CHEMICAL EQUILIBRIUM

- Some reactions progress to <u>completion</u>.

$$A \rightarrow C + D$$

- Many reactions that occur in nature, however, do not go to completion.

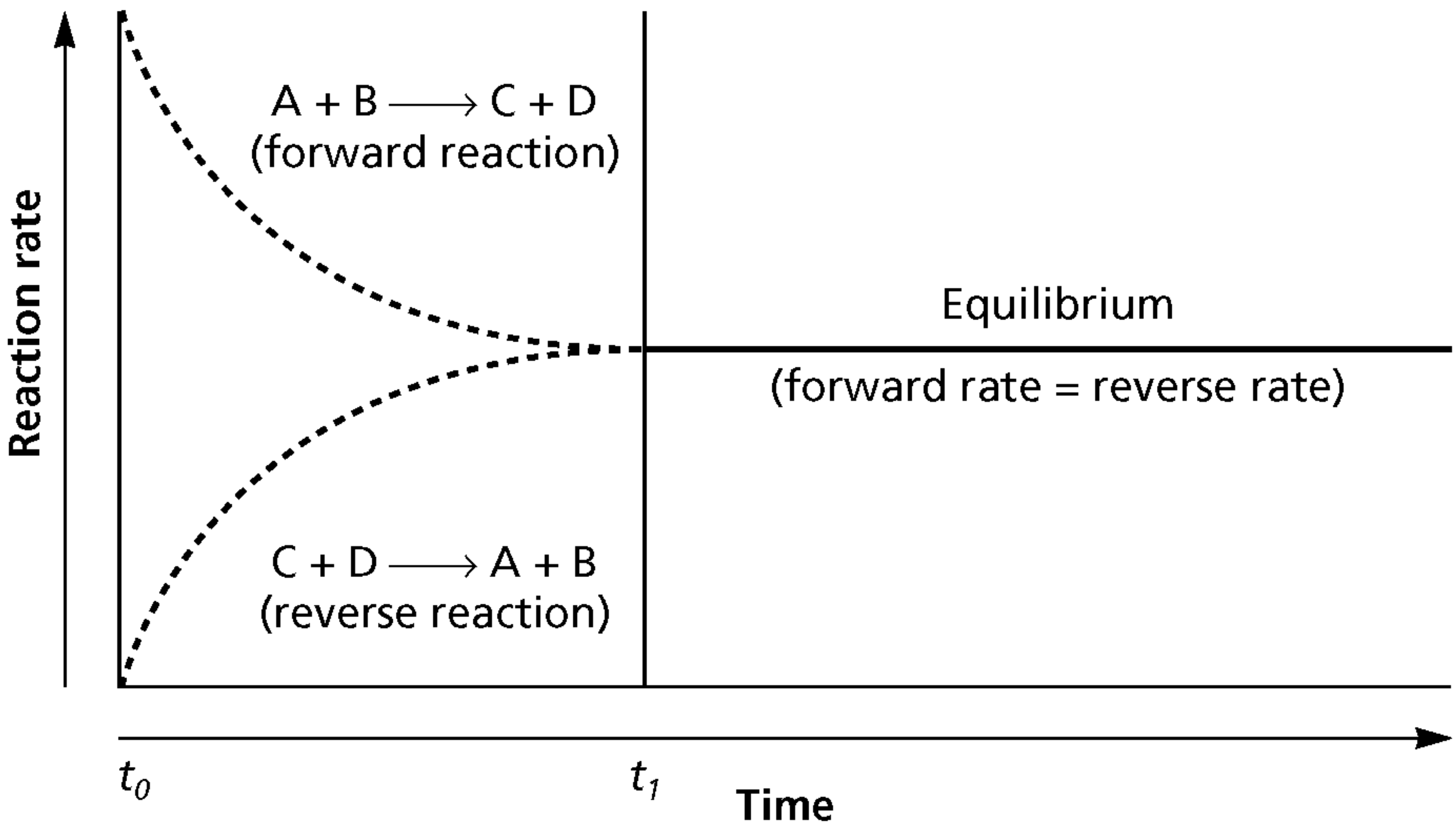
$$A + B \rightarrow C + D \quad \text{(forward)}$$

$$A + B \leftarrow C + D \quad \text{(backward)}$$

$$A + B \Leftrightarrow C + D$$

reversible reactions

Rate Comparison for the Reaction System
$A + B \rightleftharpoons C + D$



Equilibrium is a ***dynamic****, not a static, condition.*

Equilibrium Concept, continued

- In an equilibrium reaction, initially the rate of the forward reaction is very fast.
- As more products are formed, the rate of the reverse reaction speeds up.
- When the rates of the forward and reverse reactions are the same, the system is at ***equilibrium***.

$$\text{reactants} \underset{\textit{reverse reaction}}{\overset{\textit{forward reaction}}{\rightleftarrows}} \text{products}$$

Chemical equilibrium is achieved when:

- the rates of the forward and reverse reactions are equal and
- the concentrations of the reactants and products remain constant (<u>no observable concentration change</u>).

Physical equilibrium

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

Chemical equilibrium

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

Chemical Kinetics and Chemical Equilibrium

$$A + 2B \underset{k_r}{\overset{k_f}{\rightleftharpoons}} AB_2$$

$$\text{rate}_\text{f} = k_\text{f}\,[A][B]^2$$

$$\text{rate}_\text{r} = k_\text{r}\,[AB_2]$$

Equilibrium

$$\text{rate}_\text{f} = \text{rate}_\text{r}$$

$$k_\text{f}\,[A][B]^2 = k_\text{r}\,[AB_2]$$

$$\frac{k_f}{k_r} = K_{eq} = \frac{[AB_2]}{[A][B]^2}$$

Equilibrium Constant K_{eq}

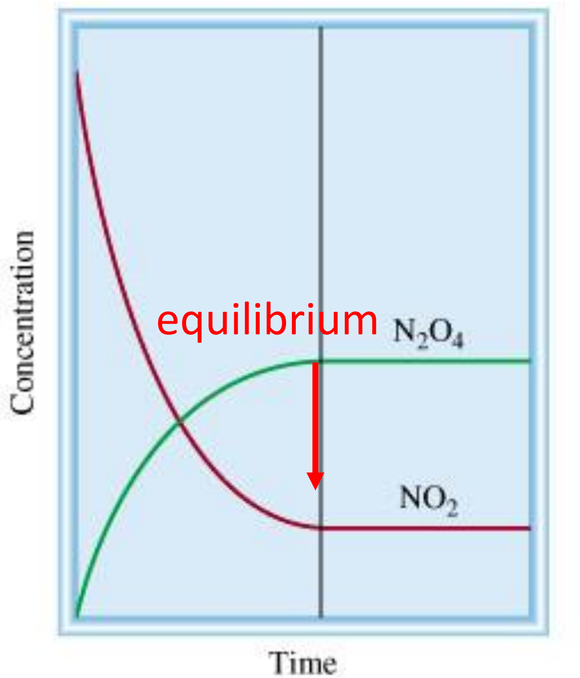
$$aA + bB \rightleftharpoons cC + dD$$

- Mathematically, we express the law of chemical equilibrium as follows:

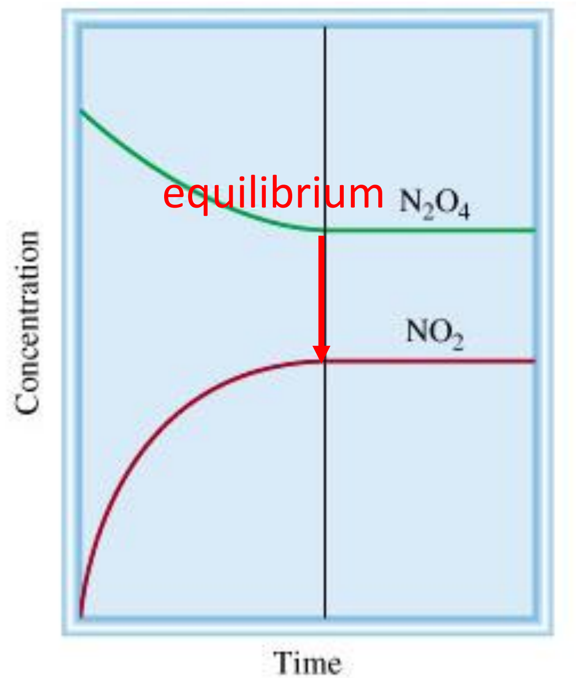
$$K_{eq} = \frac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}}$$

- The constant, K_{eq}, is the ***general equilibrium constant***.

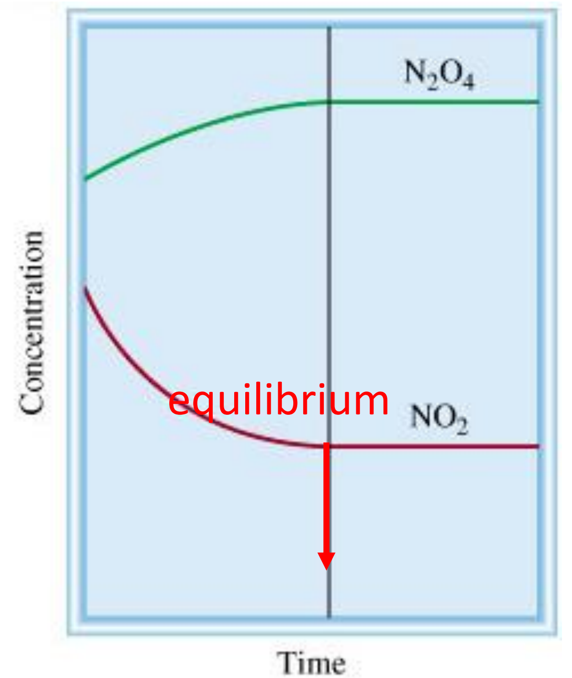
- The value of K_{eq} varies with temperature. So a given value of K_{eq} is valid only for a specific temperature.



Start with NO_2



Start with N_2O_4

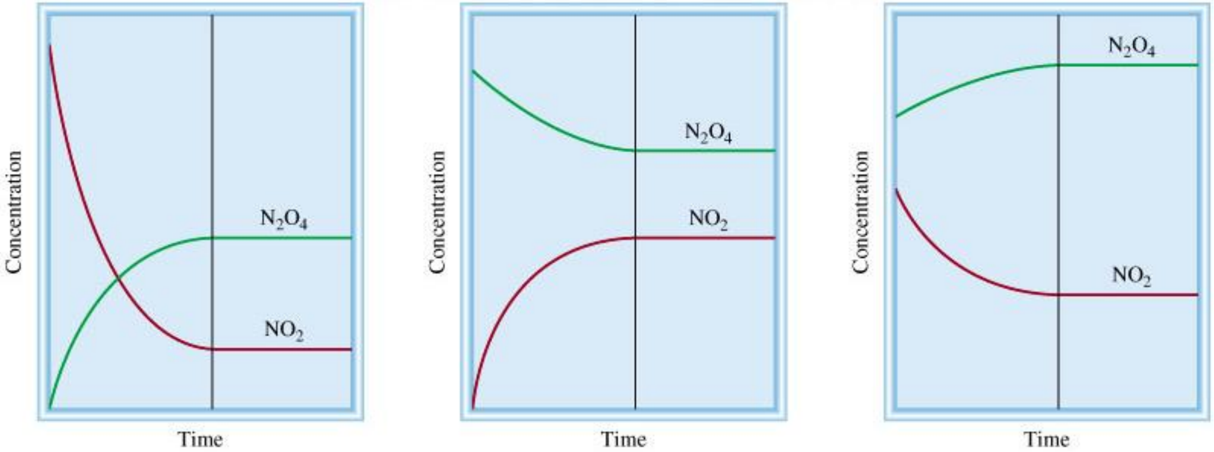


Start with NO_2 & N_2O_4

It doesn't matter how much of each substance we start with, the value of K_{eq} is always 4.63×10^{-3} .

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

$$K = \frac{[NO_2]^2}{[N_2O_4]} = 4.63 \times 10^{-3}$$



constant

TABLE 14.1 The NO_2–N_2O_4 System at 25°C

Initial Concentrations (*M*)		Equilibrium Concentrations (*M*)		Ratio of Concentrations at Equilibrium	
$[NO_2]$	$[N_2O_4]$	$[NO_2]$	$[N_2O_4]$	$\frac{[NO_2]}{[N_2O_4]}$	$\frac{[NO_2]^2}{[N_2O_4]}$
0.000	0.670	0.0547	0.643	0.0851	4.65×10^{-3}
0.0500	0.446	0.0457	0.448	0.102	4.66×10^{-3}
0.0300	0.500	0.0475	0.491	0.0967	4.60×10^{-3}
0.0400	0.600	0.0523	0.594	0.0880	4.60×10^{-3}
0.200	0.000	0.0204	0.0898	0.227	4.63×10^{-3}

Depending on the type of reaction, K may be called

- *acidity or dissociation constant for acid/base reactions,* K_a *or* K_b, K_w
- *solubility product for dissolution reaction,* K_{sp}
- *complexation constant for complexation reactions*
- *Henry's constant for gas dissolution in water, H*
- *adsorption constant for surface reactions*

Acid-base equilibrium

- How much will my river water change if an acidic waste stream starts to discharge into it?

Heterogeneous equilibria

- How much will the pH of my water change if atmospheric CO2 levels increased to 500 ppm?

  Climate Change research suggests the oceans will acidify with increased carbon dioxide levels.

- How do I get rid of the precipitates that clog the pipes?

Equilibrium Position

The composition of the reactant-product mixture at equilibrium is called the <u>equilibrium position</u>.

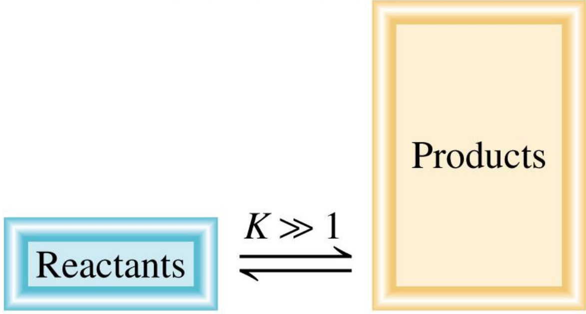
•Some reactions reach equilibrium after forming on a small amount of product.

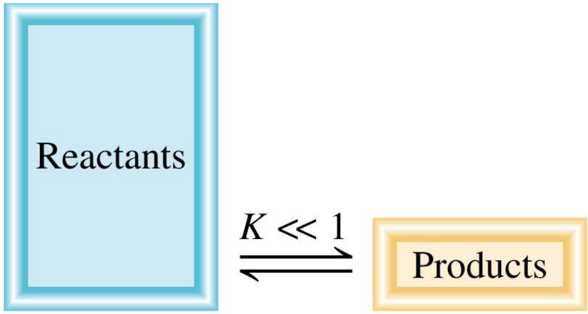
If $K_{eq} < 1$ then [products] < [reactants]

•Some proceed until only small amounts of reactant remain.

If $K_{eq} > 1$ then [products] > [reactants]

•Many reactions end up somewhere in between. (significant amounts of both reactant and product present at equilibrium)





Time to Reach Equilibrium

- *Some reactions reach equilibrium almost immediately, i.e. in fractions of a second.*
- *Other reactions proceed more slowly, taking days, decades, millennia to reach equilibrium.*
- *In this lecture we will focus on the ‘fast’ reactions.*

Le Châtelier's Principle

If an external stress is applied to a system at equilibrium, the system adjusts in such a way that the stress is partially offset as the system reaches a new equilibrium position.

- <u>Changes in Concentration</u>

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

Equilibrium shifts left to offset stress ←

↑ Add NH_3

Le Châtelier's Principle

- Changes in Volume and Pressure

$$A\,(g) + B\,(g) \rightleftharpoons C\,(g)$$

Change	**Shifts the Equilibrium**
Increase pressure	Side with fewest moles of gas
Decrease pressure	Side with most moles of gas
Increase volume	Side with most moles of gas
Decrease volume	Side with fewest moles of gas

Le Châtelier's Principle

- <u>Changes in Temperature</u>

<u>Change</u>	**<u>Exothermic Rx</u>**	**<u>Endothermic Rx</u>**
Increase temperature	K decreases	K increases
Decrease temperature	K increases	K decreases

- <u>Adding a Catalyst</u>
  - does not change K
  - does not shift the position of an equilibrium system
  - system will reach equilibrium sooner

pH of Pure Rain Water

The pH scale is used to express the acidity or hydrogen ion (H+) concentration in solution.

$$pH = -\log [H^+]$$

A solution with pH = 7 is neutral, pH < 7 is acidic, and pH >7 is basic.

The most important weak acid in nature is carbonic acid H_2CO_3

$$H_2CO_3 \underset{}{\overset{Ka_1}{\rightleftharpoons}} H^+ + HCO_3^-$$

$$HCO_3^- \underset{}{\overset{Ka_2}{\rightleftharpoons}} H^+ + CO_3^{2-}$$

All gases are also in a equilibrium between air and water

$$CO_{2(air)} \rightleftharpoons CO_{2(aqueous)}$$

$$CO_{2(aqueous)} + H_2O \rightleftharpoons H_2CO_3$$

Even in remote, unpolluted regions rainwater has a slightly acidic pH of **approximately 5.6 due to the** presence of **carbon dioxide gas** in the atmosphere. Carbon dioxide has a uniform concentration around the globe and dissolves in water to produce the weak acid, carbonic acid, as shown in the following reactions.

$$CO_2(g) \leftrightarrow CO_2(aq) \equiv H_2CO_3^0$$

(1) $H_2CO_3^0 \leftrightarrow HCO_3^- + H^+$ $\quad K_{a1} = 10^{-6.35} = \frac{[H^+][HCO_3^-]}{[H_2CO_3^0]}$

(2) $HCO_3^- \leftrightarrow CO_3^{2-} + H^+$ $\quad K_{a2} = 10^{-10.33} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$

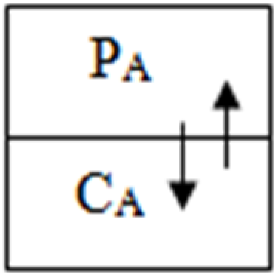
One can calculate the pH of unpolluted rainwater using reactions 1 and 2. However, to start with, what is the concentration of $H_2CO_3^0$?

How do we determine the concentration of $H_2CO_3^0$?

$$CO_2(g) \leftrightarrow CO_2(aq) \equiv H_2CO_3^0$$

An equilibrium is established between the gas in the atmosphere and the same gas dissolved in water. Therefore, use **Henry's Law**.

Henry's Law



$$H_A = \frac{P_A}{C_A}$$

P_A = partial pressure of the chemical at the system temperature (atm)

C_A = concentration of the chemical in the aqueous phase in equilibrium with the air phase (mol/L)

H_A = Henry's constant (atm.L/mol)

What is the pH of rainwater in equilibrium with atmospheric CO_2 (P_{CO_2} = $10^{-3.5}$ atm)?

H_{CO2} = 29.41 atm.L/mol

C_{CO2} = $10^{-3.5}$ atm / 29.41 atm.L/mol

C_{CO2} = 1.075 x 10^{-5} mol/L =$10^{-4.96}$ M

$$K_1 = 10^{-6.35} = \frac{M_{H^+} M_{HCO_3^-}}{M_{H_2CO_3^0}} = \frac{X^2}{10^{-4.96}}$$

$X^2 = (10^{-6.35})(10^{-4.96}) = 10^{-11.31}$

$X = [H^+] = [HCO_3^-] = 10^{-5.655} = 2.21 \times 10^{-6}$ mol/L

pH = 5.66

So the pH of pure rainwater is acidic!