Chapter 15

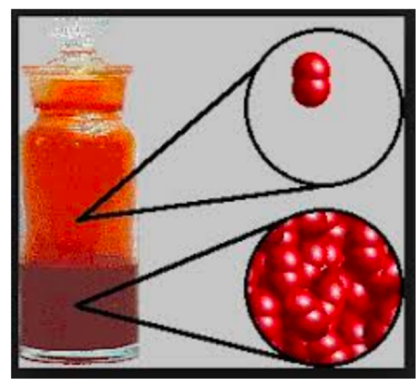
Chemical Equilibrium

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

Equilibrium: A Dynamic Process

Opposing processes occur at equal rates

- Forward & reverse reactions occur at equal rates
- No outward change is observed
- **Ratio** of reactants to products is constant
- Often temperature dependent
- Other factors can also shift equilibrium toward products or reactants
- Represented by double arrows ($\rightleftharpoons$ or $\longleftrightarrow$)



Physical Equilibrium

Ex: Equilibrium between phases

$$Br_2(l) \rightleftharpoons Br_2(g)$$

Chemical Equilibrium

Equilibrium between reactants & products

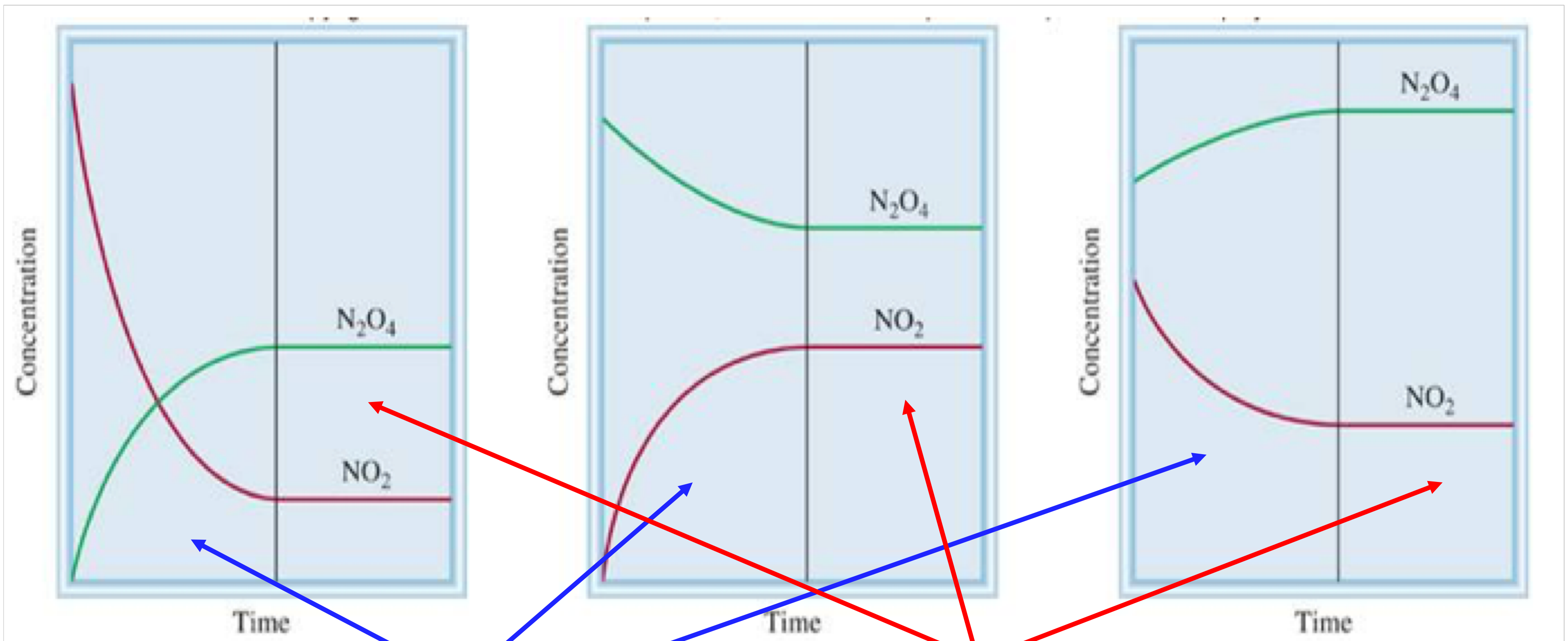
$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

Colorless Brown

Initial conditions may vary – concentrations will adjust to establish equilibrium

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

t = 0; no N_2O_4 | t = 0; no NO_2 | t = 0; N_2O_4 & NO_2



As a system approaches equilibrium, both the forward and reverse reactions are occurring

At equilibrium, the forward and reverse reactions are proceeding at the same rate, so the relative concentrations remain constant.

Equilibrium Constant (K_c)

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

At equilibrium, $[N_2O_4]$ & $[NO_2]$ are constant

- NOT EQUAL
- Not static
- Actual amounts depend on system

Rate (forward) = Rate (reverse): $k_1[N_2O_4] = k_{-1}[NO_2]^2$

$$\frac{k_1}{k_{-1}} = \frac{[NO_2]^2}{[N_2O_4]} = K_c$$

[conc]
not equal

TABLE 15.1 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}

Ratio
is equal

Equilibrium Expression

For the reaction: $aA + bB + \ldots.. \rightleftharpoons cC + dD + \ldots..$

The Equilibrium Expression is: $K_c = \dfrac{[C]^c[D]^d}{[A]^a[B]^b}$

For an Equilibrium Expression:

- Concentrations of products are in numerator
- Concentrations of reactants are in denominator
- They are the <u>concentrations at equilibrium</u>
- Exponents ARE coefficients from balanced equation
- Units generally not included
- Also known as a Mass Action Expression

Note difference from rate equation – equilibrium expression IS BASED ON BALANCED EQUATION

Impact of How an Equation is Balanced

Reaction A

$SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$

$$K_c = \frac{[SO_3]}{[SO_2][O_2]^{1/2}}$$

Reaction B

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

$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$$

Equilibrium constants change if the reaction is balanced differently

Numerical values for K_c are related, but different

K_c (reaction B) = $[K_c$ (reaction A)$]^2$

It is essential to know how the reaction was balanced

Manipulating Chemical Equations & K_c

When reversing a chemical equation, invert K_c

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

$$K_c = \frac{[A]^a[B]^b}{[C]^c[D]^d} = \frac{1}{K_c}$$

When multiplying coefficients by n, raise K_c to n^{th} power

$$n(cC + dD \rightleftharpoons aA + bB)$$

$$K_c = \frac{[A]^{na}[B]^{nb}}{[C]^{nc}[D]^{nd}} = K_c^n$$

When adding equations, multiply the K_c values

$$eE \rightleftharpoons fF$$

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

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

$$K_c = \frac{[C]^c[D]^d[F]^f}{[A]^a[B]^b[E]^e} = K_1 \times K_2$$

K_p The Pressure Version of K_c

Remember the Gas Laws – Chapter 5!

- In a closed system, pressure ∝ concentration
  - The equilibrium expression can also be written in terms of pressure
  - Very useful since gas phase reactions are often monitored via pressure

$$K_p = \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b}$$

∝ = proportional to

Writing Equilibrium Expressions

Write the equilibrium constant expression K_p and K_c for:

(a) $3\ NO(g) \rightleftharpoons N_2O(g) + NO_2(g)$

(b) $CH_4(g) + 2\ H_2S(g) \rightleftharpoons CS_2(g) + 4\ H_2(g)$

Manipulating K values

1. For the formation of NH_3 from N_2 and H_2

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

$K_p = 4.34\text{x}10^{-3}$ at 300˚C. What is the value of K_p for the reverse reaction?

A: $2.30\text{x}10^2$

2. How does the magnitude of the equilibrium constant K_p for the reaction

$$2\ HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

change if the equilibrium is written as

$$6\ HI(g) \rightleftharpoons 3\ H_2(g) + 3\ I_2(g)$$

A: K_p is cubed

3. Given that, at 700 K, K_p = 54.0 for the reaction:

$$H_2(g) + I_2(g) \rightleftharpoons 2\ HI(g)$$

and $K_p = 1.04 \times 10^{-4}$ for the reaction:

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

determine the value of K_p for the following reaction at 700K:

$$2\ NH_3(g) + 3\ I_2(g) \rightleftharpoons 6\ HI(g) + N_2(g)$$

A: 1.51×10^9

Value of Equilibrium Constants

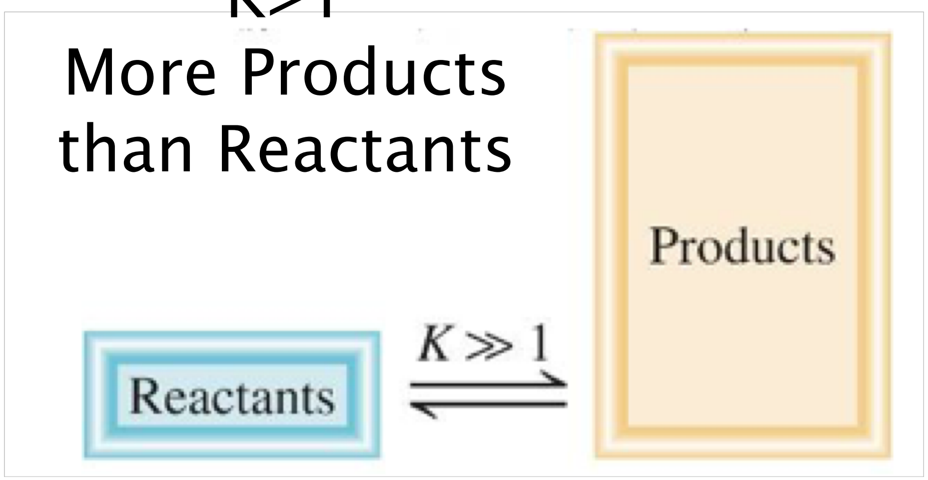
$$aA + bB \rightleftharpoons cC + dD$$

At Equilibrium:

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

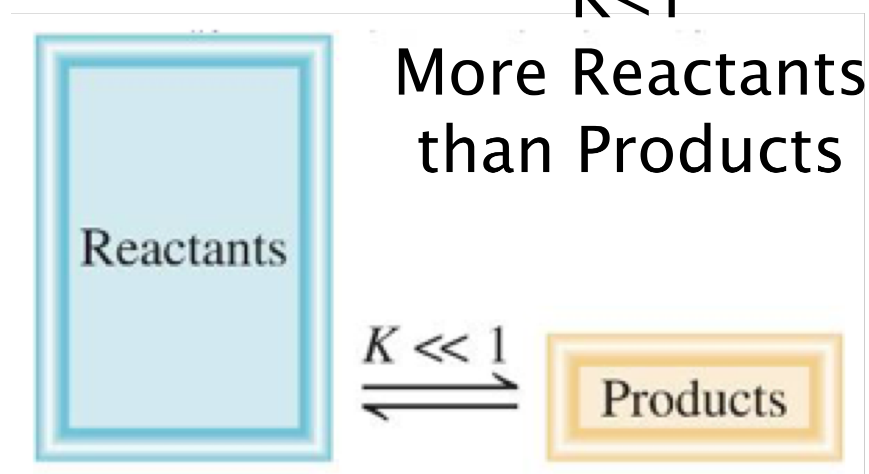
K>1

More Products than Reactants



K<1

More Reactants than Products



As K goes to infinity, reaction goes to completion.

As K goes to zero, no reaction occurs.

Analyzing K_p/K_c Values

For the reaction: $H_2(g) + I_2(g) \rightleftharpoons 2\ HI(g)$

K_p = 794 at 298K and K_p = 54 at 700K

Is the formation of HI more favored at the higher or lower temperature?

A: lower

Using the Equilibrium Expression

1. Nitrogen monoxide exists in equilibrium with nitrogen and oxygen gas. At a given temperature, 0.100 moles of NO were added to a 2.00L vessel. At equilibrium, 0.044 moles of NO were remaining. What is the value of K_c?

1. Write the balanced equation & equilibrium constant expression.

2. Find equilibrium molarities of reactants and products.

3. Calculate K_c

A: $K_c = 0.40$