UNIT II: CHEMICAL EQUILIBRIUM

I. Introduction:

- PE diagrams demonstrate forward rxns. do have the _possibility_ of reacting in a reverse rxn.

* Reading graph left to right: FORWARD RXN.
* Reading graph right to left: REVERSE RXN.
* Forward rxn: exothermic
* Reverse rxn: endothermic.

- Possibility of a reverse rxn. occurring depends on certain factors such as: (a) _energy_ of the products.
(b) Energy available for a _reverse_ rxn.
(c) Changes in the _conditions_ of the system.

- When all conditions are met, and kept _constant_, then the rxn. has the ability to " _see saw_ " between forward and reverse infinitely - This constant forward and reverse reactivity is called _EQUILIBRIUM_.

- Chemical equilibrium exists due to _energetic_ factors as well as _physical_ factors such as _ENTROPY_.

II. What is Equilbrium?

(Dynamic) Equilibrium: When observing a system at equil^{m}, there are no _macroscopic_ changes in properties, but _microscopically_, properties are constantly changing.

- **Macroscopic:** visible, or measurable properties, such as colour, temperature, pressure, etc.
- **Microscopic:** atomic or molecular level properties.

Example: N_2O_4 (g) $\leftrightarrow$ 2 NO_2 (g)
  colourless   *brown*

(a) Gas tube at room temperature: _amber_
(b) Gas tube in hot water: _dark brown_
(c) Gas tube in cold water: _pale yellow_
(d) Expected colour at equilibrium: _amber_

Conclusion: This rxn. is _endothermic_.

III. Conditions for Equil^m:

Example: A ⟷ B,   where [A] initial = 1.200M
[B] initial = 0.000M

Time (min)	RATE forward	RATE reverse	[A]	[B]
0	0.600	0.000	1.200	0.000
1	0.300	0.060	0.600	0.600
2	0.180	0.084	0.360	0.840
3	0.132	0.094	0.264	0.936
4	0.113	0.097	0.226	0.974
5	0.105	0.099	0.210	0.990
6	0.102	0.100	0.204	0.996
7	0.101	0.100	0.202	0.998
8	0.100	0.100	0.201	0.999
9	0.100	0.100	0.200	1.000
10	0.100	0.100	0.200	1.000

Time (min)	RATE forward	RATE reverse	[A]	[B]
11	0.100	0.160	0.200	1.600
12	0.130	0.154	0.260	1.540
13	0.142	0.152	0.284	1.516
14	0.147	0.151	0.294	1.506
15	0.149	0.150	0.297	1.503
16	0.150	0.150	0.299	1.501
17	0.150	0.150	0.300	1.500
18	0.150	0.150	0.300	1.500

Rate Graph:

* As system reaches equil^m
* At equil^m
* Change in conditions
* New equil^m

Concentration Graph:

* More B added
* Ratio between [A] : [B]
* Reaching equil^m
* @ equil^m
* Response to stress.
* New equil^m
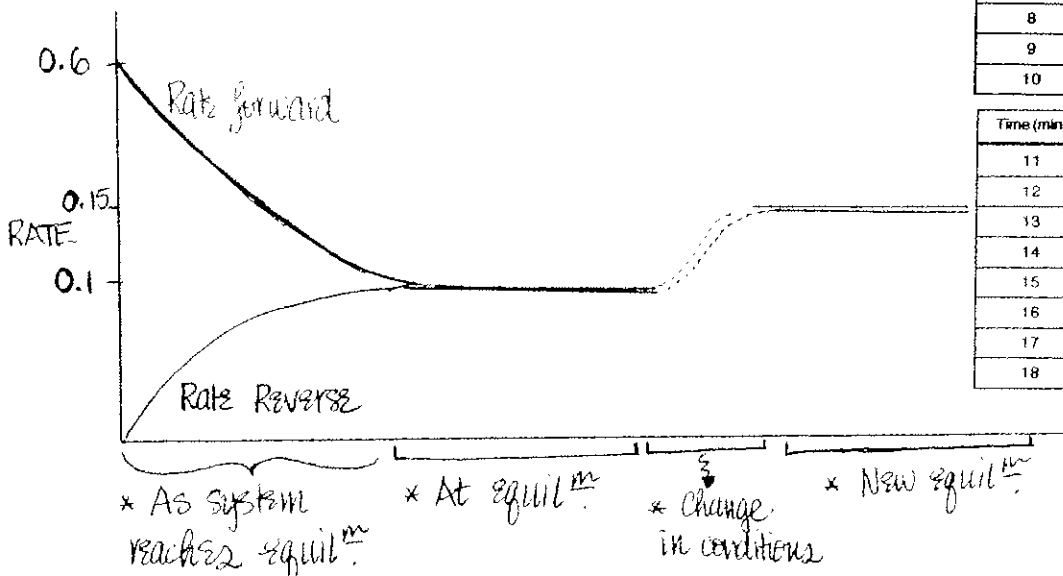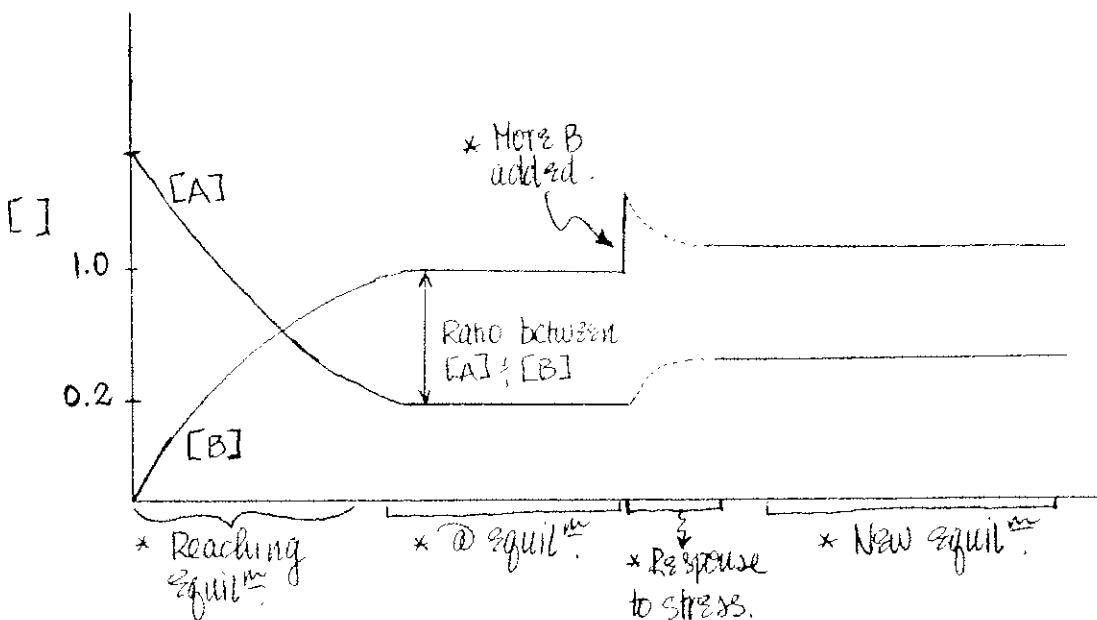
Conclusions:

AS a system reaches equil^m:

* Rate forward will decrease as rate reverse increases.
* [Reactants] will drop as [Products] rise.
* When a stress is introduced, equil^m is lost - But system will respond in a manner so as to attain a new equil^m.

System AT equilibrium:

* Rate forward = rate reverse.
* [Reactants] and [Products] remain constant.
* Ratio between [] are fixed.
* [Reactants] ≠ [Products]

NOTE:

1) Systems containing *solutions* must be **saturated** for equil^m to exist.

- **Saturated solution:** a solution where the max. amount of solute has been dissolved in a solvent.

2) Systems containing ___gases___ must be **closed** for equil^m to exist.

IV. Why Does Equil^m Exist?

Spontaneous Rxn.: a rxn. that occurs without external ___energetic___ forces ___aiding___ it.

- It **energetically** makes sense that ___endothermic___ rxns. will spontaneously undergo a reverse rxn. to attain an equil^m.

  - *But why can SOME exothermic rxns. also want to attain equilibrium?*
  - *And why do some endothermic rxns. also happen spontaneously?*

Example:

Spontaneous endo. Rxn.: Cold Packs

$$2 NH_4SCN_{(s)} + Ba(OH)_2 \cdot 8 H_2O_{(s)} \longleftrightarrow Ba^{2+}_{(aq)} + 2 SCN^-_{(aq)} + 2 NH_{3(g)} + 10 H_2O_{(l)}$$
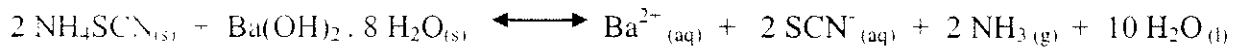
Exo. Rxn. that Form Equil^m:

$$2 NO_{(g)} + Cl_{2(g)} \longleftrightarrow 2 NOCl_{(g)} + 76 kJ$$

Aside from energetic factors, the other factor driving equil^m is ___ENTROPY___:

Entropy: The degree of ___disorder / chaos___ in a system.
All systems of the universe ___prefer___ a state of dis-order or chaos.

MOST RANDOM	←		→	LEAST RANDOM
Gases	Solutions (aq)	Liquids	Solids
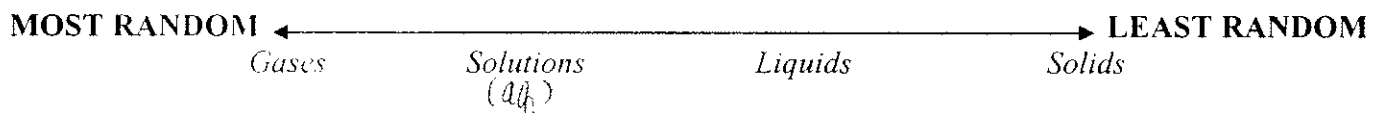
> In General: there are two factors which "drive" any rxn.:
>
> 1) Energy (H): rxns. favour the side with ___min.___ energy (Exothermic side)
> 2) Entropy (S): rxns. favour ___max.___ entropy. The more disorganized the state, the better.
>
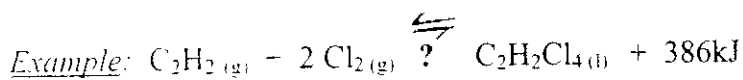> These two factors must work in ___opposition___ for equil^m to occur:

Example: $2 NH_4SCN_{(s)} + Ba(OH)_2 \cdot 8 H_2O_{(s)} + 152kJ \rightleftharpoons Ba^{2+}_{(aq)} + 2 SCN^-_{(aq)} + 2 NH_{3(g)} + 10 H_2O_{(l)}$
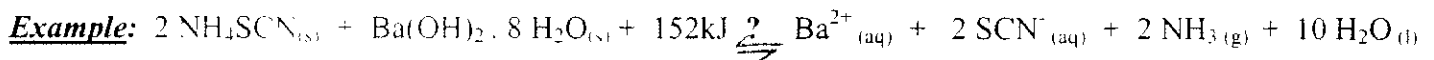
- Entropy (ΔS): ___favours products___   Enthalpy: (ΔH): ___prefers reactants___
- Conclusion: ___equil^m___
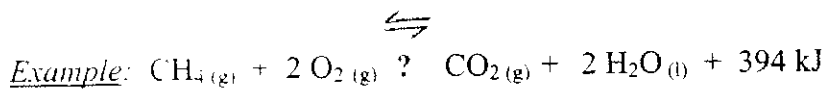
Example: $CH_{4(g)} + 2 O_{2(g)} \rightleftharpoons CO_{2(g)} + 2 H_2O_{(l)} + 394 \text{ kJ}$

- Entropy: (ΔS) *favours reactants*
- Enthalpy: (ΔH) *favours products*
- Conclusion: equil^m

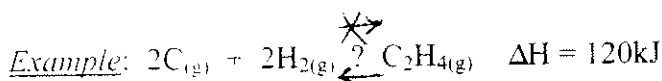*Example:* $4 Au_{(s)} + 3 O_{2(g)} + 162 \text{ kJ} \rightleftharpoons 2 Au_2O_{3(s)}$
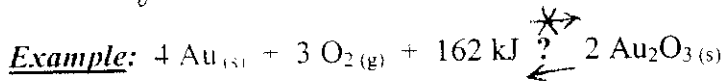
- Entropy: (ΔS) : *favours reactants*
- Enthalpy: (ΔH): *favours reactants*
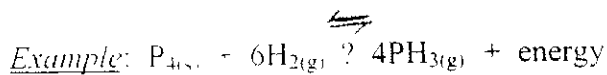- Conclusion: No rxn. (OR only reverse rxn. occurs).

Example: $C_2H_{2(g)} - 2 Cl_{2(g)} \rightleftharpoons C_2H_2Cl_{4(l)} + 386 \text{kJ}$

- Entropy: (ΔS) *favours reactants*
- Enthalpy: (ΔH) *favours products*
- Conclusion: equil^m.

Example: $NaOH_{(s)} \rightarrow Na^+_{(aq)} + OH^-_{(aq)} + \text{heat}$
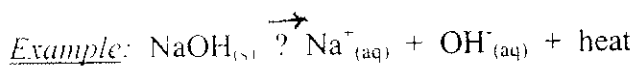
- Entropy: (ΔS) *favours products*
- Enthalpy: (ΔH) *favours products*
- Conclusion: Goes to completion.

Example: $2C_{(g)} + 2H_{2(g)} \rightleftharpoons C_2H_{4(g)}$ $\Delta H = 120 \text{kJ}$

- Entropy: (ΔS) *favours reactants* (**4** mols of gas vs. 1 mole of gas).
- Enthalpy: (ΔH) *favours reactants*
- Conclusion: No rxn. (OR only reverse rxn.)

Example: $P_{4(s)} - 6H_{2(g)} \rightleftharpoons 4PH_{3(g)} + \text{energy}$

- Entropy: (ΔS) *favours reactants*
- Enthalpy: (ΔH) *favours products*
- Conclusion: equil^m.

Example: $Cl_{2(g)} + 2 HI_{(g)} \rightleftharpoons I_{2(g)} + 2HCl_{(g)} + \text{heat}$
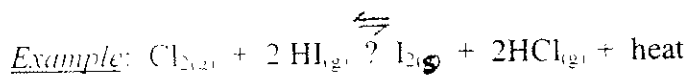
- Entropy: (ΔS) *favours reactants*   Enthalpy: (ΔH) *favours products*

(* equil^m.)

V. Factors Affecting Equil^m & Le Chatelier's Principle

Equil^m can only exist if all the desired conditions are kept constant. If one or more conditions are altered, equil^m is lost. HOWEVER, the system *shifts* towards reactant or product side to attain a new equil^m in accordance to **Le Chatelier's Principle.**

Le Chatelier's Principle: When a _____*stress*_____ is introduced to an equil^m system, the rxn. will _____*shift*_____ so as to _____*reduce*_____ the stress and _____*attain*_____ a new equil^m.

A. Change in Temperature:

1) If temp. is decreased: system will shift to create _____*more*_____ heat – *EXOTHERMIC* side.
2) If temp. is increased: system will shift _____*away*_____ from the heat source. – *ENDOTHERMIC side*

Example: $2 NO_{(g)} + Cl_{2(g)} \longleftrightarrow 2 NOCl_{(g)} + 76 kJ$

- Decrease temp.: *favours products*

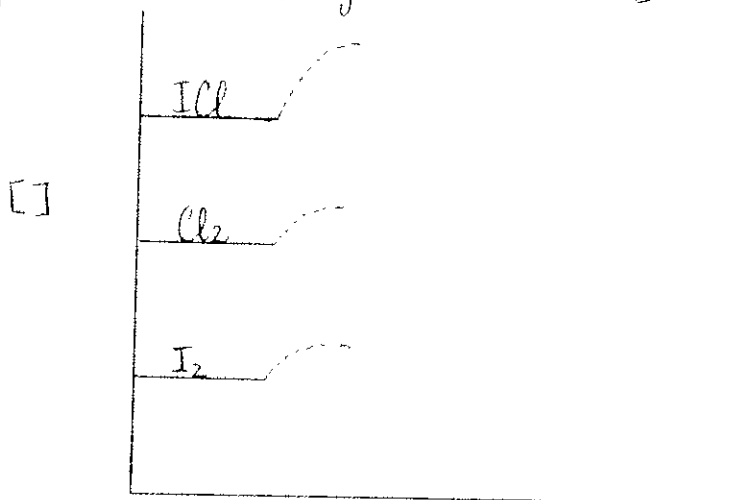- Increase temp.: *favours reactants*

Graph of Rxn. as Temp. is Decreased:
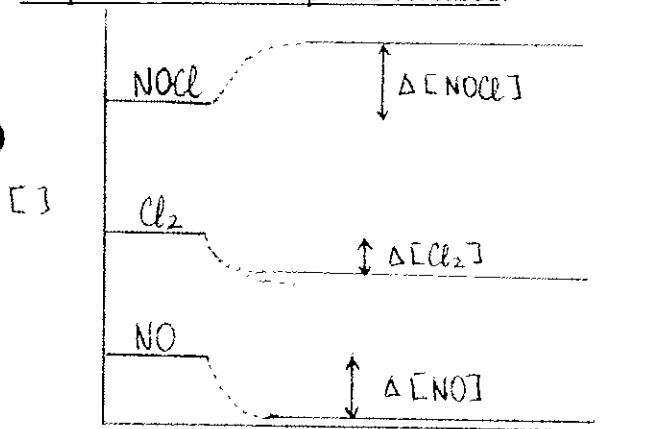
$*$ *All changes in [ ] must obey stoichiometric ratios:*
- *$\Delta[NOCl]$ is 2x that of $\Delta[Cl_2]$.*
- *$\Delta[NOCl]$ is equal to that of $\Delta[NO]$.*

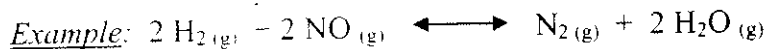*Example:* $I_{2(g)} + Cl_{2(g)} \longleftrightarrow 2 ICl_{(g)}, \Delta H = 35.0 kJ$

- Increase temp.: *favours products*

(graph) • Decrease temp.: *favours reactants*

B. Change in Concentration:

1) When [ ] of a particular species is increased, rxn. will shift to __reduce__ that species [ ].
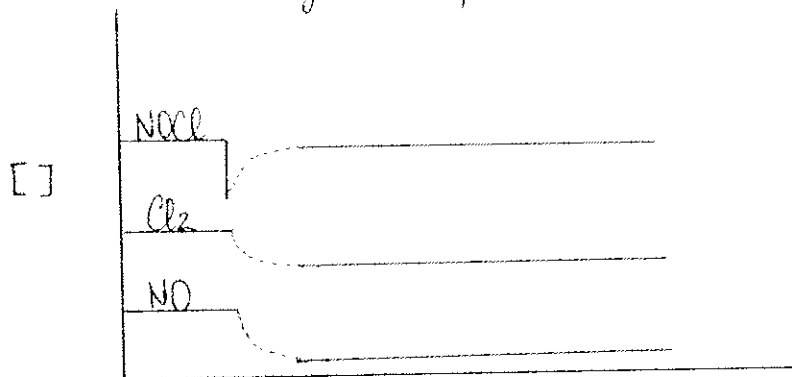
   Example: $2 H_{2(g)} + 2 NO_{(g)} \longleftrightarrow N_{2(g)} + 2 H_2O_{(g)}$

   - Increase [NO]: *favours products*

   - Decrease [H₂]: *favours reactants (system will compensate to make up for the lost H₂).*

Graph of Rxn. as [NO] increases

   Example: $2 NO_{(g)} + Cl_{2(g)} \longleftrightarrow 2 NOCl_{(g)} + 76 \text{ kJ}$
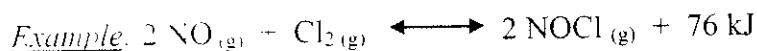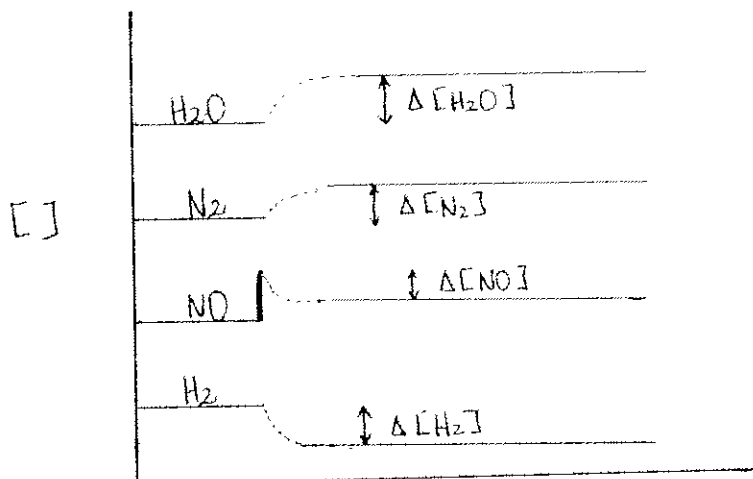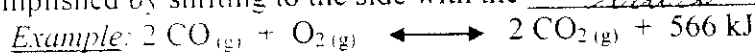
   - Increase [Cl₂]: *favours products*

(graph) - Decrease [NOCl]: *favours products*


C. Change in Pressure:

An increase in pressure (OR decrease in __volume__), will increase [ ] of __ALL__ gaseous species present.

1) If pressure is increased, rxn. will shift to __reduce__ the overall pressure of the system - This is accomplished by shifting to the side with the __least__ number of molecules.

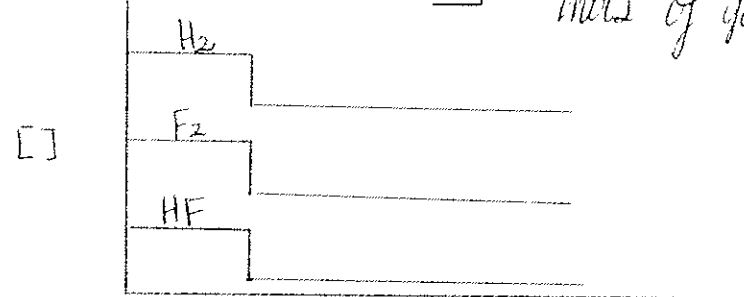   *Example:* $2 CO_{(g)} + O_{2(g)} \longleftrightarrow 2 CO_{2(g)} + 566 \text{ kJ}$

- Increase Pressure: *favours products (Only 2 mols of gas in products).*
- Decrease pressure: *favours reactants*

Graph of rxn. if pressure increased: _____

[ ]
- CO_2
- O_2
- CO

Example: $2 HF_{(g)} \longleftrightarrow F_{2(g)} + H_{2(g)}$
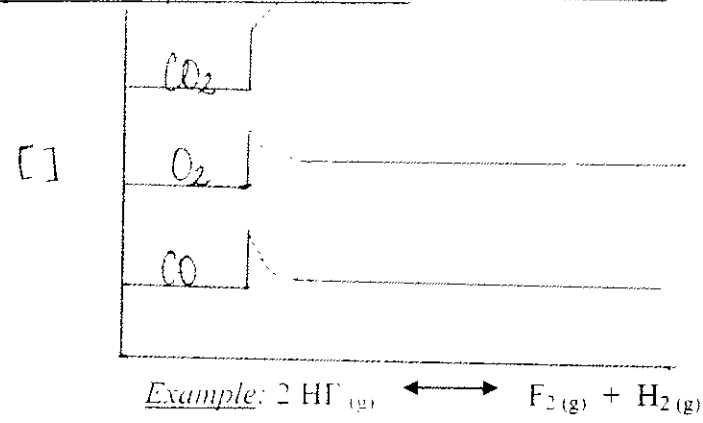
(graph) •
- Increase pressure: no effect
- Decrease pressure: no effect

Both reactants and products have the same mols of gas.

[ ]
- H_2
- F_2
- HF

## D. Addition of a Catalyst

Catalysts ___*increase*___ the rate of rxn.

1) In an equil^m system, introducing a catalyst increases ___*both*___ the forward and reverse rates of rxn. equally. As a result, equil^m is ___*not*___ disturbed.

Example: $CH_3OH_{(l)} + CH_3CH_2COOH_{(l)} \longleftrightarrow (CH_3)_2CH_2COH$
cat. H^+
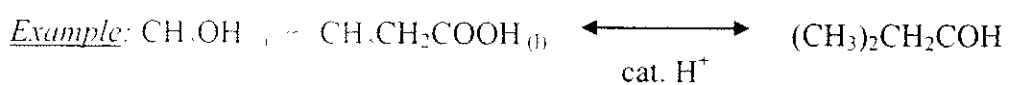
- Addition of acidic catalyst: no change on equil^m. Only change is the ___*rate*___ - Rate will increase overall. (Time needed to reach equil^m will be ___*lowered*___).

Application of Le Chatelier's Principle in Industry:

The Haber Process: During WWI, Fritz Haber needed a way to mass produce ammonia so that he could convert to nitrates for explosives.
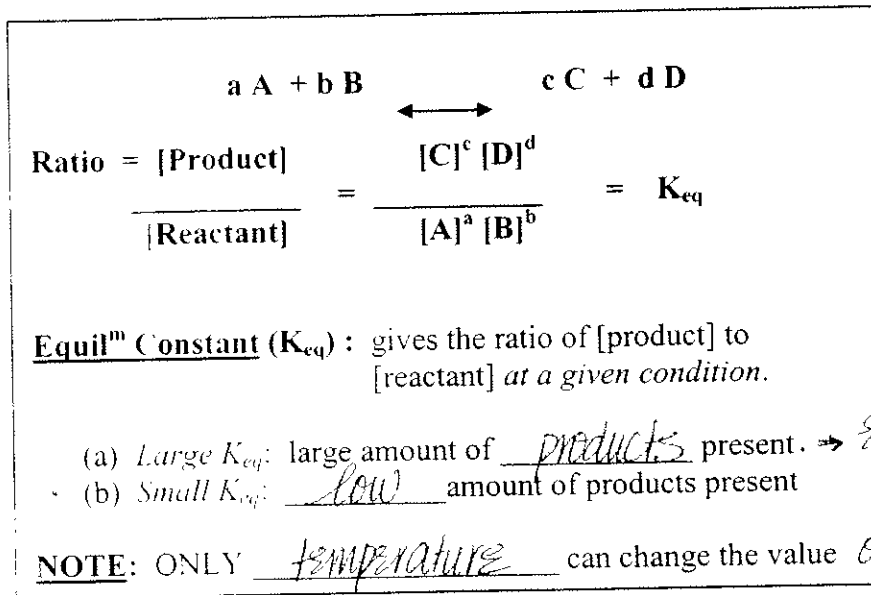
$$N_{2(g)} + 3 H_{2(g)} \longleftrightarrow 2 NH_{3(g)} + 92 \text{ kJ}$$
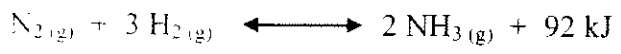
To get highest yield, he needed: (a) ___*Increase*___ pressure
(b) ___*Decrease*___ temperature
(c) High ___*concentration*___ of either reactants
(d) High temp. is needed to have faster rate of rxn. But this compromises condition (b) – Solved by using ___*catalyst*___.
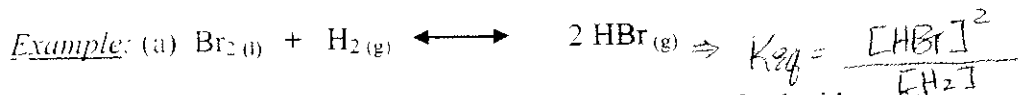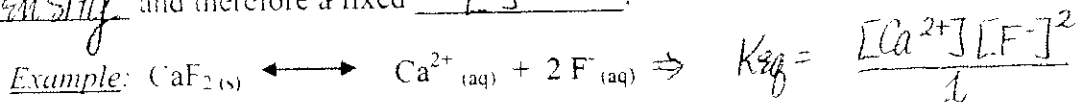
This process is still used today to manufacture ammonia for agricultural purposes.

# VI. Quantitative Analysis of Equil^m: The Equil^m Constant - K$_{eq}$

Since [products] and [reactants] are __*constant*__ @ equil^m, we would expect that the __*ratio*__ between them to be also constant.

$$a\,A + b\,B \longleftrightarrow c\,C + d\,D$$

$$\text{Ratio} = \frac{[\text{Product}]}{[\text{Reactant}]} = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b} = K_{eq}$$

Equil^m Constant (K$_{eq}$): gives the ratio of [product] to [reactant] *at a given condition*.

(a) *Large K$_{eq}$*: large amount of __*products*__ present. → *Equil^m favours forward rxn.*

(b) *Small K$_{eq}$*: __*low*__ amount of products present

NOTE: ONLY __*temperature*__ can change the value *of K$_{eq}$*.

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1) __*Solids*__ and __*pure liquids*__ do not take part in a K$_{eq}$ expression because they have a fixed __*density*__ and therefore a fixed __[ ]__.

Example: $CaF_{2\,(s)} \longleftrightarrow Ca^{2+}_{(aq)} + 2\,F^-_{(aq)}$ ⇒ $K_{eq} = \dfrac{[Ca^{2+}][F^-]^2}{1}$

Example: (a) $Br_{2\,(l)} + H_{2\,(g)} \longleftrightarrow 2\,HBr_{(g)}$ ⇒ $K_{eq} = \dfrac{[HBr]^2}{[H_2]}$

2) A liquid is considered pure IFF it is the **only** liquid which exists on both sides of the equation. If two liquids are present, they __*dilute*__ one another, thus changing the overall __[ ]__. In this case, the liquids are considered for K$_{eq}$ calculations.

$$CH_3COOH_{(l)} + Cl_{2\,(g)} \longleftrightarrow CH_3COCH_{2\,(l)} + HCl_{(g)}$$
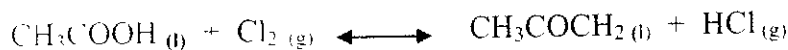
A. Equil^m Calculations:

1) Equil^m Concentrations Given:

Example: A 2.0L bulb contains 6.00 mol of $NO_{2\,(g)}$, 3.0 mol of $NO_{(g)}$ and 0.20 mol of $O_{2\,(g)}$ **at equil^m**. What is K$_{eq}$ for this rxn? $2\,NO_{(g)} + O_{2\,(g)} \longleftrightarrow 2\,NO_{2\,(g)}$

- *Determine the K$_{eq}$ expression:* $K_{eq} = \dfrac{[NO_2]^2}{[NO]^2[O_2]}$

- *Calculate [ ] of each species:*

$[NO_2] = 3.0\,M$
$[O_2] = 1.5\,M$
$[NO] = 0.10\,M$

- *Substitute into K$_{eq}$ expression:* $K_{eq} = \dfrac{(3.0M)^2}{(1.5M)^2(0.1M)} = 4.0 \times 10^1\,M^{-1}$

unit for K$_{eq}$ is usually not required.

2) Finding Equilibrium // Using "ICE" Table:

Example: 4.00 mol of NO_2 is **introduced** into a 2.00L bulb. After 5 minutes, equil^m is attained according to the equation: $2 NO_{(g)} + O_{2(g)} \longleftrightarrow 2 NO_{2(g)}$. At equil^m, 0.500 mol of NO is found. What is the K_{eq} value?

- K_{eq} *expression:*

$$K_{eq} = \frac{[NO_2]^2}{[NO]^2 [O_2]}$$

Interpreting the Problem:

- The system was at equilibrium when a ___Stress___ was introduced – The stress is
  ___$\uparrow [NO_2]$___.
- The ___reverse___ rxn. is occurring since we have 2.00 M of the product initially.
- This means that NO_2 will be ___decreasing___ over time - The change in $[NO_2]$ will be
  ___negative___.
- The reactants are being formed over time – The change in [reactants] will be ___positive___.
- All changes in [ ] must obey ___stoichiometric___ proportions.

Since K_{eq} expression uses only the **equilibrium concentrations** of the species. The [ ]$_{equilm}$ of the remaining species can be found by using an ICE table.

	2 NO	+	O_2	$\longleftrightarrow$	2 NO_2
Initial (where _Stress_ is introduced):	0		0		2.0M
Change(How system _responds_ to stress):	+ 0.250M		+ 0.125M		– 0.250M
Equil^m: (new equilibrium):	0.250M		0.125M		0.75M

- *Determine K_{eq} value:*

$$K_{eq} = \frac{(1.75M)^2}{(0.250M)^2(0.125M)} = 392 \ M^{-1}$$

Example: A 1.0L rxn. vessel contains 0.750 mol of CO and 0.275 mol of H_2O. After 1 hr., equil^m is reached according to: $CO_{(g)} + H_2O_{(g)} \longleftrightarrow CO_{2(g)} + H_{2(g)}$. Analysis shows 0.250 mol of CO_2 present at equil^m. What is the K_{eq}?

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

I	0.750M	0.275M	0	0
C	-0.250M	-0.250M	+0.250M	+0.250M
E	0.500M	0.0250M	0.250M	0.250M

$$K_{eq} = \frac{(0.250M)(0.250M)}{(0.500M)(0.0250M)}$$

$$= 5.0$$

Example: At 600.0°C. the following equilibrium occurs: $2\ BrCl_{(g)} \leftrightarrow Br_{2(g)} + Cl_{2(g)}$
At this equilibrium, the $[Br_2] = 0.752M$, $[Cl_2] = 0.235M$ and $[BrCl] = 1.25M$. If an additional 2.5mol of Br_2 is introduced to the reaction vessel, what will be the new equilibrium $[BrCl]$?   (1.0L container)   * Same Keq because no temp. stress.
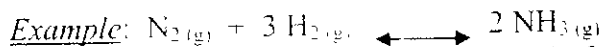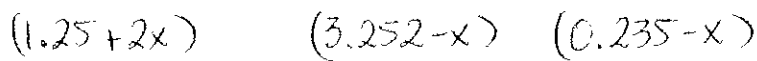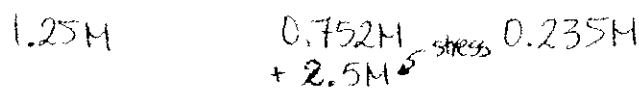
$$* K_{eq} = \frac{(0.235M)(0.752M)}{(1.25M)^2} = 0.113$$

$$0.113 = \frac{(0.235-x)(3.252-x)}{(1.25+2x)^2}$$

$$* \ x = 4.28,\ 0.148$$

$$2\ BrCl_{(g)} \rightleftharpoons Br_{2(g)} + Cl_{2(g)}$$

Reasoning: * x = 4.28 cannot work because it would give (-) concentrations.

I	1.25M	0.752M stress 0.235M	
		+ 2.5M	
C	+ 2x	- x	- x
E	(1.25+2x)	(3.252-x)	(0.235-x)

$$\therefore x = 0.148$$

$$[BrCl]_{equil^m} = 1.25 + 2(0.148)$$
$$= 1.5\ M$$

Example: $N_{2(g)} + 3\ H_{2(g)} \longleftrightarrow 2\ NH_{3(g)}$
At a certain temperature, 3.0mol of N_2, and 3.0 mol of H_2 are put into a 5.0L bulb. At equilibrium, $[NH_3] = 0.075M$. The system is then allowed to reach equilibrium. Once that has been attained, an additional 6.0mol of NH_3 was introduced, determine the new $[H_2]$.

OMIT

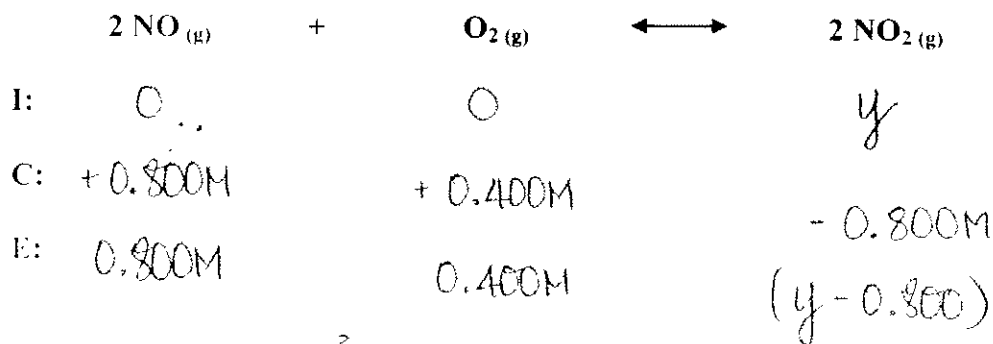**3) K_{eq} Value is Given:**

Example: A certain amount of NO_2 was introduced into a 5.00L bulb. When equil^m is reached, $[NO]$ was 0.800M. If K_{eq} is 24.0, how many moles of NO_2 was originally put into the bulb?

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

- $[NO]_{equilm} = 0.800\ M$
- $[NO_2]_{initial} = y$

$$2\,NO_{(g)} \quad + \quad O_{2\,(g)} \quad \longleftrightarrow \quad 2\,NO_{2\,(g)}$$

I: 0 0 y

C: $+0.800M$ $+0.400M$ $-0.800M$

E: $0.800M$ $0.400M$ $(y-0.800)$

$$24.0 = \frac{(y-0.8)^2}{(0.8)^2(0.4)} \quad \Rightarrow \quad *y = 3.28 \ (\text{Original } [NO_2])$$

$*\quad 3.28M \times 5.0L = 16.4 \ mol \ NO_2$

Example: $K_{eq} = 7.5$ for $2\,H_{2\,(g)} + S_{2\,(g)} \longleftrightarrow 2\,H_2S_{(g)}$. A certain amount of H_2S was added to a 2.0 L flask and allowed to reach equil^m. At equil^m, 0.072 mol of H_2 was found. How many moles of H_2S were originally added to the flask?

$$2\,H_{2(g)} + S_{2\,(g)} \longrightarrow 2H_2S_{(g)}$$

I 0 0 x

C $+0.036M$ $+0.018M$ $-0.036M$

E $0.036M$ $0.018M$ $(x-0.036)$
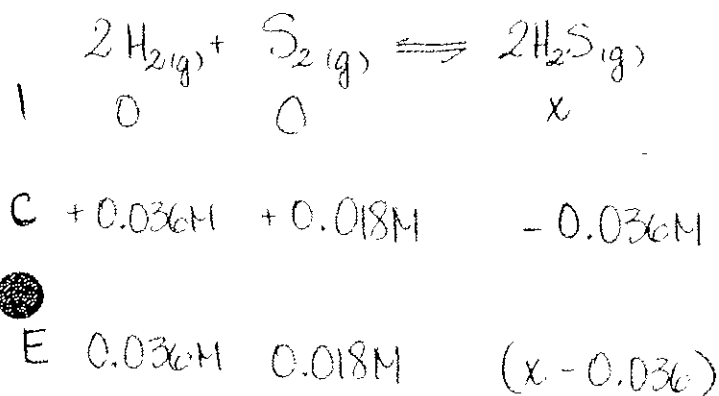
$*\quad 7.5 = \dfrac{(x-0.036)^2}{(0.036)^2(0.018)}$

$*\quad x = 0.049 \ ([H_2S] @ \text{start})$

$*\quad 0.049M \times 2.0L = 0.098 \ mol \ H_2S$

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4) Predicting Rxn. Shift to Reach Equil^m: Trial K_{eq} (Q)

Reaction Quotient (Q): a "___fake___ K_{eq} value" for a chemical equilm.
Tells us the ratio of [product] to [reactants] **at that point in time.**

1) If $Q = K_{eq}$: system "at that point in time" equals sytem at equilm.
        Therefore. equilm. exists

2) If $Q > K_{eq}$:   Then: $\dfrac{[products]}{[reactants]}$ is too **high**: **Rxn. Shifts towards** ___reactants___.

3) If $Q < K_{eq}$:   Then: $\dfrac{[products]}{[reactants]}$ is too **low**: **Rxn. Shifts towards** ___products___.

Example: $2\,NO_{(g)}\ +\ O_{2\,(g)} \longleftrightarrow 2\,NO_{2\,(g)}$ $K_{eq} = 49$

If 2.0 mol of NO, 0.20 mol of O_2 and 0.40 mol of NO_2 are put into a 2.0 L bulb, which way will the rxn, shift in order to reach equilm?

- *Calculate [ ] of all species:*

$[NO_2] =$ 0.20M $[O_2] =$ 0.10M $[NO] =$ 1.0M

- *Calculate the Q value, the value of "equilibrium" at this moment:*

$$Q = \frac{(0.20M)^2}{(0.10M)(1.0)^2} = 0.40$$

- *Compare the Q with the real K_{eq} value:*

✗ $Q < K_{eq}$: Rxn. will shift towards product to get to equil^{m}.