Unit 2 - Equilibrium

- Equilibrium is a term used to describe a **balance** between to things, hence the "equil or equal" part of the word equilibrium.
- In chemistry equilibrium is used to describe a reversible reaction where the forward rate of the reaction is equal to the rate for the reverse reaction.
- Equilibrium is shown in a reaction using double arrows. Ex. - $CO_{(g)} + Cl_{2\,(g)} \leftrightharpoons COCl_{2\,(g)}$
- An important point or realization is that when products are formed, if they escape the reaction vessel, then the products are no longer present to act as reactants and drive the reaction is reverse. As such then, for equilibrium to exist the reaction must occur in a closed system (system when nothing enters or leaves).
- Equilibrium reactions do not depend on whether there is excess reactants or products, the end result will always be the same equilibrium.
- At equilibrium no **macroscopic** changes occur. That is, no visible changes happen. However, microscopic changes are occurring.
- This reaction is said to be in ________________ ____________________.
- Reactions at equilibrium have a forward rate of reaction and a reverse rate of reaction.
- The rate of a reaction is proportional to the [reactants], so as the <u>[reactants] increases, so does the forward rate in proportion</u>!
- So, $RATE_{forward} = k_{forward}$*[reactants] where k is a constant that is given.
- Let's look at an example problem to help us picture an equilibrium reaction both "looks" and "acts".

<u>Example</u> - $A \rightleftarrows B$ and the [A] = $1.200\ M$, [B] = $0.00\ M$, $k_{forward} = 0.50$, $k_{reverse} = 0.10$

<u>Part 1</u>

The following results are produced.

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	0.990
9	0.100	0.100	0.200	1.000
10	0.100	0.100	0.200	1.000

a.) Plot the values of [A] over time and [B] over time on the same graph.

b.) When does it appear that equilibrium occurs? How do you know? What occurs at equilibrium?

c.) Is there a time when [REACTANT] = [PRODUCT]? Is [REACTANT] = [PRODUCT] at equilibrium?

d.) When is the forward rate the greatest? What happens to the rate as the [A] decreases?

e.) What is the numerical value of the ratio $\frac{[PRODUCT]}{[Reactant]}$ at equilibrium?

Part 2

- If the equilibrium is upset by adding an extra $0.6\ M$ of B at the eleventh minute, what happens?

Time (min)	$\text{RATE}_{\text{forward}}$	$\text{RATE}_{\text{reverse}}$	[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

a.) Extend your graph to include the new data. Answer b.) When is equilibrium re-established?

c.) What is the numerical value of the ratio $\frac{[PRODUCT]}{[REACTANT]}$ at equilibrium?

d.) When equilibrium is re-established, what is different from the original equilibrium? What has not changed?

- The important note to realize is that the rate of products being made is equal to the products decomposing back into reactants.

- There are two main forces that decide if a reaction will **spontaneously** proceed: Enthalpy and Entropy.
- Enthalpy (ΔH) is a term that looks at energy changes (heat), while entropy (ΔS) is a term that looks at the randomness of the particles.
- Enthalpy always favours the side of the equation that has a minimum or lower energy (heat). This is the exothermic side of the reaction. (Hint – the side with the energy statement is the lower energy side)
- Entropy always favours the side of the equation that has the more random chemical states.

- Overall the randomness of phases is ________ < ____________ < _____________ < _______

- So . . . . to increase ΔS

  1.) Evolve a gas from a solution

  $CaCO_{3\,(s)} + 2\,HCl_{(aq)} \rightarrow CaCl_{2\,(aq)} + CO_{2\,(g)} + H_2O_{(l)}$

  2.) Evolve a gas from a solid

  $2\,NaHCO_{3\,(g)} \rightarrow Na_2CO_{3\,(s)} + CO_{2\,(g)} + H_2O_{(g)}$

  3.) The # moles of gas products > # moles of gas reactants

  $4\,NH_{3\,(g)} + 5\,CO_{2\,(g)} \rightarrow 4\,NO_{(g)} + 6\,H_2O_{(g)}$

  4.) A substance dissolves in water

  $NaCl_{(s)} \rightarrow Na^+_{(aq)} + Cl^-_{(aq)}$

- There are three choices for a reaction progression

  1.) go to completion

  2.) not go at all

  3.) ______________________________________

- Ex. 1 - $Zn_{(s)} + 2\ HCl_{(aq)} \rightarrow ZnCl_{2\,(aq)} + H_{2\,(g)}$ $\Delta H = -152\ kJ$ goes to completion

  Exothermic ΔH favours →

  Evolve gas then ΔS favours →

- Ex. 2 - $3\ C_{(s)} + 3\ H_{2\,(g)} \rightarrow C_3H_{6\,(g)}$ $\Delta H = +20.4\ kJ$

  Endothermic ΔH favours ←

  Reactants more gas ΔS favours ← (more gas reactants)

- Ex. 3 - $2\ Pb(NO_3)_{2\,(s)} + 597\ kJ \rightarrow 2\ PbO_{(s)} + 4\ NO_{2\,(g)} + O_{2\,(g)}$

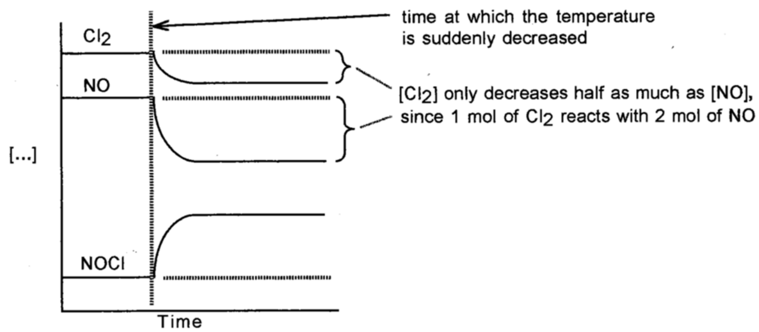
  Endothermic ΔH favours ←

  Evolve gas then ΔS favours → reaction settles somewhere in between

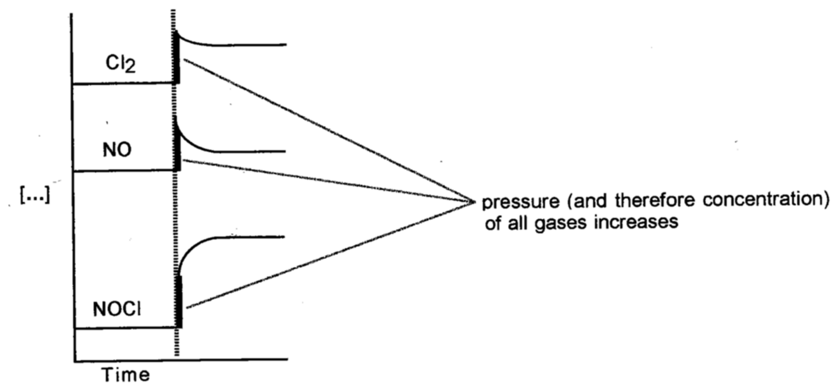
Le Chatelier's Principle

- When a reaction is in equilibrium any changes will cause the equilibrium to be disrupted by ultimately it will re-establish itself.
- "Changes" or changing conditions are the following

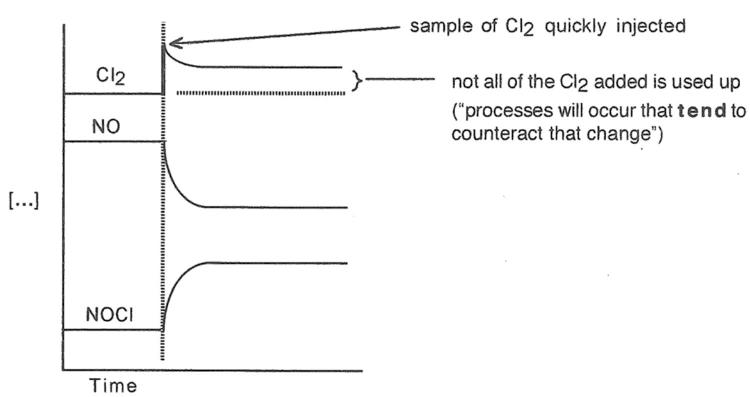
1.) Temperature effects ↑T favours endothermic reactions



2.) Pressure effects ↑P favours the side with fewer gaseous particles



3.) Concentration effects ↑[ ] favours the direction away from that chemical



4.) Catalytic effects have no effect, but speed up the rate to equilibrium.

colourless magenta

- Consider this example $2\,HI_{(g)} \rightleftharpoons H_{2\,(g)} + I_{2\,(g)}$
- If more HI is added the reaction shifts →

Equilibrium is being shifted to products to OFFSET the disturbance in equilibrium

- Le Chatelier's principle ↑

- Ex. 1 - $PCl_{3\,(g)} + Cl_{2\,(g)} \rightleftharpoons PCl_{5\,(g)}$ $\Delta H = -92.5\ kJ$ } Equilibrium system

   a.) ↑P drives the reaction to try and decrease pressure (more species on reactant side), shifting reaction to the products. So, ____.

   b.) ↑[Cl_2] drives the reaction to try and decrease [Cl_2], forces a shift away from Cl_2 (reactants), so ____.

   c.) ↑T drives the reaction to try and decrease temperature. So, the endothermic reaction is favoured, the ____.

   d.) ↑volume (= ↓Pressure) drives the reaction to try and increase pressure (more species on reactant side), shifting reaction to the reactants. So, ____.

   e.) Add catalyst. No change in equilibrium concentrations.

- Ex 2. - $CH_{4\,(g)} + H_2O_{(g)} + 49.3\ kJ \rightleftharpoons CO_{(g)} + 3\,H_{2\,(g)}$ } Equilibrium system

What would happen if . . . . . .

1.) ↑T

2.) ↓P

3.) ↓V

4.) Add a chemical which reacts with H_2O

Equilibrium Expression and Equilibrium Constant

- All reactions that reach equilibrium have an equilibrium equation as such: A + B $\rightleftharpoons$ C + D
- This generic equation is solved for experimentally by $K_{eq} = \frac{[Products]}{[Reactants]}$ $K_{eq} = \frac{[C]\times[D]}{[A]\times[B]}$

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- This expression is known as the _______________ ________________and the numerical value of K_{eq} is called the _____________________ ______________________.
- Ex. 1 - $N_{2\,(g)} + 3\,H_{2\,(g)} \rightleftharpoons 2\,NH_{3\,(g)}$ At equilibrium $[N_2] = 2.12\,M$, $[H_2] = 1.75\,M$, $[NH_3] = 84.3\,M$

  What is K_{eq}?

  Answer -

Changes to pressure, volume, or concentration have no effect to the actual value of K_{eq}.

However, temperature DOES!

- Ex. 2 - A $2.0\,L$ sealed flask contains $4.00\,mol\,NO_{2(g)}$. After a time equilibrium is attained according to this reaction $2\,NO_{(g)} + O_{2\,(g)} \rightleftharpoons 2\,NO_{2\,(g)}$. At equilibrium, $0.500\,mol\,NO_{(g)}$ is found. What is the K_{eq}?

  Answer – First, we need the K_{eq} equation.

  Second, we need the ICE box. Remember this is MOLARITY not moles!!!!

  $2\,NO_{(g)} + 1\,O_{2\,(g)} \rightleftharpoons 2\,NO_{2\,(g)}$

I	0	0	2.0
C	$+0.250$	$+0.125$	-0.250
E	0.250	0.125	1.75

  Ratio of coefficients $2:1:2$

  Thirdly, we need to solve the equation $K_{eq} = \frac{[NO_2]^2}{[O_2]\times[NO]^2}$ $K_{eq} = \frac{[1.75]^2}{[0.125]\times[0.250]^2}$ $K_{eq} = 392$

- Ex. 3 - A certain amount of $NO_{2\,(g)}$ was introduced into a $5.00\,L$ sealed flask. When equilibrium was attained according to this reaction $2\,NO_{(g)} + O_{2\,(g)} \rightleftharpoons 2\,NO_{2\,(g)}$, the concentration of $NO_{(g)}$ was $0.800\,M$. If the K_{eq} has a value of 24.0, how many **moles** of NO_2 were originally put into the flask?

  Answer –

- Ex. 4 - $K_{eq} = 49$ for 2 $NO_{(g)}$ + $O_{2\,(g)}$ ⇌ 2 $NO_{2\,(g)}$. If $2.0\ mol\ NO_{(g)}$, $0.20\ mol\ O_{2\,(g)}$, and $0.40\ mol\ NO_{2\,(g)}$ are put into a $2.00\ L$ bulb, which way will the reaction shift in order to reach equilibrium?

  Answer –

- Ex. 5 – $K_{eq} = 3.5$ for $SO_{2\,(g)}$ + $NO_{2\,(g)}$ ⇌ $SO_{3\,(g)}$ + $NO_{(g)}$. If $4.0\ mol\ SO_{2\,(g)}$ and $4.0\ mol\ NO_{2\,(g)}$ are placed in a $5.0\ L$ bulb and allowed to come to equilibrium, what concentration of all species will exist at equilibrium.

  Answer –

- Ex. 6 - A $1.0\ L$ vessel contained $1.0\ mol\ SO_2$, $4.0\ mol\ NO_{2\,(g)}$, $4.0\ mol\ SO_{3\,(g)}$, and $4.0\ mol\ NO_{(g)}$ at equilibrium according to $SO_{2\,(g)}$ + $NO_{2\,(g)}$ ⇌ $SO_{3\,(g)}$ + $NO_{(g)}$. If $3.0\ mol\ SO_{2\,(g)}$ is added to the mixture, what will be the new concentration of NO when equilibrium is reached?

  Answer –