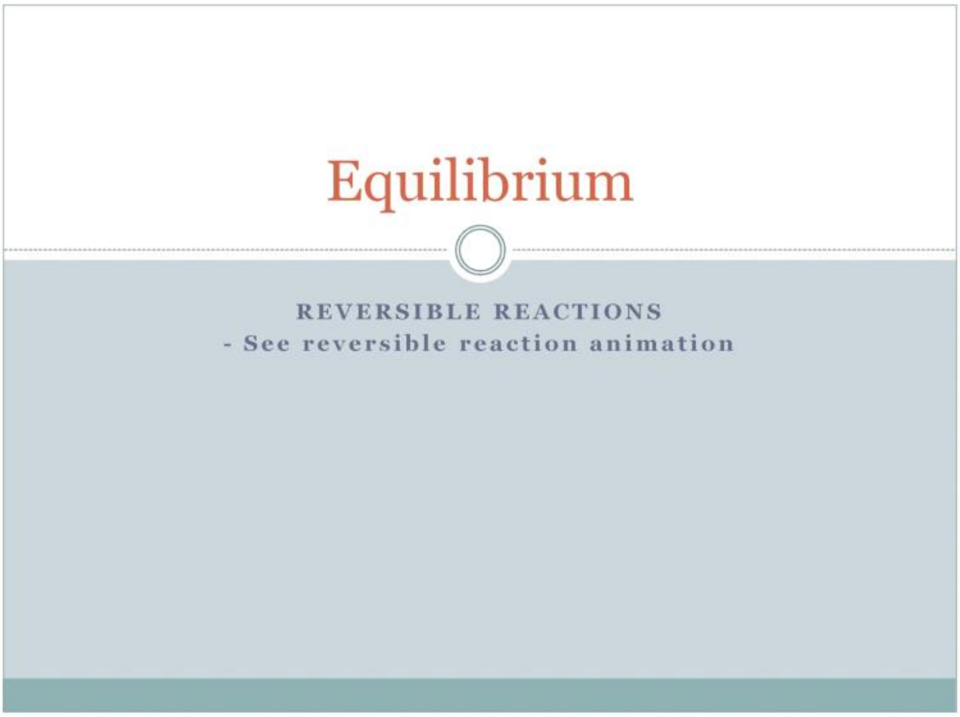
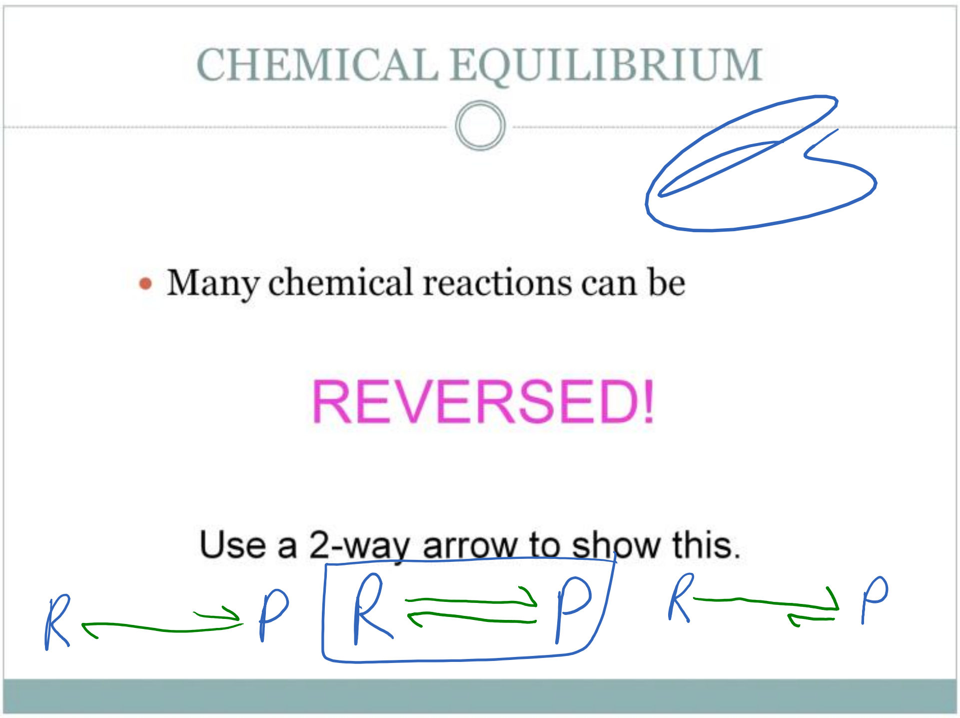
Equil notes

Monday, February 20, 2012 10:28 AM

Equilibrium

Inserted from: <file://C:\Documents and Settings\Harpal\Desktop\School Stuff\Chem 12 handouts and stuff\EQUILIBRIUM\Equilibrium.ppt>





What does this mean?

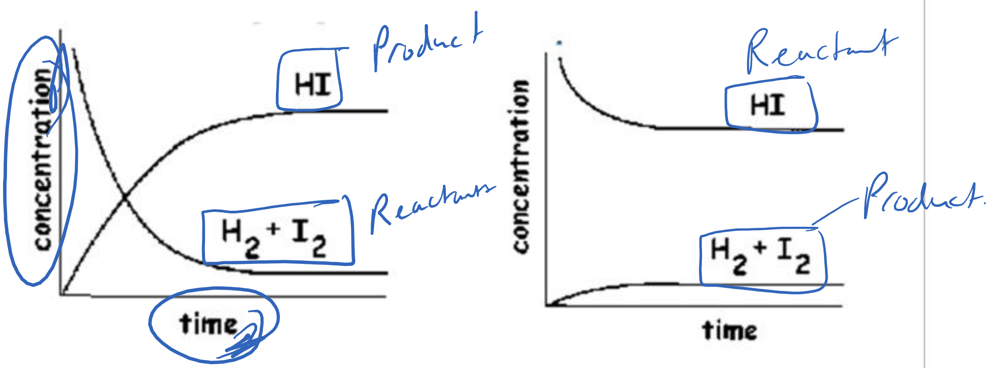
- A reaction can occur starting with REACTANTS or........

- A reaction can occur starting with PRODUCTS or……..

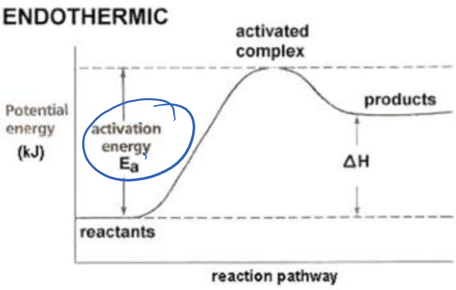
A reaction can occur starting with some REACTANTS and some PRODUCTS

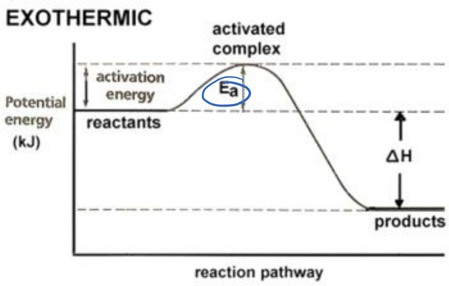
The final equilibrium is the same whether a reaction begins with reactants or products

$H_2 + I_2 \rightleftharpoons 2HI$



$N_2O_4(g)$ + energy <==> $NO_2(g)$





$N_2O_{4(g)}$ + 58 kJ <==> $NO_{2(g)}$ $NO_{2(g)}$ <==> $N_2O_{4(g)}$ + 58kJ

- A reaction system must be CLOSED to reach equilibrium

- Although a reaction occurs forward & reverse, conditions may FAVOUR one reaction over the other

Reaction Rate/Equilibrium note!

@ the Start:
- lots of reactants
  - fast fwd rate
- no products
  - slow (no) reverse rate

As the rxn proceeds
- less reactants
  - decreased fwd rate
- more products
  - increased reverse rate

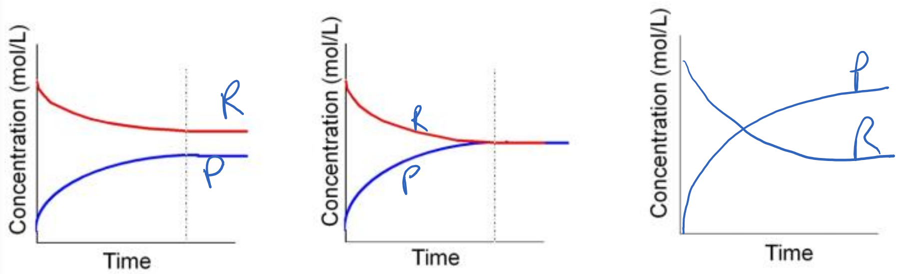
Reversibility of Reactions

Over time…
- fwd rate decreases, reverse rate increases

Eventually…
- forward rate = reverse rate

- This is EQUILIBRIUM!

Chemical Reactions…Graphically



At equilibrium:
- concentrations are constant
- fwd & reverse rates are equal

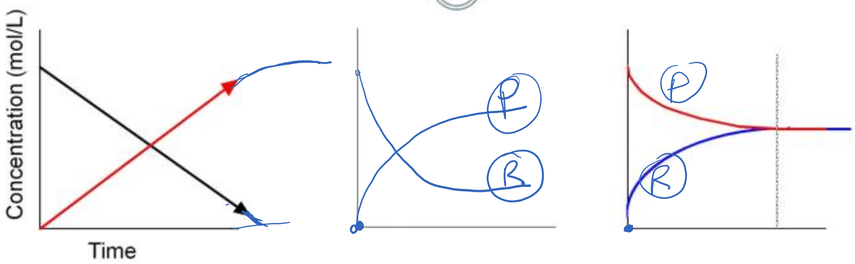
Equilibrium is established when the lines are horizontal & parallel.

Reaction Types

3 types:

- → COMPLETION
  - all reactants turn into products →
  - →
- → EQUILIBRIUM
  - reactants make products and vice versa ⇄
  - ↔
- → does NOT OCCUR (no rxn)
  - reaction will only occur in the reverse direction
  - reactants can't make products ←
  - ←

Graphical Examples of Rxn Types

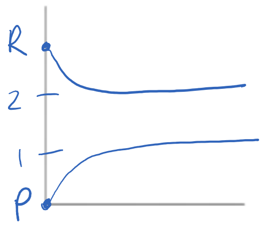


Start: [R] = 0
Goes to
completion

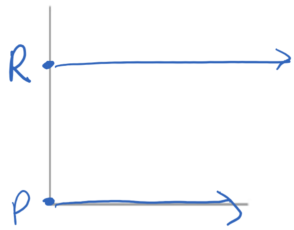
Start: [P] = 0
Goes to
equilibrium
[R] < [P]

Start: [R] = 0
Goes to
equilibrium
[R] = [P]

Start: [R] > [P]
@ eq. [R] = [2P]



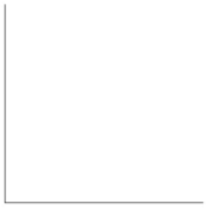
Start: [R] > [P]
Rxn does not occur



If a balanced rxn is provided...

the change in concentration is PROPORTIONAL to the COEFFICIENTS.

$N_2O_4 \leftrightarrow 2NO_2$
Start: [R] > [P]
@ eq [R] > [P]



Graphing Practice

Draw a concentration vs. time graph for each of the following conditions:

1. Start: [P] = 0
   @ eq. [P] > [R]
2. Start: [P] = [R]
   @ eq. [P] = 2[R]
3. Start: [P] > [R]
   @ eq. [P] > [R]
4. Start: [R] > [P]
   @ eq. [P] < [R]

Dynamic Equilibrium

Dynamic = changing
- rxn is occuring
- molecules are changing (reactants ←→ products)
- MICROSCOPIC properties are changing

Equilibrium = not changing
- no visible changes
- MACROSCOPIC properties not changing

Conditions @ Equilibrium

1) forward & reverse rates are EQUAL
2) concentration of reactants and products are CONSTANT
   - may or may not be equal
3) temperature is constant
4) pressure is constant
5) closed system

Equilibrium can be achieved from either direction

- can start with either reactants or products

Systems not @ equilibrium will tend toward a position of equilibrium

- they naturally will go to equilibrium

If more reagents are added, the rates will be unbalanced. The rxn will work to go back to equilbrium

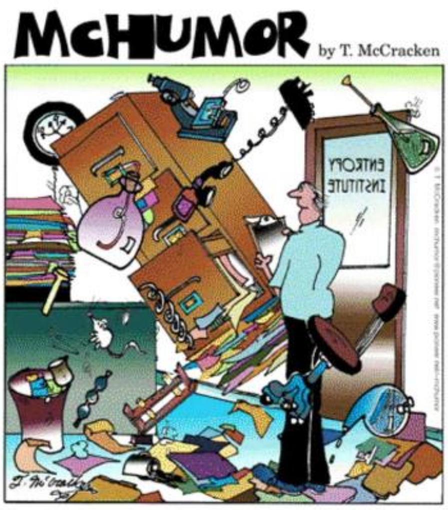
Enthalpy

Heat

- the heat content of a chemical system
- reactions tend in the direction that GIVES OFF energy (EXOTHERMIC direction)
- reaction tends in the direction of MINIMUM enthalpy

Entropy

- the randomness that exists in a system
- reactions tend in the MOST RANDOM direction
  - least random = S
  - s $\rightarrow$ l $\rightarrow$ aq $\rightarrow$ g (most random)
  - more particles of the same state = more random
- reaction tends in the direction of MAXIMUM entropy



The Entropy Institute.

Uses of enthalpy & entropy

To predict which direction of a reaction is favoured

- favoured side
  - has the greatest concentration

To know the reaction type

- completion   R ⇉ P
- equilibrium   R ⇌ P
- no reaction   R ⇇ P

Examples

1) $H_2O_{(g)} \leftrightarrow H_2O_{(l)}$ + heat
   enthalpy: →
   entropy: ←
   favours: Neither
   net result: Equilibrium
2) $2HI_{(g)}$ + 9.4 kJ $\leftrightarrow H_{2(g)} + I_{2(g)}$
   enthalpy: ←
   entropy: Neither
   favours: Left
   net result: No rxn.

3) $Na_{(s)} + H_2O_{(l)} \leftrightarrow Na^+_{(aq)} + OH^{-1}_{(aq)} + \frac{1}{2} H_{2(g)}$ + energy

Entropy →

Enthalpy →

Completion.

4) $N_{2(g)} + 2O_{2(g)} + 67.6\ kJ \leftrightarrow 2NO_{2(g)}$

← Entropy

← Enthalpy

No rxn.

5) $2NO_{2(g)} \leftrightarrow N_2O_{4(g)}$ + energy

← Entropy

Enthalpy →

Equil.

Even if ALL factors favour the same direction, the reaction may NOT OCCUR unless ACTIVATION ENERGY can be achieved!

Equilibrium Practice

Show the enthalpy & entropy direction. What type of rxn is each?

1) $Co_{(g)} + 2H_{2(g)} \leftrightarrow CH_3OH_{(l)} + 141\ kJ$ Equil
2) $2NH_{3(g)} + 92\ kJ \leftrightarrow N_{2(g)} + 3H_{2(g)}$ ~~Comp.~~ Equil.
3) $2O_{3(g)} \leftrightarrow 3O_{2(g)} + 300\ kJ$ Comp.
4) $2C_{(s)} + O_{2(g)} \leftrightarrow 2CO_{(g)}$ $\Delta H = -400\ kJ$ C
5) $Fe_2O_{3(s)} + 3CO_{(g)} \leftrightarrow 2Fe_{(s)} + 3CO_{2(g)} + 24\ kJ$ ~~NR~~ C
6) $SO_{3(g)} + H_2O_{(l)} \leftrightarrow H_2SO_{4(l)}$ + heat $\Delta H = -84\ kJ$ ~~NR~~ E ⇄
7) $BaSO_{4(s)} \leftrightarrow BaO_{(s)} + SO_{3(g)}$ $\Delta H = 225\ kJ$ E
8) $2NO_{(g)} + O_{2(g)} \leftrightarrow 2NO_{2(g)} + 113.4\ kJ$ E
9) $Ca(OH)_{2(s)} \leftrightarrow CaO_{(s)} + H_2O_{(l)}$ $\Delta H = 67\ kJ$ E

Factors Affecting Equilibrium

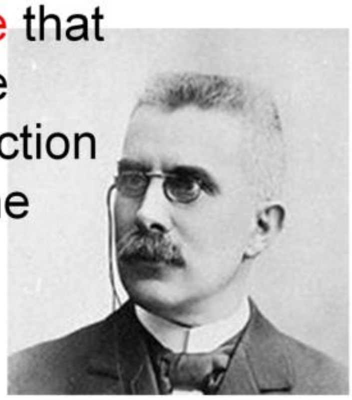
The 3 factors are:

- → concentration
- temperature
- pressure

If any one of these is changed, the reaction will try to counteract the change and re-establish equilibrium.

Le Chatelier's Principle

When a system in equilibrium is subjected to a disturbance that upsets the equilibrium, the system responds in a direction that tends to counteract the disturbance and restore equilibrium.



Concentration

Add or remove a reagent = concentration change

Make a change, the rxn will do the OPPOSITE to re-establish equilibrium.

You increase conc^n
- rxn decreases conc^n

You decrease conc^n
- rxn increases conc^n

How does a rxn RESPOND to a CHANGE?

The reaction uses up the chemical you added by SHIFTING in the direction (FAVOURING the rxn) that will use that chemical

- therefore the reagents on the other side of the rxn are produced & their concentration increases

Concentration Example

$$3H_{2(g)} + N_{2(g)} \leftarrow\rightarrow 2NH_{3(g)}$$

1. Add $H_{2(g)}$

What did you do? We added H_2

What does the rxn need to do? ↓ $[H_2]$

Which way will the rxn shift? Shifts - right

- which rxn is favoured? Rev.

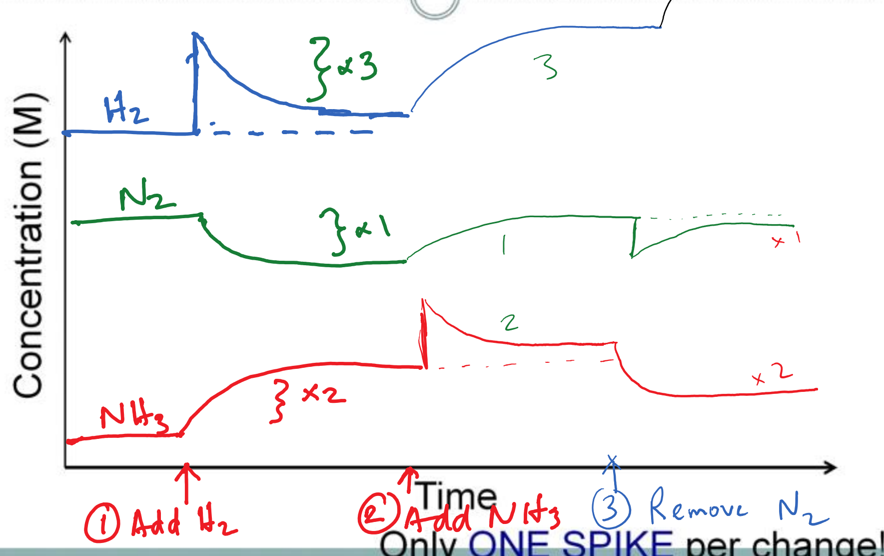
What will happen to:

- $[H_2]$? ↓ , overall ↑ why? See Graphing
- $[N_2]$? ↓
- $[NH_3]$? ↑

One change affects the whole system!

$3H_2 + N_2 \rightleftharpoons 2NH_3$

Graph it…



Only **ONE SPIKE** per change!

$$3H_{2(g)} + N_{2(g)} \leftrightarrow 2NH_{3(g)}$$

2. Add $NH_{3(g)}$

All 3 chemicals ↑ [ ]

3. Remove $N_{2(g)}$

N_2 + NH_3 ↓

H_2 ↑

Temperature

Increase or decrease the temp of the container

- can't change one reagent unless it is heated or cooled BEFORE mixing

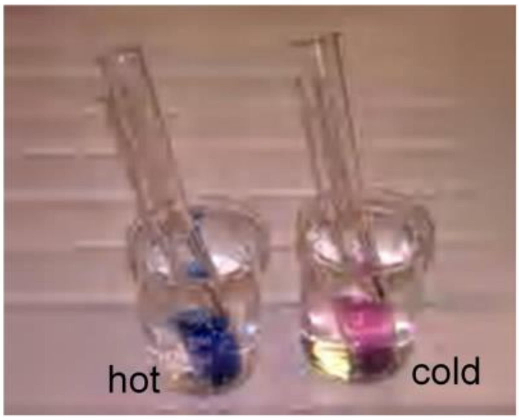
Make a change, the rxn will do the OPPOSITE to re-establish equilibrium.

You increase temp

- rxn decreases temp (endothermic shift)

You decrease temp

- rxn increases temp (exothermic shift)



Cobalt chloride solutions @ different temperatures

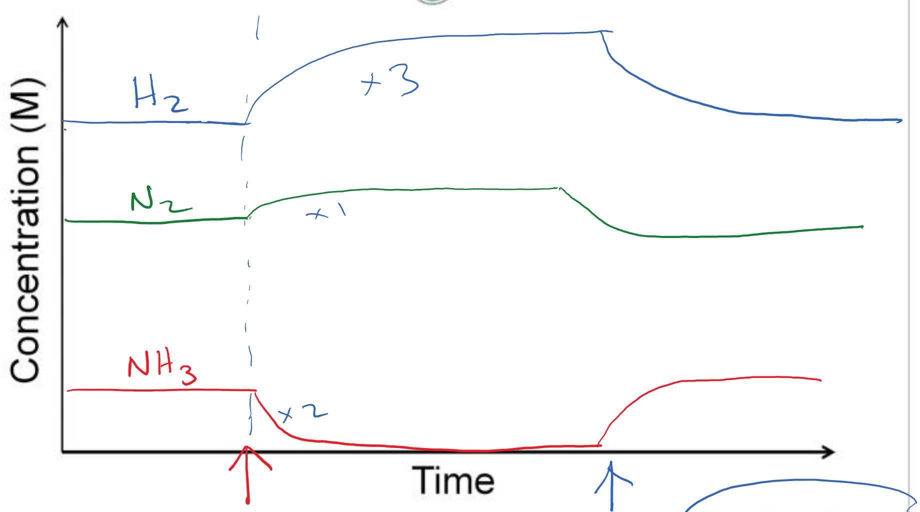
Temperature Example

$3H_{2(g)} + N_{2(g)} \leftrightarrow 2NH_{3(g)}$ + energy

1. Increase temperature
   - What did you do? ↑ temp.
   - What does the rxn need to do? ↓ temp.
   - Which way will the rxn shift? Left
     - which rxn is favoured? Left
   - What will happen to:
     - $[H_2]$? ↑
     - $[N_2]$? ↑
     - $[NH_3]$? ↓

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

Graph it…



① ↑ temp

~~No concentration~~ Δ, NO SPIKES

② ↓ temp.

$3H_{2(g)} + N_{2(g)} \leftrightarrow 2NH_{3(g)}$

2. Decrease temperature

Rxn shifts right

$[H_2] \downarrow$

$[N_2] \downarrow$

$[NH_3] \uparrow$

Pressure/Volume

Pressure & volume work in opposition

- increase pressure, decrease volume…

Change in pressure/volume causes a change in the concentration of ALL reagents

You increase pressure/decrease volume

- rxn shifts to do opposite (shifts to side with LEAST mlcls

You decrease pressure/increase volume

- rxn shifts to do opposite (shifts to side with MOST mlcls

Volume/Pressure Example

$3H_{2(g)} + N_{2(g)} \leftrightarrow 2NH_{3(g)}$ + energy

1. Decrease volume/ Increase pressure

What did you do? ↑ P

What does the rxn need to do? ↓ P

Which way will the rxn shift? Right.

- which rxn is favoured?

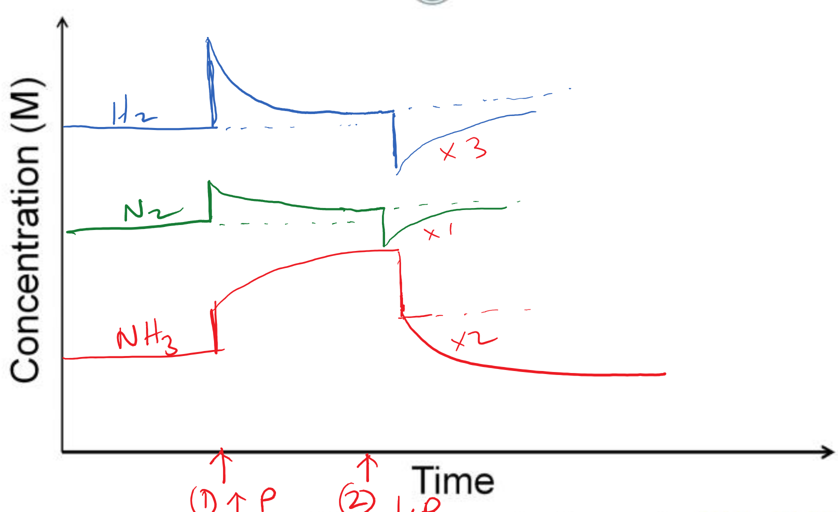
What will happen to:

- $[H_2]$? ↑
- $[N_2]$? ↑
- $[NH_3]$? ↑

① system →

① $N_{2(g)}$ + ③ $3H_{2(g)} \rightleftharpoons$ ② $2NH_{3(g)}$

Graph it... ← ②



ALL concentrations Δ, ALL SPIKE

$3H_{2(g)} + N_{2(g)} \leftrightarrow 2NH_{3(g)}$ + energy

1. Increase volume/ Decrease pressure

Low temp, High P

Maximizes NH_3 production.

States & Reaction Changes

P.10

$K_{eq} = \frac{[Products]}{[Reactants]}$

States affect

pressure Δ

g, aq, impure liquid (oil/vinegar)

Can Δ concentration

Solid (iron) + pure liquid (H_2O)

Cannot change concentration

Pure vs. Impure Liquid

Pure liquid:

- of all reagents in the rxn only ONE is liquid, it is PURE

Impure liquid:

- more than one of the reagents is a liquid, they will mix and therefore, are impure

Only graph gas, aqueous, & impure liquids on graphs, they are they only states affected by the changes.

Equilibrium Expression

Remember: @ eq. concentration of reactants & products are constant

Consider the rxn:

$$A + B \leftrightarrow C + D$$

scientists know that:

$$\frac{[C]\,[D]}{[A]\,[B]} = \text{constant} = K_{eq}$$

- called an EQUILIBRIUM EXPRESSION

Equilibrium Constant

K_{eq} = constant

- equilibrium constant
- every rxn has its own unique constant
- each constant value is for a SPECIFIC TEMPERATURE

Generally,

$$K_{eq} = \frac{[\text{products}]}{[\text{reactants}]}$$

Equilibrium Expression Examples

1. $H_2O_{(g)} + CO_{(g)} \leftrightarrow H_{2(g)} + CO_{2(g)}$

$$K_{eq} = \frac{[H_2][CO_2]}{[H_2O][CO]}$$

2. $PCl_{5(g)} \leftrightarrow PCl_{3(g)} + Cl_{2(g)}$

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

- the COEFFICIENT is written as an EXPONENT in the equilibrium expression

3. $H_{2(g)} + F_{2(g)} \leftrightarrow HF_{(g)} + HF_{(g)}$

$$K_{eq} = \frac{[HF][HF]}{[H_2][F_2]} = \frac{[HF]^2}{[H_2][F_2]}$$

or: $H_{2(g)} + F_{2(g)} \leftrightarrow 2HF_{(g)}$

- SOLIDS have a constant conc^n, therefore are NOT INCLUDED in the expression

4. $CaF_{2(s)} \leftrightarrow Ca^{+2}{}_{(aq)} + 2F^{-1}{}_{(aq)}$

Solid

$K_{eq} = [Ca^{+2}][F^-]^2$

- Substances with a constant conc^n are NOT INCLUDED in the expression. Includes:
    - solids
    - pure liquids

5. $Br_{2(l)} + H_{2(g)} \leftrightarrow 2HBr_{(g)}$

pure liquid

$$K_{eq} = \frac{[HBr]^2}{[H_2]}$$

6. $CH_3COOCH_{3(l)} + Cl_{2(g)} \leftrightarrow CH_3COCH_2Cl_{(l)} + HCl_{(g)}$

$$K_{eq} = \frac{[CH_3COCH_2Cl][HCl]}{[CH_3COOCH_3][Cl_2]}$$

7. $Cl_{2(g)} + 8H_2O_{(l)} \leftrightarrow Cl{\bullet}8H_2O_{(s)}$

$$K_{eq} = \frac{1}{[Cl_2]}$$

REMEMBER:

K_{eq} is a constant

- only changed by TEMPERATURE

Info from K_{eq}

Large K_{eq} (>1)

- rxn favours products
- rxn tends to go fwd (more than reverse)
- [P] > [R] @ eq.

Small K_{eq} (<1)

- rxn favours reactants
- rxn tends to go reverse (more than fwd)
- [P] < [R] @ eq.

K_{eq} = 1

- [P] = [R] @ eq.
- very rare

(2) $R + heat \rightleftharpoons P$

More K_{eq}

K_{eq} values can help to determine whether a rxn is exothermic or endothermic.

(1) $R \rightleftharpoons P + heat$

- (1) EXOTHERMIC rxns:
  - decrease temp = increased K_{eq}
- (2) ENDOTHERMIC rxns:
  - increase temp = increased K_{eq}

Pressure only affects gaseous systems and the number of gas mlcls must be different on each side of the rxn.

Adding a catalyst has NO EFFECT on the position of equilibrium. Just get to equilibrium faster.

K_{eq} Calculations

1. At 55°C, the K_{eq} for the following reaction is 1.15.

$$2NO_{2(g)} \leftrightarrow N_2O_{4(g)}$$

At equilibrium, there is 0.50 mol/L of $NO_{2(g)}$. Calculate the $[N_2O_4]$ at equilibrium.

$$K_{eq} = \frac{[N_2O_4]}{[NO_2]^2}$$

$$1.15 = \frac{[N_2O_4]}{(0.50)^2}$$

$[N_2O_4] = 0.29\,M$

0.22

2.3

2.9

0.29

2. Consider the following reaction:

$$N_2O_{4(g)} \leftrightarrow 2NO_{2(g)}$$

Calculate K_{eq} if, at equilibrium, $[N_2O_4] = 0.20M$ and $[NO_2] = 0.60M$.

$$K_{eq} = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(0.60M)^2}{(0.20M)} =$$

1.8

P. 130 - 136 textbook

Consider the following equilibrium:

$$2HI_{(g)} \leftrightarrow H_{2(g)} + I_{2(g)}$$

At equilibrium it was found that:

0.17M

Test	[HI]	[H_2]	[I_2]
1	0.75	0.25	0.25
2	0.50	?	?

What are the equilibrium concentrations for hydrogen and iodine in test 2?

Consider the following equilibrium:

0.025 M

$$PCl_{3(g)} + Cl_{2(g)} \leftrightarrow PCl_{5(g)}$$

What is the [Cl_2] at equilibrium if [PCl_3] is 0.50M and [PCl_5] is 1.5×10^{-5}M? The $K_{eq} = 1.2 \times 10^{-3}$.

K_{eq} Calculations with ICE Boxes

For many rxns we do NOT know the equilibrium concentrations of the chemical, we only know the initial values. Using K_{eq}, the equilibrium values can be calculated.

- use an ICE box!

I = initial concentration
C = change in concentration (as eq is re-established)
E = equilibrium concentration

I + C = E

3.00 moles of H_2 and 3.00 moles of I_2 are put together in a one litre container and allowed to reach equilibrium. What is the concentration of each substance at equilibrium? (K_{eq} = 45.9)

$$H_2 + I_2 \rightleftharpoons 2HI$$

	H_2	I_2	$2HI$
I	3.00 M	3.00 M	0
C	$-x$	$-x$	$+2x$
E	$3-x$	$3-x$	$2x$
	$3-2.32 = 0.68M$	$0.68M$	$2(2.32) = 4.64M$

$$K_{eq} = \frac{[HI]^2}{[H_2][I_2]} = \frac{(2x)^2}{(3-x)(3-x)} = \sqrt{\frac{(2x)^2}{(3-x)^2}} = \sqrt{45.9}$$

$$\frac{2x}{3-x} = \sqrt{45.9}$$

$$(3-x)\frac{2x}{3-x} = 6.77(3-x)$$

$$2x = 6.77(3-x)$$

4.00 mol of $NO_{2(g)}$ is put in a 2.00L container. After a while, equilbrium is established. At equilibrium there is 0.500 mol of $NO_{(g)}$. What is the value of K_{eq}?

$$2NO_{(g)} + O_{2(g)} \leftrightarrow 2NO_{2(g)}$$

$2NO_{(g)} + O_{2(g)} \leftrightarrow 2NO_{2(g)}$

$2x = 6.77(3-x)$

$2x = 20.31 - 6.77x$

$8.77x = 20.31$

$x = 2.32$

1.00 mol of $NH_{3(g)}$ is injected into a 1.00L flask. The equilibrium mixture has 0.300 mol of $H_{2(g)}$. What are the equilibrium concentrations of the other two chemicals? What is the value of K_{eq}?

$$2NH_{3(g)} \leftrightarrow N_{2(g)} + 3H_{2(g)}$$

In a 1.0L reaction vessel, the following equilibrium is established:

$$CO_{2(g)} + H_{2(g)} \leftrightarrow H_2O_{(g)} + CO_{(g)}$$

$K_{eq} = 2.00$

Calculate the equilibrium concentration of all reactants and products if:

a) 0.50 mol of CO_2 and 0.50 mol of H_2 are mixed.

b) 0.50 mol of H_2O and 0.50 mol of CO are mixed.

What is the value of the K_{eq} of the reverse reaction?

Equilibrium can be disturbed and re-established multiple times. Use an ICE box but:

- the "I" = [initial equilibrium]
- the "E" = [new equilibrium]

Example:

A 1.0L reaction vessel contained 1.0 mol $SO_{2(g)}$, 4.0 mol $NO_{2(g)}$, 4.0 mol $SO_{3(g)}$ and 4.0 mol $NO_{(g)}$ at equilibrium. If 3.0 mol of $SO_{2(g)}$ is added to the mixture, what will the new concentrations be when equilibrium is re-established?

$$SO_{2(g)} + NO_{2(g)} \leftrightarrow SO_{3(g)} + NO_{(g)}$$

Trial K_{eq}

Used to predict the direction (fwd or rev.) of a reaction. Calculate trial K_{eq} and compare to a real K_{eq} value. Pretend the values given are "E" values.

- no ICE box!

$R \rightleftharpoons P$

If trial K_{eq} < K_{eq}
- rxn goes FORWARD, not yet @ eq.

If trial K_{eq} > K_{eq}
- rxn goes REVERSE, rxn is past eq.

If trial K_{eq} = K_{eq}
- rxn is @ eq., no further changes occur

A mixture of 4.2 mol of N_2, 2.0 mol of H_2, and 10.0 mol of NH_3 is introduced into a 20.0L reaction vessel at 500K. At this temperature, $K_{eq} = 1.7 \times 10^2$.

$$N_{2(g)} + 3H_{2(g)} \leftrightarrow 2NH_{3(g)}$$

Is the mixture at equilibrium? If not, what is the direction of the reaction?

$$\text{Trial } K_{eq} = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(0.500)^2}{(.21)(0.1)^3} = 1.2 \times 10^3$$

K_{eq} 1.7×10^2 < Trial K_{eq} 1.2×10^3

The rxn will shift to the left in order to reach equilibrium.

K

If
N
re

$$\text{Trial } K_{eq} = \frac{[NO_2]^2}{[NO]^2[O_2]} = \frac{(.2)^2}{(1)^2(.1)} = 0.4$$

0.4 49

Trial K_{eq} < K_{eq}

Shifts Right.

Consider the following equilibrium:

$PCl_{5(g)} \leftrightarrow PCl_{3(g)} + Cl_{2(g)}$ $K_{eq} = 2.30$

A 1.0L container is filled with 0.50 mol of $PCl_{5(g)}$, 1.0 mol $PCl_{3(g)}$, and 1.0 mol $Cl_{2(g)}$. The system proceeds to the:

mol $PCl_{3(g)}$, and 1.0 mol $Cl_{2(g)}$. The system proceeds to the:

a) left because Trial $K_{eq} > K_{eq}$

b) left because Trial $K_{eq} < K_{eq}$

c) right because Trial $K_{eq} > K_{eq}$

→ d) right because Trial $K_{eq} < K_{eq}$

$$\text{Trial } K_{eq} = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

$$= 2$$

P. 138