CHEMICAL EQUILIBRIUM

Chapter 15

CHEMICAL EQUILIBRIUM

Chemical reactions normally go from reactants to products

$$A + B \rightarrow AB$$

When they do not go to completion → equilibrium

CHEMICAL EQUILIBRIUM

$$N_2 + 3\,H_2 \rightarrow 2\,NH_3$$

$$N_2 + 3\,H_2$$

$$N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3$$

Many chemical reactions are reversible

CHEMICAL EQUILIBRIUM

A system where rates of forward and reverse reactions are the same

At equilbrium, no observable changes occur

System remains in equilbrium if undisturbed

System must be closed

CHEMICAL EQUILIBRIUM

$$H_2O\,(l) \rightleftharpoons H_2O\,(s)$$

Physical equilibrium

$$N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3$$

Chemical equilibrium

Overview of Topics

Equilibrium reactions

Equilibrium expression

Equilibrium constants K_c & K_p

Reaction quotient, Q

Equilibrium calculations

Le Chatelier's Principle

Equilibrium Reactions

$$N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3$$

equilibrium arrow

THE HABER PROCESS

Friz Haber

(1868-1935)

$$N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3$$

Equilibrium Expression

$$N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3$$

Ratio of products to reactant = constant

$$K_c = \frac{[NH_3]_{eq}^{\ 2}}{[N_2]_{eq}[H_2]_{eq}^{\ 3}}$$

[ ] mean molarity

Terms raised to power of coefficient

EQUILIBRIUM EXPRESSION

In general:

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

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

Need balanced equation

Equilibrium Constant

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

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

K_c: used for molarities.
Solutions

EQUILIBRIUM CONSTANT

$$N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3$$

$$K_p = \frac{P^2_{(NH_3)}}{P_{(N_2)} \times P^3_{(H_2)}}$$

K_p: used for pressures.
Gases

Closed vrs. Open system

No

EQUILIBRIUM CONSTANT

Units for K vary

K varies with temperature

K independent of initial concentrations

Equilibrium Constant

Large K :
reactants → products

Small K:
products → reactants

EQUILIBRIUM CONSTANT

Relationship between Rates and K

At equilibrium $rate_f = rate_r$

$$\frac{k_f}{k_r} = K_c$$

REACTION QUOTIENT

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

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

Same equation as K_c

Q can be measured at any point in the reaction

REACTION QUOTIENT

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

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

Q changes as reaction proceeds: initially zero

Q increases and becomes constant at equilibrium then $Q = K_c$

CALCULATIONS

Predicting reaction direction

$Q \neq K$

reactants $\rightleftarrows$ products until equilibrium reached

CALCULATIONS

Predicting reaction direction

$Q < K$

reactants → products

until $Q = K$

"shifts to right"

CALCULATIONS

Predicting reaction direction

If Q > K
products → reactants
until Q = K
"shifts to left"

CALCULATIONS

Predicting reaction direction

If Q = K
reaction at equilibrium

CALCULATIONS

Using equilibrium equations

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

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

1. If [A], [B], [C], [D] known, can find K_c
2. If [A], [B], [C], K_c known, can find [D]

CALCULATIONS

Using equilibrium equations

aA + bB ⇌ cC + dD

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

3. If initial concentrations known, can find equilibrium concentrations

CALCULATIONS

Steps for solving #3

1. Need balanced equation & expression for Q
2. Calculate Q from given initial concentrations
3. How will changing concentrations affect equilibrium ?

CALCULATIONS

Steps for solving #3

1. Call smallest change x (Δ in book) and express other changes in terms of x
2. Substitute x terms and solve for x

CALCULATIONS

Example

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2 \quad K = 0.0211$$

A flask contains PCl_5 with a concentration of 1.00 M. Calculate the concentrations of all reactants and products when equilibrium is reached

Given: $[PCl_5]_i = 1.00M$
Find: $[PCl_5]_{eq}$ $[PCl_3]_{eq}$ $[Cl_2]_{eq}$

CALCULATIONS

$PCl_5 \rightleftharpoons PCl_3 + Cl_2 \quad K = 0.0211$

$$Q = \frac{[PCl_3]_i[Cl_2]_i}{[PCl_5]_i}$$

Given:

$[PCl_5]_i = 1.00M$

$[PCl_3]_i = 0$

$[Cl_2]_i = 0$

CALCULATIONS

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2 \quad K = 0.0211$$

$$Q = \frac{[PCl_3]_i[Cl_2]_i}{[PCl_5]_i}$$

$$Q = \frac{0 \times 0}{1.00} = 0$$

Since Q < K reaction proceeds forward

CALCULATIONS

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2 \quad K = 0.0211$$

$$K_c = \frac{[PCl_3]_{eq}[Cl_2]_{eq}}{[PCl_5]_{eq}} = 0.0211$$

Problem: have three unknowns

CALCULATIONS

$$\frac{x \times y}{z} = 10$$

Have three unknowns

If y = 4x and z = 2x ....

CALCULATIONS

$$\frac{[PCl_3]_{eq}[Cl_2]_{eq}}{[PCl_5]_{eq}} = 0.0211$$

	PCl_5	$\rightleftharpoons$	PCl_3	+	Cl_2
[initial]	1.00		0		0
Change	-x		+x		+x
[equ]	1.00-x		x		x
	$[PCl_5]_{eq}$		$[PCl_3]_{eq}$		$[Cl_2]_{eq}$

Calculations

$$\frac{[PCl_3]_{eq}[Cl_2]_{eq}}{[PCl_5]_{eq}} = 0.0211$$

$[PCl_5]_{eq} = 1.00-x$

$[PCl_3]_{eq} = x$

$[Cl_2]_{eq} = x$

CALCULATIONS

$$\frac{x \times x}{1.00 - x} = 0.0211$$

$$\Rightarrow \qquad x^2 = 0.0211 \times (1.00 - x)$$

$$\Rightarrow \qquad x^2 = 0.0211 - 0.0211x$$

$$\Rightarrow \qquad x^2 + 0.0211x - 0.0211 = 0$$

CALCULATIONS

$$x^2 + 0.0211x - 0.0211 = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \qquad ax^2 + bx + c = 0$$

see page 485

a = 1 b = 0.0211 c = - 0.0211

x = 0.135 ignore negative answer

CALCULATIONS

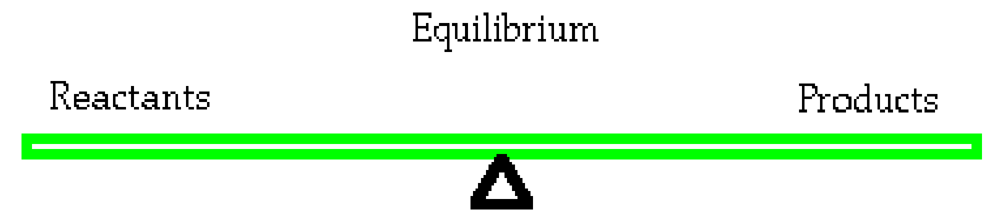
$x = 0.135$

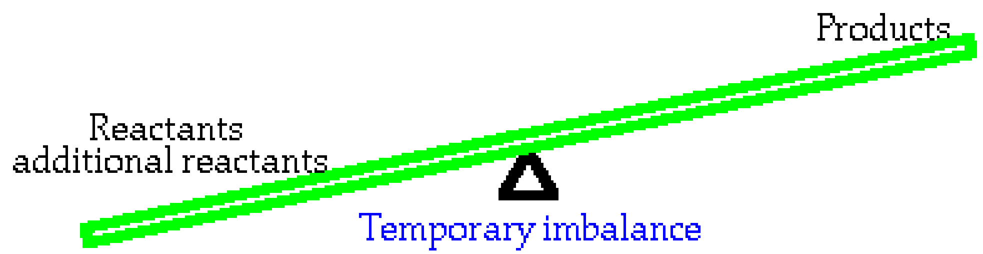
$[PCl_5]_{eq} = 1.00 - x = 0.86\ M$

$[PCl_3]_{eq} = x = 0.14\ M$

$[Cl_2]_{eq} = x = 0.14\ M$

Le Chatelier's Principle





Le Chatelier's Principle

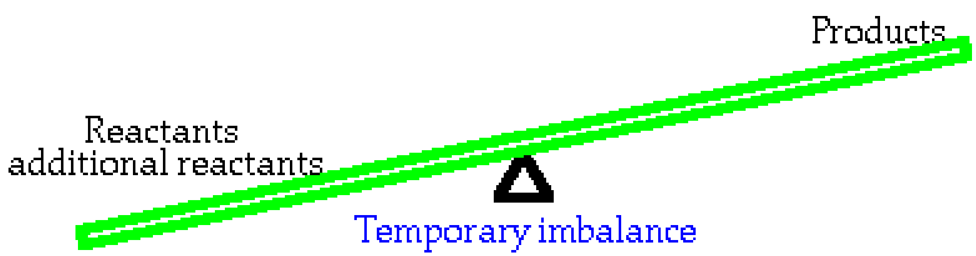
A system in equilibrium, when subjected to a change, will act to counteract the change and establish a new equilibrium

Le Chatelier's Principle

1. Changing concentration

$$A + B \rightleftharpoons C + D$$

What happens when reactants added or removed?



Le Chatelier's Principle

2. Changing pressure (gas)

Depends on number of reactant and product molecules in equation

$$H_2 + CO_2 \rightleftharpoons H_2O + CO$$

changing pressure has no effect

Le Chatelier's Principle

2. Changing pressure

$$2\ SO_2 + O_2 \rightleftharpoons 2\ SO_3$$

Increasing pressure causes shift forward

LE CHATELIER'S PRINCIPLE

3. Changing temperature

Depends on whether reaction is endothermic or exothermic

$N_2 + 3\ H_2 \rightleftharpoons 2\ NH_3 \quad \Delta H = -92.4kJ$

$N_2 + 3\ H_2 \rightleftharpoons 2\ NH_3 + 92.4kJ$

↑ T adds heat → eqm to shift back

↓ T removes heat → eqm to shift forward

Le Chatelier's Principle

4. Changing volume

$$V \propto \frac{1}{P}$$

Opposite of changing pressure

Le Chatelier's Principle

5. Addition of catalyst

Speeds up rate equilibrium reached in both directions