Chapter 15

CHEMICAL EQUILIBRIUM

(Part I)

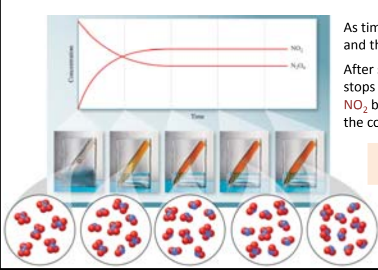
The Concept of Equilibrium

- Do all chemical reactions go to completion?
  When you start with *only reactants*, do you end up with *only products*?
- Most of chemical reactions are ***reversible***. They do not go to completion (just *products* present).
- In fact, they will be left, at some instance, with a *mixture* of *reactants* and *products*, which are in equilibrium (their concentrations are not changing).

Chemical Equilibrium

$$N_2O_4\,(g) \underset{k_r}{\overset{k_f}{\rightleftharpoons}} 2NO_2\,(g)$$

Reversible reaction



As time passes, more NO_2 is produced and the brown color intensifies.

After some time, the brown color stops changing. The concentration of NO_2 becomes constant. Same does the concentration of N_2O_4.

At this instance, does the reaction stop?

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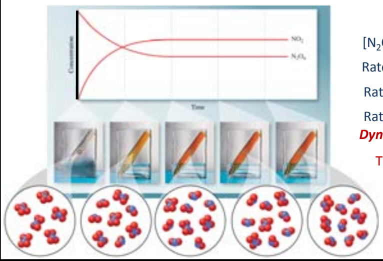
Chemical Equilibrium

$N_2O_4\,(g) \underset{k_r}{\overset{k_f}{\rightleftharpoons}} 2NO_2\,(g)$ Rate forward $= k_f[N_2O_4]$
Rate backward $= k_r[NO_2]^2$

The reaction is *reversible*, i.e. it does NOT stop but proceeds at both directions.



Reaction progress

$[N_2O_4]$ is high ; $[NO_2]$ is zero

Rate forward >> Rate backward

Rate forward > Rate backward

Rate forward = Rate backward

Dynamic equilibrium is established

The reaction does not stop. It continues running on both directions at equal rates.

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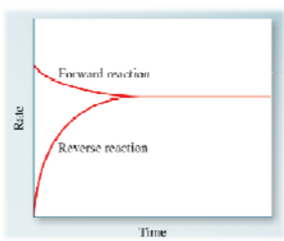
Chemical Equilibrium

$N_2O_4\,(g) \underset{k_r}{\overset{k_f}{\rightleftharpoons}} 2NO_2\,(g)$ Rate forward $= k_f[N_2O_4]$
Rate backward $= k_r[NO_2]^2$



The rates of the reaction (forward and backward rates) change over time. The forward rate gradually decreases, while the backward rate gradually increases (starting from zero). Eventually, at equilibrium, both rates become equal.

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The Equilibrium Constant

$N_2O_4\,(g) \underset{k_r}{\overset{k_f}{\rightleftharpoons}} 2NO_2\,(g)$

- At dynamic ***equilibrium***,

$$\text{rate}_{\text{forward}} = \text{rate}_{\text{reversed}}$$

or

$$k_f[N_2O_4]_{eq} = k_r[NO_2]^2_{eq}$$ Equilibrium

$$\frac{k_f}{k_r} = \frac{[NO_2]^2_{eq}}{[N_2O_4]_{eq}} = K_c$$ Molar concentration

where K_c is the ***equilibrium constant***, and the equation is called the ***equilibrium expression***.

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The Equilibrium Constant

$$N_2O_4\,(g) \underset{k_r}{\overset{k_f}{\rightleftharpoons}} 2NO_2\,(g)$$

TABLE 15.1 Initial and Equilibrium Concentrations of N_2O_4 and NO_2 at 25°C

Experiment	Initial Concentrations (*M*) $[N_2O_4]_i$	$[NO_2]_i$	Equilibrium Concentrations (*M*) $[N_2O_4]_{eq}$	$[NO_2]_{eq}$	$\frac{[NO_2]^2_{eq}}{[N_2O_4]_{eq}}$
1	0.670	0.00	0.643	0.0547	4.65×10^{-3}
2	0.446	0.0500	0.448	0.0457	4.66×10^{-3}
3	0.500	0.0300	0.491	0.0475	4.60×10^{-3}
4	0.600	0.0400	0.594	0.0523	4.60×10^{-3}
5	0.000	0.200	0.0898	0.0204	4.63×10^{-3}

Regardless the initial concentrations of N_2O_4 , the equilibrium constant (K_c) *is almost constant* at the same temperature.

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The Equilibrium Position

$$N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$$

- Each set of equilibrium concentrations is called an ***equilibrium position***.

  An ***equilibrium position*** is different than the ***equilibrium constant***.
- For a reaction system at a given temperature, there is only *one* equilibrium constant, but there are an *infinite* number of equilibrium positions.

...trations of N_2O_4 and NO_2 at 25°C

Equilibrium Concentrations (*M*) $[N_2O_4]_{eq}$	$[NO_2]_{eq}$	$\frac{[NO_2]^2_{eq}}{[N_2O_4]_{eq}}$
0.643	0.0547	4.65×10^{-3}
0.448	0.0457	4.66×10^{-3}
0.491	0.0475	4.60×10^{-3}
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0.0898	0.0204	4.63×10^{-3}

Equilibrium positions *Equilibrium constant*

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The Equilibrium Position

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

The Haber process: the most important source of ammonia worldwide.

TABLE 13.1 Results of Three Experiments for the Reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

Experiment	Initial Concentrations	Equilibrium Concentrations	$K = \frac{[NH_3]^2}{[N_2][H_2]^3}$
I	$[N_2]_0 = 1.000\ M$ $[H_2]_0 = 1.000\ M$ $[NH_3]_0 = 0$	$[N_2] = 0.921\ M$ $[H_2] = 0.763\ M$ $[NH_3] = 0.157\ M$	$K = 6.02 \times 10^{-2}$
II	$[N_2]_0 = 0$ $[H_2]_0 = 0$ $[NH_3]_0 = 1.000\ M$	$[N_2] = 0.399\ M$ $[H_2] = 1.197\ M$ $[NH_3] = 0.203\ M$	$K = 6.02 \times 10^{-2}$
III	$[N_2]_0 = 2.00\ M$ $[H_2]_0 = 1.00\ M$ $[NH_3]_0 = 3.00\ M$	$[N_2] = 2.59\ M$ $[H_2] = 2.77\ M$ $[NH_3] = 1.82\ M$	$K = 6.02 \times 10^{-2}$

Equilibrium positions *Equilibrium constant*

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The Reaction Quotient

- For the hypothetical chemical reaction:

$$a\,\text{A} + b\,\text{B} \rightleftharpoons c\,\text{C} + d\,\text{D}$$

The ***reaction quotient*** is defined as:

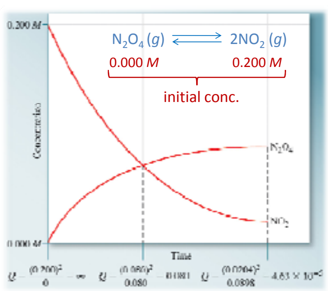
$$Q_c = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b}$$

At equilibrium:

$$Q_c = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b} = K_c$$

Law of mass action

The Reaction Quotient



- The value of Q_c :
  - o can be calculated at any time during the reaction.
  - o changes as the reaction progresses.
  - o is equal to K_c when the system is at equilibrium.

The Equilibrium Constant

- Exercise:

$$Br_2\,(g) + Cl_2\,(g) \rightleftharpoons 2BrCl\,(g)$$

The equilibrium concentrations at 100°C were found to be $[Br_2]_{eq} = 2.3 \times 10^{-3}\,M$, $[Cl_2]_{eq} = 1.2 \times 10^{-2}\,M$, and $[BrCl]_{eq} = 1.4 \times 10^{-2}\,M$.

(a) Write the equilibrium expression.

(b) Calculate the equilibrium constant at 100°C.

The Unit of Equilibrium Constant

- When we want to calculate the equilibrium constant (K_c), we leave out the units of the concentrations (or partial pressures) of the reactants and products.

  The reason is that each molar concentration (or partial pressure) of the reactants or products is divided by a reference state (1 *M* and 1 atm for molar concentrations and partial pressures, respectively). This brings up a unitless K_c.

Check pp. 622 of your textbook for more details.

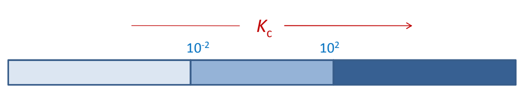
Magnitude of Equilibrium Constant

$$a\,A + b\,B \rightleftharpoons c\,C + d\,D \qquad K_c = \left(\frac{[C]^c[D]^d}{[A]^a[B]^b}\right)_{eq}$$

- For the above reaction, three outcomes are possible:
  - The reaction goes to completion. The equilibrium mixture will consist predominantly from products. — The value of K_c is very large
  - The reaction doesn't occur to any significant degree. The equilibrium mixture will consist predominantly from reactants. — The value of K_c is very small
  - The reaction occurs to a significant degree, but not to completion. The equilibrium mixture will have both reactants and products in comparable quantities. — The value of K_c is neither large nor small

Magnitude of Equilibrium Constant

$$a\,A + b\,B \rightleftharpoons c\,C + d\,D \qquad K_c = \left(\frac{[C]^c[D]^d}{[A]^a[B]^b}\right)_{eq}$$



The magnitude of K_c is very small. The reaction will almost not occur	The reaction will have an equilibrium mixture of both reactants and products.	The magnitude of K_c is very large. The reaction will go almost to completion

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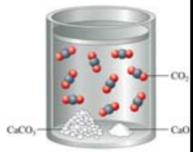
Heterogeneous Equilibria

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

$$K_c^* = \frac{[CaO]_{eq}[CO_2]_{eq}}{[CaCO_3]_{eq}}$$



Think about it. If you increase the quantity of $CaCO_3$ or CaO solids, would their concentrations change?

The concentration of a solid (or a pure liquid) is constant and can be incorporated into K_c^*.

$$\frac{K_c^*[CaCO_3]_{eq}}{[CaO]_{eq}} = [CO_2]_{eq} = K_c$$

Real equilibrium constant

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Equilibrium Expressions Involving Pressures

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$

The equilibrium expression is given by:

$$K_c = \frac{[NO_2]^2_{eq}}{[N_2O_4]_{eq}}$$

In terms of *equilibrium partial pressures* of NO_2 and N_2O_4, the equilibrium expression becomes:

$$K_P = \frac{(P_{NO_2})^2_{eq}}{(P_{N_2O_4})_{eq}}$$

Equilibrium partial pressures of NO_2 and N_2O_4 gases

Are K_c and K_P equal?

Generally, they are NOT. Because the partial pressures of reactants and products in expresses in atm are not equal to their concentrations expressed in mol/L.

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The Relationship between K_c and K_P

- Consider the reaction:

$$aA(g) \rightleftharpoons bB(g)$$

$$K_c = \frac{[B]^b}{[A]^a} \qquad K_P = \frac{(P_B)^b}{(P_A)^a}$$

Assuming ideal behavior:

$$P_A = \frac{n_A RT}{V} = \frac{n_A}{V} RT = [A]RT$$

Similarly:

$P_B = [B]RT$

Substitution in K_P gives => $K_P = \dfrac{([B]RT)^b}{([A]RT)^a} = \underbrace{\dfrac{[B]^b}{[A]^a}}_{K_c}(RT)^{b-a}$

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The Relationship between K_c and K_P

- Consider the reaction:

$$aA(g) \rightleftharpoons bB(g)$$

$$K_c = \frac{[B]^b}{[A]^a} \qquad K_P = \frac{(P_B)^b}{(P_A)^a}$$

Since: $b - a = \Delta n$

Then:

$$K_P = \frac{[B]^b}{[A]^a}(RT)^{\Delta n} = K_c(RT)^{\Delta n}$$

where: Δn = moles of gaseous products – moles of gaseous reactants

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The Equilibrium Expression

- Exercise:

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

The value of K_c of the reaction above is 2.3×10^{-2} at 25°C. Calculate K_P for the reaction at this temperature.

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Manipulating Equilibrium Expressions

- For any chemical reaction, if something gets changed about how its equilibrium is being expressed, the equilibrium expression must also change accordingly.

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

$$K_c = \frac{[NO_2]^2_{eq}}{[NO]^2_{eq}[O_2]_{eq}}$$

At 500 K, $K_c = 6.9 \times 10^5$.

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Manipulating Equilibrium Expressions

- For any chemical reaction, if something gets changed about how its equilibrium is being expressed, the equilibrium expression must also change accordingly.
- By reversing the reaction, we get:

$$2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$$

$$K'_c = \frac{[NO]^2_{eq}\,[O_2]_{eq}}{[NO_2]^2_{eq}}$$

At 500 K, the new equilibrium constant (K'_c) will be the reciprocal of K_c .

$$K'_c = 1/(6.9 \times 10^5) = 1.5 \times 10^{-6}$$

Manipulating Equilibrium Expressions

- For any chemical reaction, if something gets changed about how its equilibrium is being expressed, the equilibrium expression must also change accordingly.
- By multiplying the original reaction by 2:

$$4NO(g) + 2O_2(g) \rightleftharpoons 4NO_2(g)$$

$$K''_c = \frac{[NO_2]^4_{eq}}{[NO]^4_{eq}\,[O_2]^2_{eq}}$$

At 500 K, the new equilibrium constant (K''_c) will be $(K_c)^2$.

$$K''_c = (6.9 \times 10^5)^2 = 4.8 \times 10^{11}$$

Manipulating Equilibrium Expressions

At 500 K

$$2NO_2(g) \rightleftharpoons 2NO(g) + \cancel{O_2(g)} \qquad K_{c_1} = 1.5 \times 10^{-6}$$

$$2H_2(g) + \cancel{O_2(g)} \rightleftharpoons 2H_2O(g) \qquad K_{c_2} = 2.4 \times 10^{47}$$

$$2NO_2(g) + 2H_2(g) \rightleftharpoons 2NO(g) + 2H_2O(g)$$

$$K'_c = \frac{[NO]^2_{eq}\,\cancel{[O_2]_{eq}}\,[H_2O]^2_{eq}}{[NO_2]^2_{eq}\,[H_2]^2_{eq}\,\cancel{[O_2]_{eq}}} = \frac{[NO]^2_{eq}\,[H_2O]^2_{eq}}{[NO_2]^2_{eq}\,[H_2]^2_{eq}}$$

In fact when two reactions (one is with an equilibrium constant K_{c_1} , and the other is with an equilibrium constant K_{c_2}) are added:

$$K'_c = K_{c_1} \times K_{c_2}$$

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Manipulating Equilibrium Expressions

- In summary:

TABLE 15.2 Manipulation of Equilibrium Constant Expressions

$A(g) + B(g) \rightleftharpoons 2C(g)$ $\quad K_{c_1} = 4.39 \times 10^{-3}$

$2C(g) \rightleftharpoons D(g) + E(g)$ $\quad K_{c_2} = 1.15 \times 10^{4}$

Equation	Equilibrium Expression	Relationship to Original K_c	Equilibrium Constant
$2C(g) \rightleftharpoons A(g) + B(g)$ Original equation is reversed.	$K'_{c_1} = \frac{[A]_{eq}[B]_{eq}}{[C]^2_{eq}}$	$\frac{1}{K_{c_1}}$	2.28×10^{2} New constant is the reciprocal of the original.
$2A(g) + 2B(g) \rightleftharpoons 4C(g)$ Original equation is multiplied by a number.	$K''_{c_1} = \frac{[C]^4_{eq}}{[A]^2_{eq}[B]^2_{eq}}$	$(K_{c_1})^2$	1.93×10^{-5} New constant is the original raised to the same number.
$\frac{1}{2}A(g) + \frac{1}{2}B(g) \rightleftharpoons C(g)$ Original equation is divided by 2.	$K'''_{c_1} = \frac{[C]_{eq}}{[A]^{1/2}_{eq}[B]^{1/2}_{eq}}$	$\sqrt{K_{c_1}}$	6.63×10^{-2} New constant is the square root of the original.
$A(g) + B(g) \rightleftharpoons D(g) + E(g)$ Two equations are added.	$K_{c_3} = \frac{[D]_{eq}[E]_{eq}}{[A]_{eq}[B]_{eq}}$	$K_{c_1} \times K_{c_2}$	50.5 New constant is the product of the two original constants.

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Manipulating Equilibrium Expressions

- Exercise:

  At 500°C, $K_P = 2.5 \times 10^{10}$ for,

  $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

  Compute K_P for each of the following reactions at 500°C :

  (a) $SO_2(g) + 1/2O_2(g) \rightleftharpoons SO_3(g)$

  (b) $3SO_3(g) \rightleftharpoons 3SO_2(g) + 3/2\ O_2(g)$

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