Module 9. Principles of Chemical Equilibrium
Lecture 2

Learning Objective	Openstax 2e Chapter
Equilibrium Constant (K)	13.2

Suggested Practice Problems

Chapter 13 Exercises – Questions: 22, 24, 27, 30

Answers can be found in the Chapter 13 Answer Key

K expressions for Heterogeneous Systems

Q1: Write the equilibrium constant expression for the reaction (using activities):

$$Cl_2(g) + H_2O(l) \rightleftharpoons HOCl(aq) + H^+(aq) + Cl^-(aq)$$

$$K = \frac{a(HOCl)\ a(H^+)\ a(Cl^-)}{a(Cl_2)\ \cancel{a(H_2O(l))}} = \frac{a(HOCl)\ a(H^+)\ a(Cl^-)}{a(Cl_2)}$$

For pure liquid, a =1.

Q2: Write the equilibrium constant expression for the reaction (using activities):

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

$$K = \frac{a(CO_2)\ \cancel{a(CaO)}}{\cancel{a(CaCO_3)}} = a(CO_2)$$

For pure solid, a = 1.

Pure liquids and pure solids can be omitted from K expressions, because their activities are always equal to 1.

K expressions for Heterogeneous Systems

Q3: Write the equilibrium constant expression for the reaction (using activities):

$$2H_2O(\ell) \rightleftharpoons 2H_2(g) + O_2(g)$$

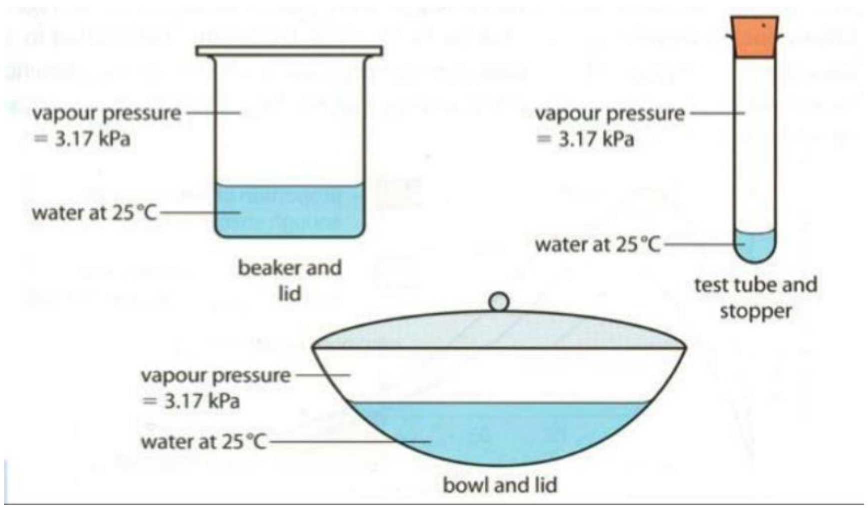
$$K = \frac{a(H_2(g))^2\, a(O_2(g))}{a(H_2O(l))^2}$$

Recall that the activity of a pure liquid is 1.

$$= a(H_2(g))^2\, a(O_2(g))$$

K expressions for Heterogeneous Systems

Recall that we learned about water vapor pressure in the Fall.



Water vapor pressure is independent of the amount of water and the shape and volume of the container.

TABLE 6.4 Vapor Pressure of Water at Various Temperatures

	Vapor Pressure	
t, °C	kPa	mmHg
15.0	1.706	12.79
17.0	1.938	14.54
19.0	2.198	16.49
21.0	2.448	18.66
23.0	2.811	21.08
25.0	3.170	23.78
30.0	4.247	31.86
50.0	12.35	92.65

Now we can write the *K* expression for this process as:

$$H_2O(l) \rightleftharpoons H_2O(g)$$

$$K = \frac{a(H_2O(g))}{a(H_2O(l))} = a(H_2O(g)) = \text{Pressure}/100\text{ kPa} = 3.17\times10^{-2} \text{ at } 25\ ^\circ\text{C}$$

The amount liquid water does not appear in the *K* expression!

However, why does *K* depend on *T*; to be learned later.

Relationship of K to the balanced equations

Provide K expression for the following reactions

(1) $A + B \rightleftharpoons C$ $\qquad K_1 = \frac{[C]}{[A][B]}$

(2) $C \rightleftharpoons A + B$ $\qquad K_2 = \frac{[A][B]}{[C]} = (K_1)^{-1}$

(3) $2\,A + 2\,B \rightleftharpoons 2\,C$ $\qquad K_3 = \frac{[C]^2}{[A]^2[B]^2} = (K_1)^2$

(4) $1/2\,A + 1/2\,B \rightleftharpoons 1/2\,C$ $\qquad K_4 = \frac{[C]^{1/2}}{[A]^{1/2}[B]^{1/2}} = (K_1)^{1/2}$

- The value of K depends on the expression of the given reaction

Multi-step reactions: Solve for overall *K*

In one reaction vessel

(1) $A \rightleftarrows \cancel{B}$ has constant K_1

(2) $\cancel{B} \rightleftarrows C$ has constant K_2

Overall reaction: (1)+(2) = (3) $A \rightleftarrows C$ has constant $K_3 = K_1 * K_2$

Proof for the expression of K_3

$$K_1 = \frac{[B]}{[A]}$$

$$K_2 = \frac{[C]}{[B]}$$

$$K_3 = K_1 * K_2 = \frac{\cancel{[B]}}{[A]} \times \frac{[C]}{\cancel{[B]}} = \frac{[C]}{[A]}$$

Practice Question 1

We know the equilibrium constants of reactions (1) and (2) and want to know the equilibrium constant for the overall reaction (3).

(1) $N_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons N_2O(g)$ $\quad K_1 = 5.4\times10^{-19}$

(2) $N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g)$ $\quad K_2 = 4.6\times10^{-31}$

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(3) $N_2O(g) + \frac{1}{2}O_2(g) \rightleftharpoons 2\,NO(g)$ $\quad \boldsymbol{K_3 = ?}$

A) Write expressions for K_1 , K_2 , and K_3

B) How is the overall equation (3) related to reactions (1) and (2)?

C) Solve for K_3 *(of the overall reaction)*

Practice Question 1 - Answer

We know the equilibrium constants of reactions (1) and (2) and want to know the equilibrium constant for the overall reaction (3).

(1) $N_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons \boxed{N_2O(g)}$ $\quad K_1 = 5.4\times10^{-19} = \dfrac{[N_2O]}{[N_2][O_2]^{1/2}}$

(2) $N_2(g) + O_2(g) \rightleftharpoons \boxed{2\ NO(g)}$ $\quad K_2 = 4.6\times10^{-31} = \dfrac{[NO]^2}{[N_2][O_2]}$ A)

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(3) $\boxed{N_2O(g)} + \frac{1}{2}O_2(g) \rightleftharpoons \boxed{2\ NO(g)}$ $\quad$ **K_3 = ?** $\quad = \dfrac{[NO]^2}{[N_2O][O_2]^{1/2}}$

B) Overall reaction (3) involves reaction (2) and the reverse of reaction (1)

(-1) $N_2O(g) \rightleftharpoons \cancel{N_2(g)} + \cancel{\frac{1}{2}O_2}(g)$ $\quad K_{-1} = 1/K_1 = 1/5.4\times10^{-19} = 1.9\times10^{18}$

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(2) $\cancel{N_2(g)} + \frac{1}{2}O_2(g) \rightleftharpoons 2\ NO(g)$ $\quad K_2 = 4.6\times10^{-31}$

C) $K_3 = K_2 \times K_{-1} = (4.6\times10^{-31}) \times (1.9\times10^{18}) = 8.5\times10^{-13}$

or

$K_3 = K_2 / K_1\ (4.6\times10^{-31})/(5.4\times10^{-19}) = 8.5\times10^{-13}$

Practice Question 1 – Answer – Extra proof

We know the equilibrium constants of reactions (1) and (2) and want to know the equilibrium constant for the overall reaction (3).

(1) $N_2(g) + \frac{1}{2}O_2(g) \rightleftarrows \boxed{N_2O(g)}$ $\quad K_1 = 5.4\times10^{-19} = \dfrac{[N_2O]}{[N_2][O_2]^{1/2}}$

(2) $N_2(g) + O_2(g) \rightleftarrows \boxed{2\ NO(g)}$ $\quad K_2 = 4.6\times10^{-31} = \dfrac{[NO]^2}{[N_2][O_2]}$

(3) $\boxed{N_2O(g)} + \frac{1}{2}O_2(g) \rightleftarrows \boxed{2\ NO(g)}$ $\quad$ $\boldsymbol{K_3 = ?}$ $\quad = \dfrac{[NO]^2}{[N_2O][O_2]^{1/2}}$

Proof for equation:

$$K_3 = K_2 / K_1 = \dfrac{\dfrac{[NO]^2}{[\cancel{N_2}][\cancel{O_2}]}}{\dfrac{[N_2O]}{[\cancel{N_2}][\cancel{O_2}]^{1/2}}} = \dfrac{[NO]^2}{[N_2O][O_2]^{1/2}}$$

Practice Question 2

In the Ostwald process for oxidizing ammonia gas to $NO_2(g)$ and water, a variety of products are possible. One possibility is:

$$NH_3(g) + \frac{5}{4} O_2(g) \rightleftharpoons NO(g) + \frac{3}{2} H_2O(g) \qquad K_1 = 2.11 \times 10^{19}$$

At high temperatures (700K), NO_2 also degrades to NO.

$$NO_2(g) \rightleftharpoons NO(g) + \frac{1}{2} O_2(g) \qquad K_2 = 0.524$$

Determine the equation for the overall oxidation of NH_3 to NO_2 and calculate K_3.

$$K_3 = ?$$

$$\rightleftharpoons$$

Practice Question 2 - Answer

In the Ostwald process for oxidizing ammonia gas to $NO_2(g)$ and water, a variety of products are possible. One possibility is:

$$NH_3(g) + \frac{5}{4}O_2(g) \rightleftharpoons \cancel{NO}(g) + \frac{3}{2}H_2O(g) \qquad K_1 = 2.11 \times 10^{19}$$

At high temperatures (700K), NO_2 also degrades to NO.

$$NO_2(g) \rightleftharpoons NO(g) + \frac{1}{2}O_2(g) \qquad K_2 = 0.524$$

Determine the equation for the overall oxidation of NH_3 to NO_2 and calculate K_3.

Rewrite 2nd equation towards NO_2 (Reverse)

$$\cancel{NO}(g) + \frac{1}{2}O_2(g) \rightleftharpoons NO_2(g) \qquad K_{-2} = 1/K_2 = 1/0.524 = 1.91$$

5/4 + 1/2 =5/4 + 2/4 = 7/4

$$NH_3(g) + \frac{7}{4}O_2(g) \rightleftharpoons NO_2(g) + \frac{3}{2}H_2O(g)$$

$$K_3 = K_1 \times K_{-2} = (2.11 \times 10^{19}) \times 1.91 = 4.03 \times 10^{19}$$

Magnitude of the Equilibrium Constant

$$2\,H_2(g) + O_2(g) \rightleftarrows 2\,H_2O(l)$$

$$K_{(298K)} = \frac{a(H_2O)^2}{a(H_2)^2\ a(O_2)} = \frac{1}{a(H_2)^2\ a(O_2)} = 1.4 \times 10^{83}$$

Denominator must be very small!

If K is very large ($K > 10^{10}$) the reaction, as written, exhibits a strong tendency to go to completion. At equilibrium, the reaction mixture contains almost *entirely products*.

Warning: A very large *K* does NOT mean that this reaction would occur automatically. $H_2(g)$ and $O_2(g)$ mixed in a test tube would never react to produce H_2O until triggered by a spark.

Magnitude of the Equilibrium Constant

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$$

Numerators must be very small!

$$K_{(298K)} = \frac{a(H_2)\, a(CO)}{a(H_2O)} = 1.6 \times 10^{-21}$$

If K is very small ($K < 10^{-10}$) the reaction, as written, exhibits almost no tendency to occur. At equilibrium, the reaction mixture contains almost entirely *starting materials*.

Warning: A very small K does NOT mean that this reaction would not be useful in producing products. The Haber process for ammonia synthesis has a rather small K_p (see last lecture). But this process is used to produce 300 million metric tons of ammonia in the world every year!