	$CN^-(aq)$
Initial concentration (*M*)	0.15	0	0
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium concentration (*M*)	$0.15 - x$	x	x

Approximation Example

$$K_c = \frac{(x)(x)}{0.150 - x} \approx \frac{x^2}{0.150}$$

$$x = \sqrt{0.150K_c} = \sqrt{(0.150)(4.9 \times 10^{-10})} = 8.6 \times 10^{-6}\ \mathrm{M}$$

$$[\mathrm{HCN}] = 0.150 - x = 0.150 - (8.6 \times 10^{-6}) = 0.14999\,\mathrm{M} \approx 0.150\,\mathrm{M}$$

$$[\mathrm{H^+}] = [\mathrm{CN^-}] = \mathrm{x} = 8.6 \times 10^{-6}\ \mathrm{M}$$