1 Introduction

Chemical Reactions (Rx) usually do not go to completion.

For example, dimerization of NO₂:

\[
2\text{NO}_2(g) \rightarrow \text{N}_2\text{O}_4(g)
\]

(brown) (colorless)

Start: 2.0 mol 0.0 mol

Start with 2.0 mol of NO₂ and 0.0 mol of N₂O₄:

\[
2\text{NO}_2(g) \rightarrow \text{N}_2\text{O}_4(g)
\]

(brown) (colorless)

Start: 2.0 mol 0.0 mol

After the Rx is done — at chemical equilibrium – some N₂O₄(g) is produced but some NO₂ remains:

moles of NO₂ > 0.0 and moles of N₂O₄ < 1.0

At equilibrium a light brown color is observed (not colorless).

Question of interest: How much N₂O₄(g) and NO₂ remains? (at a given Temp. T)
• A system in chemical equilibrium experiences no changes (over time) in the concentrations of any species – reactants or products.

• Concentration of species X is denoted by [X] in mol/L (e.g. \([\text{NO}_2]=2.0 \text{ mol/L} - 2.0 \text{ M}\))

• Chemical equilibrium can be achieved in a short period (seconds) of time or a very-very long time (years) – depends on the chemical kinetics.

• Chemical equilibrium is described by the equilibrium constant \(K\) – a constant at a specified \(T\). (Some books denote it by \(K_{eq}\))

1.1 Rxs can go to the left or right

Consider again the Rx, where at some \(T\) we find:

\[
\begin{align*}
\text{2NO}_2(g) & \longrightarrow \text{N}_2\text{O}_4(g) \\
\text{start:} \quad 2.0 \text{ mol} & \quad 0.0 \text{ mol} \\
\text{end:} \quad 1.0 \text{ mol} & \quad 0.5 \text{ mol}
\end{align*}
\]

So at the end when the reaction stops – at equilibrium – half of the 2 moles of NO\(_2\) has been converted to 0.5 moles of N\(_2\)O\(_4\).

However, the Rx can also be run in reverse – starting with 1.0 moles of N\(_2\)O\(_4\):

\[
\begin{align*}
\text{2NO}_2(g) & \longleftarrow \text{N}_2\text{O}_4(g) \\
\text{start:} \quad 0.0 \text{ mol} & \quad 1.0 \text{ mol} \\
\text{end:} \quad 1.0 \text{ mol} & \quad 0.5 \text{ mol}
\end{align*}
\]

• We say, in this case, the reaction went to the left

• We still obtain the same number of moles of NO\(_2\) and N\(_2\)O\(_4\) at equilibrium!

• Hence, Rxs can run to the right or to the left, and this state of affairs is denoted by a double arrow:

\[
\begin{align*}
\text{2NO}_2(g) & \longleftrightarrow \text{N}_2\text{O}_4(g)
\end{align*}
\]
2 Equilibrium constant $K$ (or $K_{eq}$)

2.1 Mathematical definition of $K$

Consider the generic Rx:

$$mA + nB + \cdots \rightleftharpoons pC + qD + \cdots$$

for $m$ mol of $A$, $n$ mol of $B$, and so on. The equilibrium constant is

$$K = \frac{[C]^p[D]^q}{[A]^m[B]^n} \cdots,$$  \hspace{1cm} (1)

where ... $[C]$ is concentration of $C$ at equilibrium,

... $[D]$ is concentration of $D$ at equilibrium and so on.

For example: $2\text{NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_4(g)$ has

$$K = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2}$$  \hspace{1cm} (2)

- Large $K$ favors products (get a lot of $\text{N}_2\text{O}_4$)

- Small $K$ favors reactants (only a little $\text{N}_2\text{O}_4$)

- Note that in the Rx $2\text{NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_4(g)$:

$[\text{NO}_2]$ and $[\text{N}_2\text{O}_4]$ are not constant! – they can have different values.

Only the quotient, given by

$$K = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2}$$  \hspace{1cm} (3)

is constant! (At a given $T$).

- In general, $K$ is constant, however individual concentration $[\ldots]$ are not constant.
2.2 How to compute $K$

Consider the Haber Process:

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

$$K = \frac{[NH_3]^2}{[N_2][H_2]^3}$$  \hspace{1cm} (4)

$$[NH_3] = 0.031 \text{ mol/L}$$  \hspace{1cm} (5)
$$[N_2] = 0.85 \text{ mol/L}$$  \hspace{1cm} (6)
$$[H_2] = 0.0031 \text{ mol/L}.$$  \hspace{1cm} (7)

$$K = \frac{[0.031]^2}{(0.85)(0.0031)^3} = 3.8 \times 10^4$$  \hspace{1cm} (8)

$K$ in unitless, so remove mol/L factors.

Also, if we know $K$, $[N_2]$, and $[H_2]$ we can compute $[NH_3]$:

$$[NH_3] = \sqrt{K[N_2][H_2]^3}$$  \hspace{1cm} (9)

2.3 Only $K$ is constant, not the concentrations

$K$ is constant, not the concentrations.

Consider the Rx:

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

The equilibrium constant $K$:

$$K = \frac{[SO_2]^2[O_2]}{[SO_3]^2} = 4.8 \times 10^{-3} \hspace{1cm} (at \ T = 700 \degree C)$$  \hspace{1cm} (10)

The concentration (in mol/L) – $[SO_2]$, $[O_2]$, and $[SO_3]$ are at equilibrium – they are not changing over time.

Different reaction vessels (say 1 L containers) can have different concentrations, but $K$ is always constant.

Different Equilibrium positions for $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$:
We can write:

\[ K = \frac{[\text{SO}_2]^2[\text{O}_2]}{[\text{SO}_3]^2} = [\text{O}_2] \left( \frac{[\text{SO}_2]}{[\text{SO}_3]} \right)^2 = 4.8 \times 10^{-3} \]  \hfill (11)

1) \[ [\text{O}_2] = 4.8 \times 10^{-3} \text{ mol/L} \]  \hfill (12)
\[ [\text{SO}_2] = 1.0 \text{ mol/L} \]  \hfill (13)
\[ [\text{SO}_3] = 1.0 \text{ mol/L} \]  \hfill (14)

2) \[ [\text{O}_2] = 4.8 \times 10^{-3} \text{ mol/L} \]  \hfill (15)
\[ [\text{SO}_2] = 9.0 \text{ mol/L} \]  \hfill (16)
\[ [\text{SO}_3] = 9.0 \text{ mol/L} \]  \hfill (17)

• Both 1) and 2) give same \( K = 4.8 \times 10^{-3} \)!
• 1) and 2) are different *equilibrium positions*.

### 3 Reaction Quotient \( Q \)

• Just like \( K \), but not at equilibrium – concentrations are still changing
• The Reaction Quotient \( Q \) depends on time, \( Q(t) \)
• By comparing \( K \) and \( Q(t) \) at \( t \) tells the course of the Rx.
• Calculated the same way as \( K \):

\[ mA + nB + \cdots \rightleftharpoons pC + qD + \cdots \]

gives

\[ Q = \frac{[C]^p[D]^q \cdots}{[A]^m[B]^n \cdots} \]  \hfill (18)

• \([C], [D], \ldots \) are concentrations

But
• [C], [D], ... are not at equilibrium!

• Q defined at any time during a Rx – not just at equilibrium

• Just like K but (usually) not at equilibrium.

3.1 Q changes as the Rx approaches equilibrium

If \( Q < K \) reaction proceeds to the right \( \rightarrow \) (for more product)

If \( Q = K \) reaction stops – equilibrium.

If \( Q > K \) reaction goes to the left \( \leftarrow \) (for less product)

3.2 Calculate \( Q \) to predict Rx direction: An example

\[ 2\text{SO}_3(\text{g}) \rightleftharpoons 2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \]

\[ K = 4.8 \times 10^{-3} \quad (T = 700 \degree \text{C}) \]

At some point in time the concentrations are measured:

\[
\begin{align*}
[\text{SO}_3] &= 0.60 \text{ mol/L} \\
[\text{SO}_2] &= 0.15 \text{ mol/L} \\
[\text{O}_2] &= 0.025 \text{ mol/L}
\end{align*}
\]

First Calculate \( Q \):

\[
Q = \frac{[\text{SO}_2]^2[\text{O}_2]}{[\text{SO}_3]^2} = \frac{(0.15)^2(0.025)}{(0.60)^2}
\]

We get

\[ Q = 1.6 \times 10^{-3} \]

Hence

\[ 1.6 \times 10^{-3} < 4.8 \times 10^{-3} \]

\[ Q < K \]
\[
2\text{SO}_3(g) \leftrightarrow 2\text{SO}_2(g) + \text{O}_2(g)
\]

• Since \( Q < K \), Rx proceeds to the right \( \rightarrow \)

• \([\text{SO}_2]\) and \([\text{O}_2]\) increases,

• \([\text{SO}_3]\) decreases

Later, when \( Q = K \) the reaction stops, at equilibrium

### 3.3 Summarizing: How to use \( Q \)

• During a Rx the concentrations change [...]

• We can calculate \( Q \) at any time to predict the future:

  e.g.,

  \[
  2\text{SO}_3(g) \leftrightarrow 2\text{SO}_2(g) + \text{O}_2(g)
  \]

• If \( Q < K \) reaction proceeds to the right \( \rightarrow \): ↓ \([\text{SO}_3]\) ↑ \([\text{O}_2]\) ↑ \([\text{SO}_2]\)

• If \( Q = K \) reaction stops – equilibrium (no changes)

• If \( Q > K \) reaction goes to the left \( \leftarrow \): ↑ \([\text{SO}_3]\) ↓ \([\text{O}_2]\) ↓ \([\text{SO}_2]\)

• \( Q \) is calculated the same way as \( K \), but concentrations are NOT at equil.

### 3.4 Calculate \( Q \) to predict Rx direction: example #2

\[
2\text{SO}_3(g) \leftrightarrow 2\text{SO}_2(g) + \text{O}_2(g):
\]

\[
Q = \frac{[\text{SO}_2]^2[\text{O}_2]}{[\text{SO}_3]^2} = [\text{O}_2]\left(\frac{[\text{SO}_2]}{[\text{SO}_3]}\right)^2
\]

\[
K = 4.8 \times 10^{-3}
\]  \( \quad (26) \)

At some point in time – not at equilibrium – the concentrations are measured:

\[
[\text{O}_2] = 5.0 \times 10^{-3} \text{ mol/L} \quad (28)
\]

\[
[\text{SO}_2] = 1.0 \text{ mol/L} \quad (29)
\]

\[
[\text{SO}_3] = 1.0 \text{ mol/L} \quad (30)
\]
\[ Q = 5.0 \times 10^{-3} \quad (31) \]

• Since \( Q > K \), Rx proceeds to the left ←
• \([\text{SO}_3]\) increases; \([\text{SO}_2]\) and \([\text{O}_2]\) decrease
• Only later, when \( Q = K \) does the reaction stops, at equilibrium

4 Heterogeneous Equilibrium

One phase system — Homogeneous (gas, liquid, or solid)

Two or more phases – heterogeneous systems (solid + gas)

EXAMPLE:
Consider a reaction vessel (a container) with Sulfur (S) gas. If we put a chunk of solid carbon into the vessel, at the surface of the carbon the following Rx occurs:
\[
\text{C}(s) + \text{S}_2(g) \quad \rightleftharpoons \quad \text{CS}_2(g)
\]

• After the reaction is complete we will have equilibrium concentrations of S and \( \text{CS}_2 \) gas.

• If we have an excess of Carbon – some solid remains in the vessel, then ...

... leave out \([C]\) within \( K \) and \( Q \) expressions:

\[ K = \frac{[\text{CS}_2]}{[\text{S}_2]} \quad (32) \]

• In general: Liquid or solid component, in excess, are left out of \( Q \) and \( K \)

5 Identities for \( K \) and \( Q \)

Consider again the generic Rx:
\[
mA + nB + \cdots \quad \rightleftharpoons \quad pC + qD + \cdots
\]
The equilibrium constant is

\[ K = \frac{[C]^p[D]^q \cdots}{[A]^m[B]^n \cdots} \]  

(33)

Now consider the reverse Rx:

\[ pC + qD + \cdots \rightleftharpoons mA + nB + \cdots \]

• The equilibrium constant for this Rx, denoted by \( K_r \), is just

\[ K_r = \frac{1}{K} \]  

(34)

For example: \( 2\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g}) \) has

\[ K = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2} \]  

(35)

Reverse Rx: \( \text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g}) \) has

\[ K_r = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} \]  

(36)

• Hence: \( K_r = \frac{1}{K} \)

Also, if we multiply the Rx by a factor \( d \):

\[ dmA + dnB + \cdots \rightleftharpoons dpC + dqD + \cdots \]

• The equilibrium constant, denoted by \( K' \), is then given by

\[ K' = K^d \]  

(37)

Example: \( 4\text{NO}_2(\text{g}) \rightleftharpoons 2\text{N}_2\text{O}_4(\text{g}) \) has

\[ K' = \frac{[\text{N}_2\text{O}_4]^2}{[\text{NO}_2]^4} \]  

(38)

Hence \( (K' = K^2) \)
6 Le Châtelier’s Principle:

What happens to a system at equilibrium if something changes:

• Does the Rx shift to the left or right when ...

1) some of the concentrations are changed
2) the volume is changed
3) the temperature is changed (considered later after thermodynamics)

6.1 Equilibrium shift by concentration change: #1

Consider the Haber Process at equilibrium:

\[ \text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g) \]

\[ K = \frac{[\text{NH}_3]^2}{[[\text{N}_2][\text{H}_2]^3]} \]  \hspace{1cm} (39)

• Now 1) increase concentration \([\text{NH}_3]\) by \(x\) mol/L, and 2) compute \(Q\):

\[ Q = \frac{([\text{NH}_3] + x)^2}{[[\text{N}_2][\text{H}_2]^3]} \]  \hspace{1cm} (gives \(Q > K\))  \hspace{1cm} (40)

• Hence \(Q > K\); so, the Rx:

\[ \text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g); \hspace{0.5cm} \text{goes to the left} \rightleftharpoons \]

• for simplicity let \((V = 1L)\), so \(x\) is equal to the number of moles of \(\text{NH}_3\) that is added

Since the Rx goes left \(\rightleftharpoons\) after adding the \(x\) moles:

1) some of the \(x\) added \(\text{NH}_3\) is consumed

2) \([\text{N}_2]\) and \([\text{H}_2]\) are increased

Note: Not all of the \(x\) moles is consumed – only some of it
6.2 Equilibrium shift by concentration change: #2
Again Consider: \( \text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g}) \)

NOW Decrease concentration \([\text{NH}_3]\) by \(x\) mol/L ...

... and Again compute \(Q\):

\[
Q = \frac{([\text{NH}_3] - x)^2}{[\text{N}_2][\text{H}_2]^3}
\] (41)

Hence \(Q < K\), so the Rx goes to the right \(\rightarrow\):

1) more \([\text{NH}_3]\) is produced, (partial compensation for \(x\) removed)

2) \([\text{N}_2]\) and \([\text{H}_2]\) are decreased

6.3 Equilibrium shift by concentration change: #3
Again, consider: \( \text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g}) \)

\[
K = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}
\] (42)

Now increase concentration \([\text{H}_2]\) by \(x\) mol/L; compute \(Q\)

\[
Q = \frac{[\text{NH}_3]^2}{[\text{N}_2] ([\text{H}_2 + x])^3}
\] (43)

Hence \(Q < K\) so Rx goes to the right \(\rightarrow\):

1) some of the \(x\) added \(\text{H}_2\) is consumed

2) \([\text{N}_2]\) decreases

3) more \([\text{NH}_3]\) is produced

6.4 General case
Consider the generic Rx:

\[
mA + nB + \cdots \rightleftharpoons pC + qD + \cdots
\]
Shift always reduces concentration of added component

If [A] or [B] is increased: shift to the right →
If [C] or [D] is increased: shift to the left ←

Shift always enlarges concentration of removed component

2 If [A] or [B] is decreased: shift to the left ←
4 If [C] or [D] is decreased: shift to the right →

**Le Châtelier’s Principle:**

If an equilibrium system is disturbed ... ... it adjusts to reduce the change ... it (partially) counters the change

6.5 The volume is changed

The concentration [...] is inversely proportional to the volume \( V \)

\[ [X] = \frac{n_x}{V} \]

where \( n_x \) is the moles of \( X \)

Consider the Rx

\[ 2\text{NO}_2(g) \rightarrow \text{N}_2\text{O}_4(g); \ V = 1\text{L} \]

At equilibrium the concentrations are

\[ [\text{NO}_2] = [\text{NO}_2]_{\text{eq}} \quad [\text{N}_2\text{O}_4] = [\text{N}_2\text{O}_4]_{\text{eq}} \]

Hence

\[ K = \frac{[\text{N}_2\text{O}_4]_{\text{eq}}}{[\text{NO}_2]_{\text{eq}}^2} \quad (44) \]

If the Volume is halved (1/2 L) *all* concentrations double

\[ [\text{NO}_2] = 2[\text{NO}_2]_{\text{eq}} \quad [\text{N}_2\text{O}_4] = 2[\text{N}_2\text{O}_4]_{\text{eq}} \]

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The Rx quotient for $(2\text{NO}_2(g) \rightarrow \text{N}_2\text{O}_4(g))$:

$$Q = \frac{2[N_2\text{O}_4]_{\text{eq}}}{(2[\text{NO}_2]_{\text{eq}})^2} = \frac{K}{2} \quad (45)$$

Hence $Q < K$ and the reaction goes right $\rightarrow$

**Le Châtelier’s Principle for volume change:**

If the volume *decreases* the reaction goes in the direction of *less* total moles.

Sequence of events:

1) The volume is suddenly reduced ($T$ is fixed)

2) The pressure $P$ increases (recall: $P = n/V \times RT$)

   System does “not like” added pressure (it increases its energy), so

3) Equilibrium shifts so the total number of moles ($n$) is less

4) This causes the $P$ to reduce some (recall again: $P = n/V \times RT$)

**NOTE:** the original (low) pressure will not be restored; it only partially compensates

**Le Châtelier’s (other) Principle for volume change:**

If the volume *increases* the reaction goes in the direction of *more* total moles.

**Example # 1,**

$$\text{2NO}_2(g) \rightarrow \text{N}_2\text{O}_4(g)$$

left side 2 moles, right side 1 mole

• decrease $V$, Rx goes right $\rightarrow$

• increase $V$, Rx goes left $\leftarrow$

**Example # 2,**
Consider again the Haber Rx:

\[ \text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g) \]

(4 moles) (2 moles)

4 moles on the left, 2 on the right

• decrease \( V \), Rx goes right \( \rightarrow \) or • increase \( V \), Rx goes left \( \leftarrow \)

Example # 3,

\[ 2\text{SO}_3(g) \rightarrow 2\text{SO}_2(g) + \text{O}_2(g) \]

moles: 2 on the left, 3 on the right

• decrease \( V \), Rx goes left \( \leftarrow \)
• increase \( V \), Rx goes right \( \rightarrow \)

Special case # 1

• If the total number of moles on the left and right are equal. e.g.,

\[ \text{I}_2(g) + \text{Cl}_2(g) \rightleftharpoons 2\text{ICl}(g) \]

2 moles on left and right

**there is no shift when the volume changes**

- system cannot respond to \( V \) change

Special case # 2

• Solid (s) phases (in excess) do not count. e.g.,

\[ 3\text{Fe}(s) + 4\text{H}_2\text{O}(g) \rightleftharpoons \text{Fe}_3\text{O}_4(s) + 4\text{H}_2(g) \]

• *ignore* \( \text{Fe}(s) \) and \( \text{Fe}_3\text{O}_4(s) \)

4 moles on both sides *in the gas* (g) *phase*

**ALSO**

Added inert gases (Argon) does not change equilibrium
e.g., If we add some Ar gas in a reaction vessel, where
\[ \text{I}_2(g) + \text{Cl}_2(g) \leftrightarrow 2\text{ICl}(g) \]

- Added Ar gas does not change concentrations of other components – the \( \text{I}_2, \text{Cl}_2, \text{ICl} \) are not influenced by the Ar gas

- Added Ar gas – or any other inert gas – *only* changes the total pressure within the vessel (partial pressures of other components do not change)

- An inert gas is like an ideal gas and does not interact (to a significant extent) with the other molecules – usually a small-sized atom or molecule with no dipole moment (e.g., He)