Unit 8B Equilibrium

What is Equilibrium? Lesson 1

EQUILIBRIUM is a dynamic [ever changing] condition where rates of opposing processes are equal.

- o Can only take place in a closed container/space

- Types of Equilibrium:
  - o Physical Equilibrium: ____________________________ and _____________________________
  - o Chemical Equilibrium

Phase Equilibrium

- Rate of one ______________ ___________ is equal to the rate of the opposing phase change.
- Occurs when two phases exist at the same temperature.
  - o Think about those heating/cooling curves and the plateaus where Melting/Freezing and Condensing/Vaporizing took place

In an open container
All liquid molecules will eventually convert to a gas and leave the container
In a closed container
The liquid converts into a vapor but remains just above the remaining liquid (due to the closed lid of the container) creating vapor pressure.

Dynamic Equilibrium

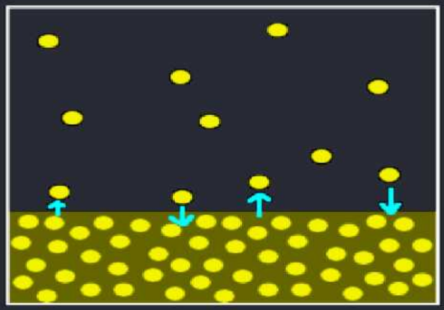
→ Molecules initially escape from ____________.

→ As the vapor builds up some vapor __________ back to a liquid.

→ Eventually the rate of the forward reaction equals that of the reverse reaction.

Vapor Pressure

→ The pressure of the _________ above a liquid



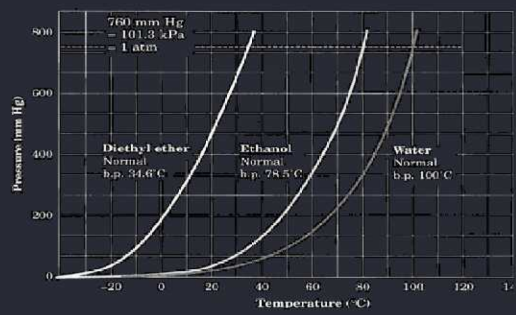
Factors That Affect Vapor Pressure

→ Intermolecular Forces

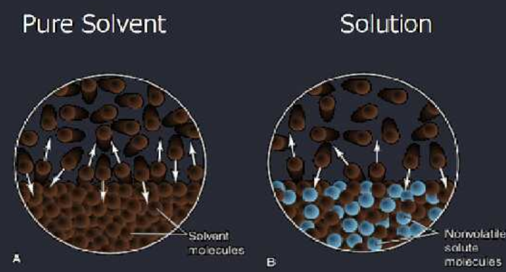
- o The forces between _________________________
  - ▪ *The stronger the intermolecular forces the lower the vapor pressure and vice versa*
- o Strong Forces such as ________________ ____________ and dipole forces are harder to break creating a ___________ vapor pressure
- o Weak forces such as London dispersion forces are easier to break creating a ________ vapor pressure.

→ Temperature

- o As temperature increase, molecules have more ___________ ____________ to break their intermolecular forces between liquid molecules



- This is due to the solvent not being able to convert to a gas as often

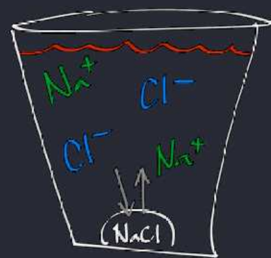


→ **Adding a solute to a solvent**
- Lowers the vapor pressure of a liquid

→ **What Factors <u>CANNOT</u> Affect Vapor Pressure?**
1) Changing the container size
2) Adding more of the solvent to the container

Solution (Physical) Equilibrium

- Rate of ______________ = rate of __________________
  - Meaning that the rate of the compound decomposing [separating] equals the rate ions reconnecting into ionic compounds as shown in the diagram to the right.
- Occurs in saturated solutions



Equilibrium in Chemical Reactions

→ SO far, we have only talked about chemical reactions that proceed in one direction, from Reactants to Products and then STOP

$$A + B \rightarrow C$$

- Equilibrium is not reached if one of the products is withdrawn as quickly as it is produced and no new reactants are added.
- Reaction __________________ until reactants are used up.

→ BUT most chemical reactions are able to proceed in both directions under the appropriate conditions. (closed container) They are REVERSIBLE!
Example:

$$Fe_3O_{4\,(s)} + 4\,H_{2\,(g)} \leftrightarrow 3\,Fe_{(s)} + 4\,H_2O_{(g)}$$

→ ***WHEN DOES IT STOP?*** ***It doesn't.***

Reversible Reactions

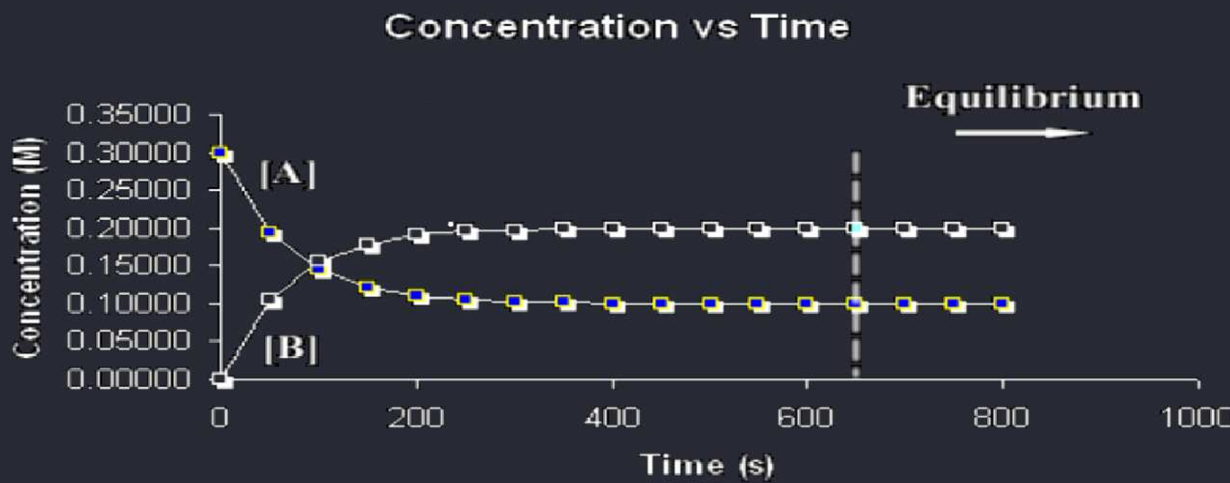
→ Represented by a double arrow between reactants and products ↔

→ In a closed system, as products are produced they will react in the reverse reaction until the ___________ of the forward and reverse reactions are ______________.

$$Rate_{fwd} = Rate_{rev}$$

→ This is called _________________ _______________.
- Rate depends on concentration

- The forward rate of a reaction decreases over time
- The reverse rate of a reaction increases over time
- Eventually the 2 rates become equal



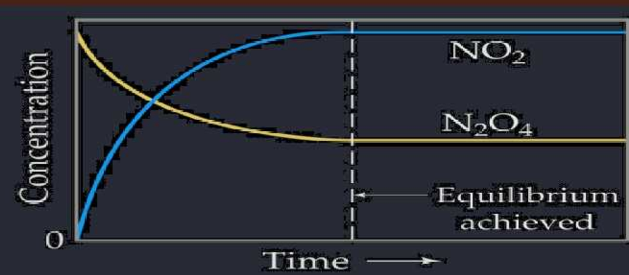
The Concept of Equilibrium

→ Once equilibrium is achieved, the amount of each reactant and product remains constant

→ CON CON REQUAL: Concentration of reactants and products are ____________ , not necessarily equal. Rates are Equal!

→ Depicting Equilibrium

- A __________ __________ identifies that a reaction is in equilibrium.



$N_2O_{4\,(g)} \rightleftharpoons 2\ NO_{2\,(g)}$

Lesson 2 Writing Equilibrium Equations

→ The equilibrium expression is **ratio of _____________ over _____________.**

→ **Only use _______________ or ____________** substances in the expression; never use pure solids or liquids

Writing an Equilibrium Expression

$$aA + bB \leftrightarrow cC + dD$$

The equilibrium expression for this reaction would be...

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

The lower case letter = ***coefficent***

The upper case = ***chemical formula***

K *is the equilibrium constant*

Practice: Write Equilibrium expressions

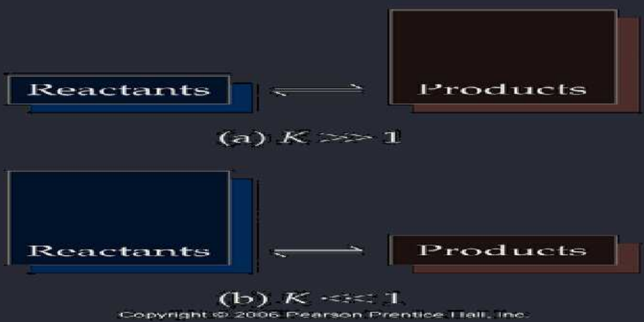
1. SnO_2 (s) + 2CO (g) ↔ Sn (s) + $2CO_2$ (g)

2. $CaCO_3$ (s) ↔ CaO (s) + CO_2 (g)

3. Zn (s) + Cu^{2+} (aq) ↔ Cu (s) + Zn^{2+} (aq)

What Does the Value of *K* Mean?

- If *K* >> 1, the reaction is *product-favored;* product predominates at equilibrium.
- If K << 1, the reaction is *reactant-favored;* reactant predominates at equilibrium



Equilibrium Can Be Reached from Either Direction

As you can see, the ratio of $[NO_2]^2$ to $[N_2O_4]$ remains constant at this temperature no matter what the initial concentrations of NO_2 and N_2O_4 are.

Lesson 3: Le Chatelier's Principle

- Whenever a _______________ is applied to a reaction at equilibrium, the reaction will ___________ its point of equilibrium to offset the stress.
- Stresses include:
  - Change Temperature
  - Change Pressure
  - Changes concentrations [product or reactant]

Change in Concentrations [of a Reactant or Product] **ADD AWAY, TAKE TOWARDS**

- Adding a reactant or product shifts the equilibrium away from the ___________________.
  - Increase product – makes more reactant
  - Increase reactant – makes more product
- Removing a reactant or product shifts the equilibrium towards the ___________________.
  - Decrease product – makes more product
  - Decrease reactant – makes more reactant

Example: The Haber process [Change in Concentration]

$$N_2\,(g) + 3H_2\,(g) \leftrightarrow 2NH_3\,(g)$$

If H_2 is added while the system is at equilibrium, the system must respond to counteract the added H_2

- That is, the system must consume the H_2 and produce products until a new equilibrium is established.

Therefore, $[H_2]$ and $[N_2]$ will decrease and $[NH_3]$ increases.

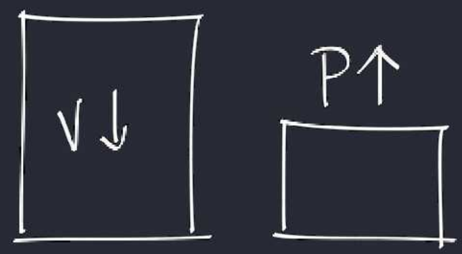
Effects of Volume & Pressure on Gaseous Equilibrium.

→ Volume & pressure have a inverse relationship

→ Increasing pressure (decrease in ________________) favors the direction that has fewer moles of gas.

→ Decreasing _______________ (increase in volume) favors the direction that has greater moles of gas.

→ In a reaction with the same number of products and reactant moles of gas, pressure has no effect.



Example: Increase Volume **Change to Pressure and ADD AWAY, TAKE TOWARDS MORE MOLES**

$$N_2O_4\,(g) \leftrightarrow 2NO_2\,(g)$$

If the volume of the container increases while the system is at equilibrium (pressure of the gas decreases), the system must respond to counteract the decreased pressure

- That is, the system will shift to the right ;more moles of product will form until a new equilibrium is established.- this raises the pressure back to where it originally was
- Therefore, $[NO_2]$ will increase and $[N_2O_4]$ decreases.

Example: Increase Pressure -**ADD AWAY TAKE TOWARDS MORE MOLES**

$$N_2O_4\,(g) \leftrightarrow 2NO_2\,(g)$$

An increase in pressure (by decreasing the volume) favors the formation of colorless N_2O_4.

- The instant the pressure increases, the system is not at equilibrium and the concentration of both gases has increased.
- The system moves to reduce the number moles of gas: shifts left
- A new equilibrium is established!

Effects of Temperature Change=
Add the word "heat" to the correct side Then ADD AWAY, TAKE TOWARDS

→ The equilibrium constant is temperature dependent.

- For an _______________ reaction, $\Delta H >$ or ΔH is positive (+); heat can be considered as a reactant.
- For an _______________ reaction, $\Delta H < 0$ or ΔH is negative (-); heat can be considered as a product.

→ Removing heat (i.e. cooling the vessel), favors towards the decrease:

- if _______________, cooling favors the reverse reaction,
- If _______________, cooling favors the forward reaction.

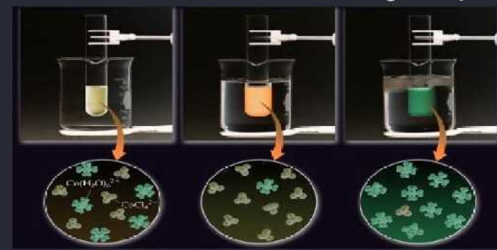
→ Adding heat (i.e. heating the vessel) favors away from the increase:

- If _______________, adding heat favors the forward reaction,
- If _______________, adding heat favors the reverse reaction.

Example:

ΔH =+50KJ; If the temperature is lowered, the reaction will shift to the left and the solution will change to pink making more $Co(H_2O)_6^{2+}$

$$Cr(H_2O)_6(aq) + 4Cl^-(aq) \rightleftharpoons CoCl_4^{2-}(aq) + 6H_2O(l)$$



Example: The Haber process **$N_2\ (g) + 3H_2\ (g) \leftrightarrow 2NH_3\ (g)$**

Stress Added	Shift	Stress Added	Shift
[a] Increase [N_2]	________	[e] Increase pressure	________
[b] Decrease [H2]	________	[f] Increase volume	________
[c] Increase [NH3]	________	[g] Increase temperature	________
[d] Decrease [NH3]	________	[h] Decrease temperature	________

OVERVIEW: Equilibrium shifts due to stresses:

- Concentration increase ____________________ from increase
- Concentration decrease **shift toward** decrease
- Increase [↑] in pressure **shifts in direction of ______________________________.**
- Decrease [↓] in pressure **shifts in direction of more gas molecules**
- Increase [↑] in temperature favors endothermic reaction ____________________ **from heat**
- Decrease [↓] in temperature favors exothermic reaction **shift towards heat**

Effect of Catalyst:

→ Addition of __________________ increases the rate of both the forward and reverse reactions.

- o There is no change in concentrations but equilibrium is reached more rapidly.

→ **Does not __________________ the value of K [aka no shift to reaffirm equilibrium]**

The Haber Process: Industrial Production of Ammonia

→ Application of Le Chatelier's Principle: ***$N_{2\,(g)} + 3\ H_{2\,(g)}$ $2\ NH_{3\,(g)} + 92\ kJ$***

Increase pressure	Shift Right
Decrease Temp	Shift Right
Remove NH_3 add N_2 and H_2	Shift Right

Maximum yields of NH_3 occurs under high pressures, low temperatures and by constantly removing NH_3 and adding N_2 & H_2