II. 1 and II.2 – Dynamic Equilibrium

Goals:
1. Realize that reactions can go both in forward and in reverse.
2. Define equilibrium.
3. Understand the concept of dynamic equilibrium.
4. State the characteristics of a system at equilibrium

We know that many reactions are REVERSIBLE!

\[
\text{Reactants} \rightarrow \text{Products} \quad \text{or} \quad \text{Reactants} \leftarrow \text{Products}
\]

Reactants form Products

Products form Reactants

A system is said to be at “Equilibrium” when the \( \text{forward rx rate} \) EQUALS the \( \text{reverse rx rate} \)!

use “\( \rightleftharpoons \)” or “\( \leftrightarrow \)” to show a reversible rx.

Ex: Consider the reaction below in a CLOSED system:

\[ \text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2 \]

Colourless brown gas

gas.

When 2 molecules of \( \text{N}_2\text{O}_4 \)
collide with each other, the bonds between the “N”s break and each molecule splits up into two molecules of \( \text{NO}_2 \).
Imagine we are watching this reaction in the lab. We are measuring the rate of the forward reaction by measuring the Δ[reactant]. At the beginning of the reaction (t= 0), there is a high \([N_2O_4]\) and the rate decreases (fewer reactant molecules, fewer collisions) as slope of the line of the graph will get more gradual (less steep).

As the reaction starts, the reactant is consumed so \([N_2O_4]\) decreases and the rate goes down (fewer reactant molecules, fewer collisions).

Let's stop here and consider the REVERSE reaction: (N₂O₄ ↝ 2NO₂)

2 molecules of NO₂ collide with the proper energy and collision geometry and form a molecule of N₂O₄.
If we graphed the rate of the reverse reaction, it would look like this:

At \( t = 0 \), there is no \( \text{NO}_2 \).

As \( \text{NO}_2 \) accumulates, those molecules can collide and form \( \text{N}_2\text{O}_4 \).

Around \( t = 3 \), the rate begins to slow.

Let's **compare the forward and reverse reaction rate graphs**:

At \( t = 4 \) min, the rates are **EQUAL**

**Rate of forward reaction = rate of reverse reaction**

This system is at **dynamic equilibrium**!

\( \Delta \frac{[\text{N}_2\text{O}_4]}{\Delta \text{time}} = 0 \)

because

\( [\text{N}_2\text{O}_4] = \text{constant} \)

\( [\text{NO}_2] = \text{constant} \)

\( \text{NO}_2 \) is being used up at the SAME rate as it is being formed

\( \text{N}_2\text{O}_4 \) is being formed at the SAME rate as it is being consumed

\( \text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2 \)
Things you need to know about **DYNAMIC EQUILIBRIUM**:

- The reaction has not **stopped!** (even though slope = 0)
- Forward and reverse reaction continue at **equal rates**.
- Changes are microscopic. No **macroscopic** changes occur (no visible, large scale changes so it appears as if nothing is happening).
- All observable properties are **constant** (temp, [react], [prod], pressure, colour)
- A system at equilibrium is a **CLOSED** system.
- If we changed the temp, it would affect the equilibrium.
  \[ \text{temp is constant}. \]

<table>
<thead>
<tr>
<th>4 Characteristics of a System at Equilibrium</th>
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<tbody>
<tr>
<td>1. The <em>rate</em> of the <em>forward</em> reaction = The <em>rate</em> of the <em>reverse</em> reaction</td>
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<td>2. <em>Microscopic</em> processes. <strong>No macroscopic changes</strong></td>
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<td>3. The system is <strong>closed</strong> and the <em>temperature</em> is <strong>constant</strong> and <em>uniform</em> throughout.</td>
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<td>4. The equilibrium can be approached from the <em>left</em> (starting with <em>reactants</em>) or from the <em>right</em> (starting with <em>products</em>).</td>
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- If sufficient $E_a$ is available, systems not at equilibrium will tend to move towards equilibrium.

http://www.absorblearning.com/media/item.action?guick=w8

**STATIC EQUILIBRIUM**: is the opposite of dynamic equilibrium. It will not move at all unless it is “pushed” in some way. Essentially, nothing is happening (system is balanced but particles are at rest).

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marbles stationary vs. marbles rolling usually discussed more in physics.
At equilibrium...

\[ \text{[reactants]} \neq \text{[products]} \quad (\text{not equal in general}) \]

* they could be in some cases.

**Analogy: if you have coins in your pockets (3 twoonies, 20 loonies)**

* you exchange 1T for 2 L.
* then you exchange the other way.

Overtime, the back and forth rate is the same. The amount of money is each pocket has not changed. But the amount of money in each pocket is different! [twoonies] doesn’t equal [loonies].

Ex: \( A \rightarrow B \) (See page 40, Q 6)

Rate forward = \( \text{k}_{\text{forward}} \text{[Reactants]} \)
Rate reverse = \( \text{k}_{\text{reverse}} \text{[Products]} \)

See the table of data.

a) Plot the values of \([A]\) vs time, and \([B]\) vs time:
b) When are the RATES equal? (look at data)

@ 8 min (both rates = 0.100)

What does this look like on the graph? Are the concentrations the same? @ 8 min, both lines are "level":

\[ \frac{[A]}{[B]} = \text{constant}, \quad \frac{[B]}{[A]} = \text{constant} \]

\[ \frac{[A]}{[B]} \neq \frac{[B]}{[A]} \]

c) When does \([A] = [B]\)? at 1 min

Is the systems at equilibrium when \([A] = [B]\)? NO. \(\text{rates are not equal} \)

d) When is the forward rate the greatest? early in rx \(\text{high} \frac{[A]}{[B]} \)

e) What is the numerical value of the ratio \([\text{products}] / [\text{reactants}]\) at equilibrium?

\[ \text{at} \text{EQ: } \frac{[\text{prod}]}{[\text{react}] = \frac{[\text{B}]}{[\text{A}]} = \frac{1.000}{0.200} = 5} \]

At equil, there is 5 mol B: 1 mol A

Ex 2) \(\text{H}_2 + \text{Br}_2 \rightleftharpoons \text{2 HBr}\)

Will the ratio of \([\text{HBr}] / [\text{H}_2]\) be 2/1 (or 2:1) at equilibrium? \(\text{Not necessarily}\)

\[ \text{Ratio at equil} = \frac{[\text{prod}]}{[\text{react}] = ? \text{ Depends on the} \quad [\text{HBr}] \text{ and } [\text{H}_2] \]

But... 1 mol H\(_2\) produces 2 mol HBr

so \[ \frac{\text{mol HBr reacting}}{\text{mol H}_2 \text{ reacting}} = \frac{2}{1} \]

But it is true to say that ratio of moles of HBr reacting to moles of H\(_2\) reacting is 2:1

Do Questions p. 43 #8 – 13 in Hebden