Unit 8 (Thermodynamics & Kinetics) Test Review Sheet

Dynamic Equilibrium

Equilibrium is a state of balance between two opposing (opposite) processes occurring at the same time (simultaneously).

When equilibrium is reached in a system:

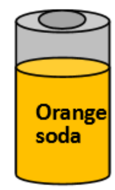
- *Rate* of the forward process is *equal* to rate of the reverse process
- *Concentrations* (or amounts) of substances remain *constant*

Equilibrium can only occur in a closed system in which changes that are taking place are *reversible*. A closed system is a system in which nothing is allowed in or out. For an example, if a soda can is left closed, carbon dioxide gas will not be able to get inside the can from the outside, or allowed to escape out of the can to the outside. Inside the can, carbon dioxide will move in and out of the liquid of the soda can. If left undisturbed, equilibrium will be reached when the movements of carbon dioxide gas into the liquid (*dissolving*) and out of the liquid (*undissolving*) is occurring at the same rate. (see next page).

Equations showing a reversible process at equilibrium always contain a double ended arrow. (<——> or <=====>)

$$CO_2(g) \underset{\text{Reverse}}{\overset{\text{Forward}}{\rightleftarrows}} CO_2(aq)$$

Both physical and chemical changes can reach a state of equilibrium.



Closed can
Equilibrium process will occur in this can.

Open soda can
Equilibrium process CANNOT occur in this can.

Chemical equilibrium occurs in chemical changes that are reversible. *Recall* that chemical changes lead to changes in composition of substances. Chemical equilibrium, therefore, occurs in changes in which one or more substances are changing to other substances.

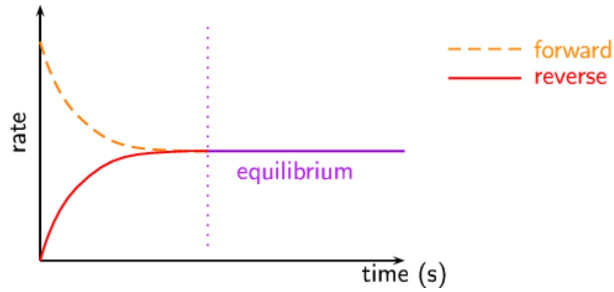
$$N_2(g) \quad + \quad 3H_2(g) \underset{\text{Reverse reaction}}{\overset{\text{Forward reaction}}{\rightleftarrows}} 2NH_3(g)$$

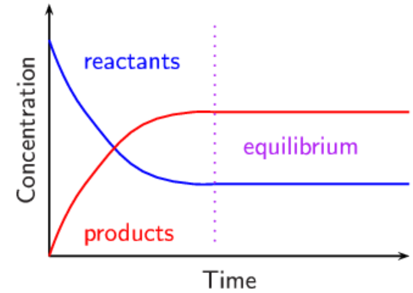
Consider the *Haber process* reaction above:
At the start of the reaction the reactants, N_2 and H_2, will combine to produce NH_3 in the forward reaction. As NH_3 is being produced, the reverse reaction, in which NH_3 is decomposing to produce N_2 and H_2 will start. The speed (or rate) of this reverse reaction will be slow at first. As more and more NH_3 are being produced, the forward reaction will slow down, while the reverse reaction will speed up. Eventually, the forward and reverse reactions will be occurring at the same rate (equal speed). This means that if at a given time period 10 molecules of NH_3 are being produced, there will be 10 other molecules of NH_3 breaking up to produce N_2 and H_2. When the rates of the reactions (forward and reverse) are equal, the reaction is said to have reach a state of **equilibrium.**

At equilibrium:

- *Rate* of forward is *equal* to the rate of reverse.
- *Concentrations* of N_2, H_2, and NH_3 will be *constant* (unchanged).

We can graph reactions as they proceed to chemical equilibrium, as shown below





Phase equilibrium occurs in a *closed system* in which phase changes are occurring. Recall that temperature is important to phase changes. At a specific temperature of a substance, a state of balance (equilibrium) can be reached between two opposing phase changes of the substance. The temperature at which a particular phase equilibrium is reached is different for different substances.
Phase change equilibrium in water are described below.

Ice / water equilibrium: at 0°C or 273 K (melting and freezing points of water at normal pressure)

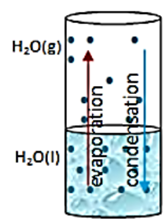
- Equilibrium exists between ice melting and liquid freezing
- *Rates* of melting and freezing are *equal*
- *Amounts* of ice and water remain *constant*

$H_2O(s) \underset{\text{freezing}}{\overset{\text{melting}}{\rightleftharpoons}} H_2O(\ell)$ Ice/liquid water equilibrium equation

Water /steam (vapor) equilibrium: at 100°C or 373 K (boiling point of water at normal pressure)

- Equilibrium exists between liquid evaporating and steam condensing
- *Rates* of evaporation and condensation are *equal*
- *Amounts* of liquid and steam remain *constant*

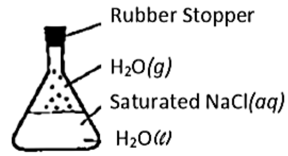
$H_2O(\ell) \underset{\textit{condensation}}{\overset{\textit{evaporation}}{\rightleftharpoons}} H_2O(g)$ water/steam equilibrium equation



Solution equilibrium occurs in a closed system in which a substance is dissolving in a liquid.
Two examples of solution equilibriums are described below.

Solid in liquid equilibrium: In a saturated solution

- Equilibrium exists between dissolved particles and undissolved particles
- *Rates* of dissolving of solid and crystallization of ions are equal
- *Amounts* of solid and ions remain *constant* in the solution



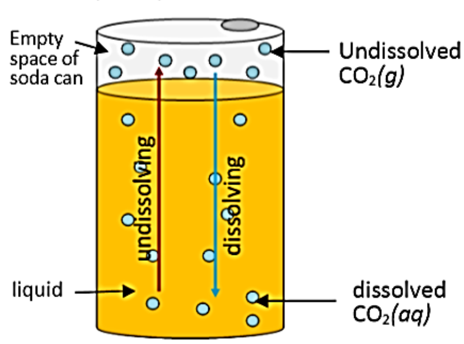
$NaCl(s) \underset{\textit{crystallizing}}{\overset{\textit{dissolving}}{\rightleftharpoons}} Na^+(aq) + Cl^-(aq)$

Gas in liquid equilibrium: In a gaseous solution

- Equilibrium exists between dissolved gas in the liquid and undissolved gas above the liquid
- *Rates* of dissolving and undissolving of gas are *equal*
- *Amounts* of undissolved gas (above liquid) and dissolved gas (in liquid) remain constant

$CO_2(g) \underset{\textit{undissolving}}{\overset{\textit{dissolving}}{\rightleftharpoons}} CO_2(aq)$

Gas in liquid equilibrium in a closed soda can.



Enthalpy (ΔH) Heat of Reaction

A summary of exothermic and endothermic reactions is given below. Use this table for a quick study and comparison of the two reactions.

Reaction	*Potential Energy of Reactants*	*Potential Energy of Products*	*Energy Change*	*Temperature of Surrounding*	*Heat of Reaction (ΔH)*
Exothermic	Higher	Lower	Released	Increases	Negative (-ΔH)
Endothermic	Lower	Higher	Absorbed	Decreases	Positive (+ΔH)

Heat of Reaction is the difference between the potential energy of the products and reactants as shown below:

$\Delta H = PE_{PRODUCTS} - PE_{REACTANTS}$

ΔH is positive (+) for an endothermic reaction

ΔH is negative (-) for an exothermic reaction

***Table I is a list of Heats of Reaction at a Specific Pressure and Temperature**

Examples of Reading Table I

Ex 1: N_2 (*g*) + $3H_2$ (*g*) → $2NH_3$ (*g*) shows a ΔH value of -91.8 kJ
This reaction is "exothermic" since ΔH is negative
Since the value of ΔH is negative it also means that the products have less potential energy than the reactants. The difference in energy was released to the surroundings in the form of heat.

Ex 2: N_2 (*g*) $2O_2$ (*g*) → $2NO_2$ (*g*) shows a ΔH value of +66.4 kJ
This reaction is "endothermic" since ΔH is positive
Since the value of ΔH is positive it also means that the products have more potential energy than the reactants. The difference in energy was absorbed from the surroundings.

MUST KNOW HOW TO WRITE THE HEAT OF REACTION IN A CHEMICAL EQUATION
Example for Exothermic: *A* + B → *C* + heat (Amount of heat is on the right side)
Example for Endothermic: *A* + B heat → *C* (Amount of heat is on the left side)

Sample Problem of Writing Heat in Chemical Equations

Ex 1: Write the amount of heat into the equation for N_2 (*g*) + $3H_2$ (*g*) → $2NH_3$ (*g*) based on Table I
Answer: N_2 (*g*) + $3H_2$ (*g*) → $2NH_3$ (*g*) + 91.8 kJ

Ex 2: Write the amount of heat into the equation for N_2 (*g*) + $2O_2$ (*g*) → $2NO_2$ (*g*) based on Table I
Answer: N_2 (*g*) $2O_2$ (*g*) + 66.4kJ → $2NO_2$ (*g*)

Calculating Total Heat Released or Absorbed in a Reaction

Example: How much heat is produced when 1 mol of ammonia is synthesized from its elements?

$N_2\ (g) + 3H_2\ (g) \rightarrow 2NH_3\ (g) + 91.8\ kJ$

To solve this problem, set up the problem as a proportion:

2 mol NH_3 /91.8 kJ = 1 mol N_2 / X kJ Solve for X kJ =45.9kJ

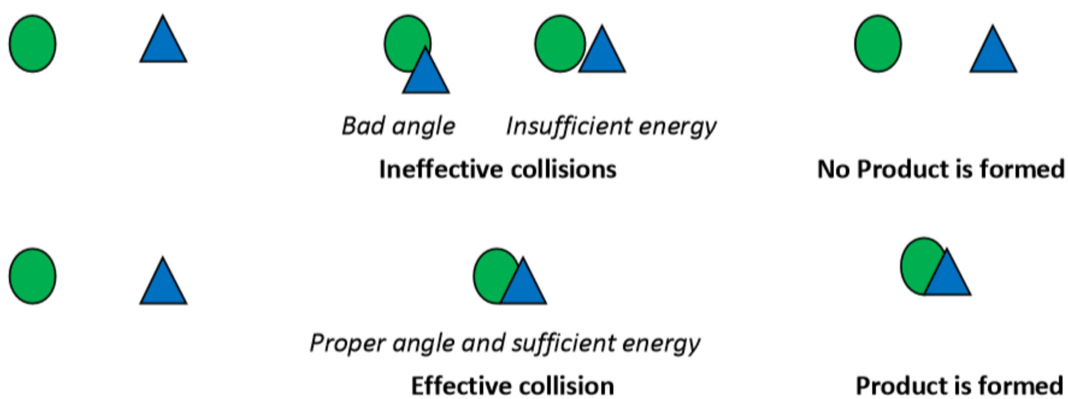
Collision Theory

-Reactants must collide in a reaction to produce products

-Collisions must have the correct orientation

-Collisions must occur with enough energy

-Minimum amount of energy is called the "activation energy"



Activation energy is the energy needed to start a chemical reaction.

- All chemical reactions, both endothermic and exothermic, require some amount of activation energy.
- Chemical reactions that require low activation energy are faster than those that require high activation energy.
- Any factor that can change the amount of activation energy needed for a reaction will change the rate of that reaction.
- Any substance that can lower the activation energy for a reaction will increase (speed up) the rate for that reaction.

A **catalyst** is a substance that can increase the speed (rate) of a reaction by lowering the activation energy

- A catalyst in a reaction provides an alternate (lower activation energy) pathway for a reaction to occur faster.

and $\mathbf{O_2}$ react (burn) to produce MgO as shown in equation below.

$$2Mg + O_2 \rightarrow 2MgO$$

However, Mg strip must be lit with a Bunsen burner before it can burn with O_2.

The flame provides the activation energy needed to start the reaction.

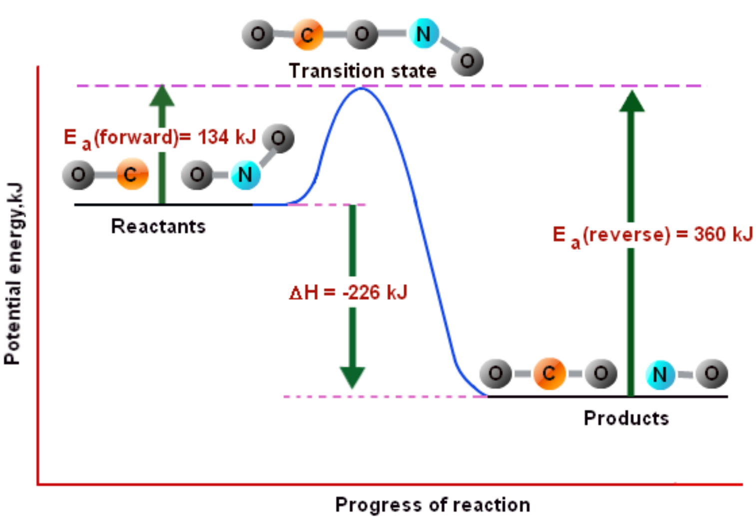
Factors that will increase reaction rate	*Reasons why rate increases*
1. ***Increasing*** **concentration** of reactants	Increases number of reacting particles. Increases frequency of effective collisions between reacting particles.
2. ***Increasing*** **temperature** of reactants	Increases kinetic energy of reacting particles. Increases frequency of effective collisions.
3. ***Increasing pressure*** on the reaction	Decreases volume of gaseous reactants. Increases concentration of gaseous reactants. Increases frequency of effective collisions.
4. ***Increasing surface area*** of reacting solids	Exposes more area for reactions to occur. Increases frequency of effective collisions.
5. ***Addition of a catalyst*** to a reaction	Provides a lower activation energy (alternate) pathway for a reaction to occur.

Reaction Potential Energy Diagrams

Exothermic diagram: **Potential energy of products less than reactants**
Endothermic diagram: **Potential energy of products more than reactants**

Know the different parts of both the Exothermic and Endothermic Potential Energy Diagrams, Including:

Potential Energy of Reactants
Potential Energy of Products
Potential Energy of Activation Complex (Transition State)
Activation Energy of Forward and Reverse Reactions (Catalyst reduces height of the activation energy)
Heat of Reaction is the difference between the potential energy of the products and reactants.



Exothermic PE Diagram Example

Entropy & Spontaneous Processes

During chemical and physical changes, particles of a substance may rearrange from one phase to another. Particles can become more or less organized depending on the type of change the substance has gone through.

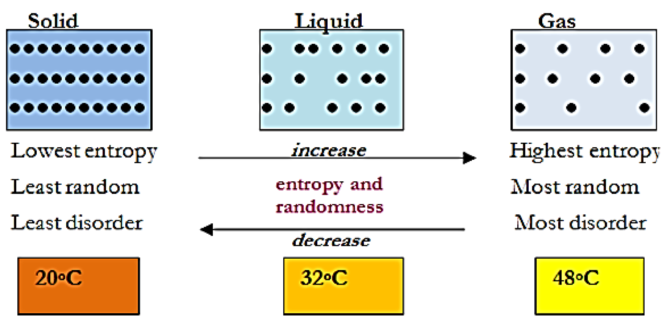
Entropy is a measure of randomness or disorder of a system.

In chemistry, a system refers to any chemical or physical process that is taking place.

Entropy of chemical and physical systems is relative, meaning that randomness or disorder of one system can only be described when compared to another system.

- Entropy increases from solid to liquid to gas
- Entropy decreases from gas to liquid to solid
- As temperature increases, so does the entropy of the system
- As pressure increases, entropy of the system decreases
- Entropy of free elements is higher than entropy of compounds

Change in Entropy



- A physical or chemical change tends to occur by itself (spontaneously) if the ***change leads to a greater entropy and a lower enthalpy (energy) state.***

In physical changes, entropy increases as a substance changes from:

solid to liquid to gas

Ex: $CO_2(s) \xrightarrow[\text{increase entropy}]{} CO_2(g)$

In chemical changes, entropy increases if the reactants are changed in any of the orders listed below.

solid to liquid to aqueous to gas

Ex. $C(s) + O_2(g) \xrightarrow[\text{increase entropy}]{} CO_2(g)$

smaller moles of reactants to greater moles of products.

Ex $\underline{2}H_2O(g) \xrightarrow[\text{increase entropy}]{} \underline{2}H_2(g) + \underline{1}O_2(g)$

a compound reactant is changed to free elements

Ex $2AB \xrightarrow[\text{increase entropy}]{} A_2 + B_2$

Entropy decreases if any of the above changes is reversed.

Spontaneous Processes

- **Spontaneous**: process that ***does*** occur under a specific set of conditions
- **Nonspontaneous**: process that ***does not*** occur under a specific set of conditions

Le Chatelier's Principle

A **stress** is any change in concentration, temperature or pressure to an equilibrium reaction. Questions on chemical equilibrium often involve determining a result of a stress to an equilibrium reaction, or determining which stress will cause a particular change to a reaction.

Le Chatelier's Principle states that when a stress is introduced into a reaction at equilibrium, the reaction will change by speeding up in one direction and slowing down in the other direction to bring back or re-establish the reaction to a new equilibrium point. The concentrations of the substances at the new equilibrium point will be different from those at the old equilibrium point. There will be an increase in concentration of some substances, and a decrease in others.

LE CHATELIER'S PRINCIPLE

STRESS	SHIFT	WHY?
increase concentration of a substance	*away* from substance	extra concentration needs to be used up
decrease concentration of a substance	*towards* substance	need to produce more of substance to make up for what was removed
increase pressure of system	towards *fewer* moles of gas	for gas: pressure increase = volume decrease
decrease pressure of system	towards *more* moles of gas	for gas: pressure decrease = volume increase
increase temperature of system	*away* from heat/ energy *exothermic* reaction is favored	extra heat/ energy must be used up
decrease temperature of system	*towards* heat/ energy *exothermic* reaction is favored	more heat/ energy needs to be produced to make up for the loss
add a catalyst	NO SHIFT	The rates of both the forward and reverse reactions are increased by the same amount.