

CHEMICAL EQUILIBRIUM occurs **when**

Also referred to as

TWO IMPORTANT CHARACTERISTICS OF A SYSTEM AT EQUILIBRIUM:

(1)

(2)

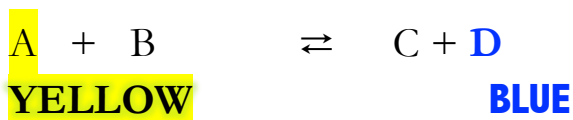
EQUILIBRIUM CAN BE DETERMINED **when**

Example:

If it is a reaction in which a solution is turning a particular colour, the colour will be getting darker or more intense before equilibrium, but once the equilibrium is established, the colour will become constant. This does NOT imply that the reaction has stopped.

Using radioactive isotopes in labeling experiments, it has been experimentally shown that **equilibrium is**

Instead of the reaction stopping, what has happened is **that**



At equilibrium, as a D molecule is produced, one D molecule is used up, therefore **the colour you observe**

EQUILIBRIUM CAN BE ALTERED by either changing the concentration of the reactants or products, or by changing the temperature.

Note: changing pressure only affects gaseous reactions. The pressure of a gas is directly proportional to its concentration at a constant temperature. I gave you a mathematical proof of this in Unit 1, when discussing the effect of concentration on the rate of a reaction.

From the $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$ reaction example at the beginning of this topic, the acid catalyst is not a stress on the equilibrium; it allows the equilibrium to be achieved in a *shorter period of time, or by following a alternate pathway.*

In order for a physical process (eg. change of state) or a reversible chemical reaction to be at equilibrium, it must be in a **closed system**.

In an **open system**, the products or reactants would leave the reaction vessel, and equilibrium could not be achieved.

In a chemical equilibrium, no NET chemical reaction occurs.

With **REVERSIBLE REACTIONS**, this is achieved when the opposing reactions reach a balance. This is the **DYNAMIC EQUILIBRIUM**

With **IRREVERSIBLE REACTIONS**, this is achieved at the completion of the transformation. This is called **STATIC EQUILIBRIUM**

eg. baking a cake



Dynamic equilibrium is reached when the **REACTION RATE** *products* equals **REACTION RATE** *reactants* in a closed system during a reversible transformation.

Dynamic equilibrium is characterized by:

- constant macroscopic properties (T, P, M, colour, ppt...)
- continuing microscopic activity (opposing reactions continue)
- reversibility: rate F = rate R
- closed system [cannot exchange mass or energy with its surroundings - this is most difficult to achieve as most systems are open eg. glass of coke, planet earth (open atmosphere; sunlight, etc.)]

Perfect dynamic equilibrium is not practically achievable, however, we can approximate it closely in our labwork and industrial processes.

EXAMPLES:

1. It is very difficult to achieve a truly CLOSED SYSTEM wrt to the loss or gain of Heat, Light and Mass
2. Water bottle: microscopic activity. Is the system at equilibrium?
3. $\text{CO (g)} + \text{Cl}_2 \text{ (g)} \rightleftharpoons \text{COCl}_2 \text{ (g)}$
Can this reaction produce pure phosgene, $\text{COCl}_2 \text{ (g)}$?

HW Before next class:

REVIEW/PREVIEW: read 5.4, 5.10, 5.11 in text (ENTHALPY AND ENTROPY)
do review questions at the end of each of these sections
KEEPING UP: read sections 7.1, 7.2, 7.3 & do review questions
at the end of each of these sections

IN YOUR TEXTBOOK READING, YOU SHOULD HAVE REVIEWED:**5.4:**

Recall the definitions of exothermic and endothermic reactions.
 ΔH values for each.

exo: releases heat to surroundings, negative ΔH

endo: absorbs heat from surroundings, positive ΔH

5.10:

Recall the definition of Spontaneous reactions.

If a reaction occurs at all it is called Spontaneous.

eg. chemical change: combustion of methane with oxygen

physical change: weathering of rocks, melting

TWO DRIVING FORCES IN A SPONTANEOUS REACTION:

a) a drive to minimum enthalpy ΔH

b) a drive to maximum entropy S

Recall the definition of Entropy.

Entropy is the degree of disorder or randomness.

The law of disorder states that a spontaneous reaction in an isolated system always proceeds in the direction of increasing entropy.

(in text they give an example of Kits Beach - sodium and chloride ions will not form sodium chloride and precipitate out of solution from the ocean water. Ions in solution have higher entropy than ions in crystal lattice structure)

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more review next pages!

5.11:

Recall GIBBS FREE ENERGY

A reaction with neg ΔH and pos S will always be favoured because it satisfies both conditions that drive a rxn to spontaneity.

(A reaction with pos ΔH and neg S will NEVER BE SPONTANEOUS) - AN ENDOTHERMIC RXN will only occur if it has increasing entropy.

RECALL FROM UNIT 1:

Entropy can be defined as the measure of the randomness of a chemical system. A large value for entropy means very random. If entropy increases during a chemical reaction, it means the system is becoming more random or disordered.

These two variables are related in the Gibb's free energy equation which says:

$$\Delta G^\circ = \Delta H - T\Delta S^\circ$$

$^\circ$ indicates standard state conditions.

where ΔG is a measure of the energy available to do useful work from a chemical reaction.

ΔG has units of Joules (J).

T is temperature.

If $\Delta G < 0$, the reaction is spontaneous to the right and useful work can be done.

If $\Delta G > 0$, the reaction as written is not spontaneous to the right but the reverse reaction would be spontaneous.

If $\Delta G = 0$ then the chemical system is at equilibrium.

(the rate of the forward rxn equals the rate of the reverse rxn so no useful work can be obtained from this system).

A "MUST" for understanding:

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THERMODYNAMICS:

-THE STUDY OF ENERGY AND ITS POTENTIAL TO DO WORK.

More exactly it is the physical science discipline which studies energy conversion and energy transfer

FIRST LAW OF THERMODYNAMICS:

Principle of Conservation of Energy:

"Energy may be converted from one form to another, but it cannot be created or destroyed. The total energy in the Universe is constant."

SECOND LAW OF THERMODYNAMICS:

"Energy cannot be used to do work without some loss to the surrounding environment."

This energy loss is a loss to entropy since the energy lost is unavailable to do useful work. The energy loss results in a more chaotic system or environment since it is employed in counter-productive ways.

Resulting corollaries are:

"A machine cannot be 100% efficient"

"Work cannot be done without paying a price to entropy"

eg. light a candle: PE stored in chemical bonds is changed to heat and light when candle is lit.

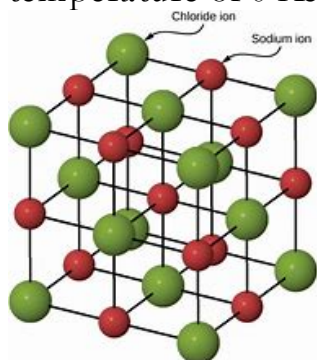
losses to: sound, deformation of candle, smoke/fuel loss, chaotic air flow around candle

eg. CAR: PE stored in chemical bonds of HC fuel. PE converted to KE, electrical, and sound energy.

losses to: heat, engine vibration, sound energy, friction (engine, wheels), atmosphere (pollution increases), electrical resistance, fuel loss, self destruction due to heat and friction

THIRD LAW OF THERMODYNAMICS:

"The entropy of a perfect crystalline material of a pure substance is zero at a temperature of 0 Kelvin. (absolute zero)"



If any atom is out of place in the "grid" of the crystalline structure, entropy is inevitable!

Corollary:

MOST ORGANIZED----- > LEAST ORGANIZED
(low S) solids liquids gas & solutions **(high S)** plasma

APPLICATION OF MINIMUM ENTHALPY AND MAXIMUM ENTROPY TO CHEMICAL EQUILIBRIUM:

These two tendencies decide where the balance will be struck between PRODUCTS and REACTANTS during a chemical or physical change.

Entropy and energy (ENTHALPY) determine which side of the reaction wins and how much it wins by...

eg. 20% reactants and 80% products at 300K

OR 40% reactants and 60% products at 200K

Since S and H tend to oppose each other, most reactions are **reversible and incomplete**. This is a facet of Chemistry not considered prior to Chem 12. (recall in Chem 11 when we calculated theoretical yields...we assumed that if 40 moles of a limiting reagent were used, we could accurately determine the moles of product used, based on a mole ratio).

The tendency to lowest energy (Enthalpy) is dominant at **low temperature**.

The tendency to highest Entropy is dominant at **High temperature**.

Only temperature influences the S vs. H struggle.

eg. $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g}) + \text{kJ}$

→ minimum enthalpy

PE diagram:

← maximum entropy

(more moles,
more variety of molecules)

Example of Entropy increasing:
(based on the over simplification that entropy is basically the chaos model)

- more moles (more particles in motion)
- more variety of molecules
- more phases of matter (heterogeneity)
- temp. increases (KE of molecules increases causing higher entropy)
- more moles of the more random phase

EXAMPLES of this bullet point:

LIQUID vs. SOLID

-melting (more random arrangement of particles...recall KMT Gr 8)

GAS vs. LIQUID

-vapourization (more random arrangement of particles; increased translational energy)

GAS vs. SOLID

-sublimation (more random arrangement of particles; increased translational energy)

SOLUTION vs. LIQUID

-two miscible liquids

-solute dissolved in solution

(particles become scattered amongst one another - see pic p. 217)

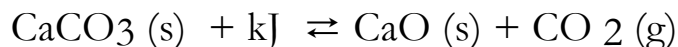
IONS vs. ATOMS

MORE COMPLEX BONDING = higher entropy!

The heavier and more complex a molecule is, the greater its compound's entropy.

(more chance for variability in atoms)

AN ADDITIONAL SAMPLE QUESTION:



←

minimum enthalpy

→

maximum entropy

SAMPLE EXERCISES

S vs. H

PREDICT WHICH DIRECTION entropy AND enthalpy PREFER IN THE FOLLOWING REVERSIBLE REACTIONS (“at equilibrium”). BE SURE TO JUSTIFY YOUR CHOICE WITH A CLEAR REASON (OR TWO!) FOR min. H and max. S IN EACH CASE!

