Chemical Equilibrium

When the rate of two opposing processes are equal, the condition is called *equilibrium.*

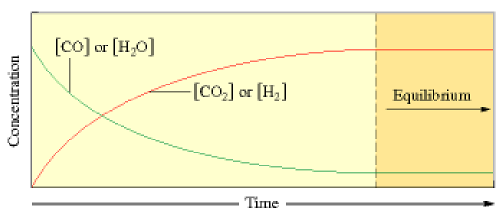
<u>Characteristics of Equilibrium</u>

- dynamic
- reactions are reversible
- if one driving force favors the forward process and the other driving force favors the reverse process the process is reversible
- rate of the forward and reverse processes are equal
- concentrations of reactants and products are constant at equilibrium (not equal)
- occurs in a closed system
- the nature of equilibrium is the same no matter which direction equilibrium is approached
- the equilibrium constant (K) is temperature dependent
- the *equilibrium position* (equilibrium concentrations of reactants and products) can be changed at constant temperature but K will remain constant

The change in concentrations with time for the reaction:

$H_2O_{(g)} + CO_{(g)} \leftrightarrow H_{2(g)}\ CO_{2(g)}$

when equilmolar quantities of water and carbon monoxide are mixed.



Equilibrium Expression:

$\mathbf{H_2 + I_2 \rightleftharpoons 2HI}$

The rate expression for the **forward** reaction is: rate = $k_f [H_2] [I_2]$

The rate expression for the **reverse** reaction is: rate = $k_r [HI]^2$

At equilibrium, the rates of these two reactions are equal:

$k_f [H_2] [I_2] = k_r [HI]^2$

$$\frac{[HI]^2}{[H_2][I_2]} = k_f / k_r$$

Since both k_f and k_r are constants, the ratio k_f / k_r is also a constant.

This new constant is the equilibrium constant, *K*$_{eq}$

$$K_{eq} = \frac{[\text{ Products }]}{[\text{ Reactants }]}$$

Equilibrium constant expression:

- **In the hypothetical balanced equation**, aA + bB ⇌cC + dD, coefficients are represented by small letters and chemical symbols are represented by capital letters.

The equilibrium constant expression for the equation is:

$$K_{eq} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

The exponents are the same as the coefficients in the balanced equation.

- **Pure solids**--do not appear in expression
- **Pure liquids**--do not appear in expression
- **Water**--as a liquid or reactant, does not appear in expression

Example:

$2\ HgO_{(s)} \leftrightarrow 2\ Hg_{(l)} + O_{2(g)}$ $\quad$ $K = [O_2]$

Interpreting K_{eq}

- If K_{eq} is much greater than 1, the reaction will approach completion.
- If K_{eq} is much less than 1, equilibrium is established before much product is formed.
- Each chemical reaction has a unique K_{eq} for every temperature.

K_c and K_p

Equilibrium problems are a common type of problem in Chemistry which involve the equilibrium constant *K*. More specifically, K_c is used when the equilibrium constant is written in terms of concentrations, and K_p is appropriate for a gas reaction if partial pressures of gases are given.

$$K_p = K_c(RT)^{\Delta n}$$

For a reaction

$$a\,A + b\,B \leftrightarrow c\,C + d\,D$$

K_c is defined to be

$$K_c = \left(\frac{[C]^c[D]^d}{[A]^a[B]^b}\right)_{\text{(at equilibrium)}}$$

where all concentrations are equilibrium concentrations. The double arrow in the equation indicates the reaction goes in both directions (and never reaches completion). At equilibrium, the rates of the forward and reverse reactions are equal, and there is no further change in concentration. K_c is a constant for a given reaction at a given temperature.

$$K_p = \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b}$$

How to Solve Equilibrium Problems

Methods for solving equilibrium problems are best shown with examples.

Example 1

Calculate the equilibrium constant K_c at 25 °C for the reaction

$$2\,NOCl(g) \leftrightarrow 2\,NO(g) + Cl_2(g)$$

using the following information. In one experiment 2.00 mol of NOCl is placed in a 1.00 -L flask, and the concentration of NO after equilibrium is achieved is 0.66 mol/L.

Method:
(a) Calculate the initial concentration of NOCl from the information given.
(b) Form an equilibrium table and fill in all known quantities. Represent unknown quantities with variables. Use the information in the table to calculate the concentration of NOCl and Cl_2 at equilibrium.
(c) Form the K_c equation and fill in all known information. Calculate K_c.

Solution:
Step(a): The initial concentration of NOCl is

$$[\text{NOCl}]_0 = \frac{2.0 \text{ mol}}{1.00 \text{ L}} = 2.00 \text{ M}$$

Step(b): The equilibrium table is:

Balanced Equation	**2 NOCl(g) ↔**	**2 NO(g) +**	**Cl_2(g)**
Initial Concentrations (M)	2.00	0	0
Change (M)	- 2x	2x	x
Equilibrium Concentrations (M)	(2.00 - 2x)	2x = 0.66	x

From the table we have

$$[\text{NO}] = 2x = 0.66 \text{ M}$$
$$x = 0.33 \text{ M}$$

Thus

$$[\text{NOCl}] = (2.00 - 2x) \text{ M} = (2.00 - 2(0.33)) \text{ M} = 1.34 \text{ M}$$

$$[\text{Cl}_2] = x = 0.33 \text{ M}$$

Step(c): We now have the information we need to calculate K_c:

$$K_c = \left(\frac{[\text{NO}]^2[\text{Cl}_2]}{[\text{NOCl}]^2}\right)_{\text{(at equilibrium)}} = \frac{(0.66)^2(0.33)}{(1.34)^2} = 0.080$$

Example 2
When solid ammonium carbamate sublimes, it dissociates completely into ammonia and carbon dioxide according to the equation

$$N_2H_6CO_2(s) \leftrightarrow 2\ NH_3(g) + CO_2(g)$$

At 25 ^{o}C, experiment shows that the total pressure of the gases in equilibrium with the solid is 0.116 atm. What is the equilibrium constant K_p?

Method:
The steps are:
(a) Form an equilibrium table and fill in all known quantities. Represent unknown quantities with variables.
(b) Use the table together with the rule that the sum of the partial pressures equals the total pressure to find the partial pressures of NH_3 and CO_2 at equilibrium.
(c) Form the K_p equation and fill in all known information. Calculate K_p.

Solution:
Step (a): The equilibrium table is:

Balanced Equation	**$N_2H_6CO_2(s)$ ↔**	**2 $NH_3(g)$ +**	**$CO_2(g)$**
Initial Partial Pressures (atm)	(solid!)	0	0
Change (atm)	*not applicable*	$2x$	x
Equilibrium Partial Pressures (atm)	*not applicable*	$2x = p(NH_3)$	$x = p(CO_2)$

Step (b): The total pressure at equilibrium (given as 0.116 atm) equals the sum of the partial pressures. The last line of the equilibrium table allows us to express $p(NH_3)$ and $p(CO_2)$ in terms of x. Thus we have

$$p_{Total} = p(NH_3) + p(CO_2)$$

$$0.116 \text{ atm} = 2x + x = 3x$$

$$x = 0.03867 \text{ atm}$$

It follows that

$$p(NH_3) = 2x = 2\ (0.0387 \text{ atm}) = .07734 \text{ atm}$$
$$p(CO_2) = x = 0.03867 \text{ atm}$$

Step (c): Now we have the information needed to calculate K_p:

$$K_p = \left(p_{NH_3}^2\ p_{CO_2}\right)_{(\text{at equilibrium})} = \left((0.07734)^2(0.03867)\right) = 2.31 \times 10^{-4}$$

EXTERNAL FACTORS AFFECTING EQUILIBRIA

I. **Le Chatelier's Principle**: Shifts in direction occur to reestablish equilibrium positions.
II. Temperature--exothermic⇒heat is a product; endothermic⇒heat is a reactant.
III. Changing reagent and product amounts:
   A. Adding a reagent--shift tries to consume additional material by favoring forward reaction.
   B. Removing a reagent—shift tries to replace material by favoring reverse reaction.
   C. Adding product—shift tries to consume—favor reverse reaction
   D. Removing product—shift tries to replace—favor forward reaction
IV. Pressure--increase favors the side with the least # of gas moles; the converse is also true.
V. catalysts--NO EFFECT on K; just gets to equilibrium faster!

Practice problems are on the next page:

1. Write the equilibrium expression for each of the following: Where possible, express both K_c and K_p.

a)2 NaN_3 (s) $\rightleftharpoons$ 2 Na (s) + 3 N_2 (g)

b) 4 NH_3 (g) + 5 O_2 (g) $\rightleftharpoons$ 4 NO (g) + 6 H_2O (g)

c) 2 HCl (aq) + $Ca(OH)_2$ (aq) $\rightleftharpoons$ 2 H_2O (l) + $CaCl_2$ (aq)

2. For equation 1b, would $K_c = K_p$? Explain.
No, different number of moles on reactant side and product side.
3. Determine the equilibrium concentrations for each species in the equation:

H_2 (g) + I_2 (g) $\rightleftharpoons$ 2 HI (g)
if the initial concentrations of H_2 and I_2 are 1.0 M and $K_c = 54.3$ at 430°C.

4. Given the reaction below:

H_2 (g) + I_2 (g) $\rightleftharpoons$ 2 HI (g)
If the initial concentrations of H_2 and I_2 are 1.0 M and the initial concentration of HI is 0.5 M (Kc = 54. 3 at 430°C), is the reaction at equilibrium? If not, which way will the reaction proceed?

Reaction is not at equilibrium, more reactants than should be at euqilibrium, the equilibrium would proceed to the right.

5. According to Le Chatelier's Principle,
a) what effect would the addition of Cl^- have on the equilibrium below?

$CoCl_2$ + 2 Cl^- $\rightleftharpoons$ $CoCl_4^{2-}$
Shifts the equilibrium to the right, increase in the Cl^- concentration creates stress on the reactant side. To relieve the stress, more $CoCl_4^{2-}$ is formed.
b) what effect would the addition of Ag^+ have on the equilibrium in problem 5a if the Ag^+ precipitates as AgCl?
Shifts the equilibrium to the left, the Ag^+ ion removes Cl^-, to compensate for loss of Cl^-, the $CoCl_4^{2-}$ dissociates to generate more Cl^-.

Answers

1.

$K_c = [N_2]^3$ $K_p = P_{N_2}^3$

$$K_c = \frac{[NO]^4[H_2O]^6}{[NH_3]^4[O_2]^5} \qquad K_p = \frac{P_{NO}^4 P_{H_2O}^6}{P_{NH_3}^4 P_{O_2}^5}$$

$$K_c = \frac{[CaCl_2]}{[HCl]^2 [Ca(OH)_2]}$$

No K_p

2. No, different number of moles on reactant side and product side.

3.

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(2x)^2}{(1.0 - x)(1.0 - x)}$$

solve for x, x = 0.79

$[H_2] = [I_2] = 0.21M$; $[HI] = 1.58M$

4.

$$Q = \frac{[HI]_o^2}{[H_2]_o[I_2]_o} = \frac{(0.5)^2}{(1.0)(1.0)} = 0.25$$

$Q < K_c$

5. Reaction is not at equilibrium, more reactants than should be at euqilibrium, the equilibrium would proceed to the right.

Shifts the equilibrium to the right, increase in the Cl^- concentration creates stress on the reactant side. To relieve the stress, more $CoCl_4^{2-}$ is formed.

b) Shifts the equilibrium to the left, the Ag^+ ion removes Cl^-, to compensate for loss of Cl^-, the $CoCl_4^{2-}$ dissociates to generate more Cl^-.