



CHEMISTRY

25th class Date : 18-10-2021

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Chapter II - Physical chemistry



- ☐ Thermodynamics : U, Q, W, T, H, S, ΔG , Gibbs-Helmholtz equation
- ☐ Chemical equilibrium and solubility product
- ☐ Electrochemistry : Nernst equation, Applications
- ☐ Corrosion : Types, Pourbaix diagram

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Last class..

- ☐ Thermodynamics : Introduction, Laws, U, Q, W, H, S

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In this class

- ☐ Thermodynamics : U, Q, W, H, S, continuation

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Thermodynamics



- ❑ The study of heat and work and the transformation of one into the other
- ❑ Deals with very practical phenomenon, e.g., engines, power generation systems
- ❑ Based on observations of energy exchanges between macroscopic systems
- ❑ **Macroscopic** – systems with very large numbers of particles → in 1 m³ there are over 10²⁵ air molecules

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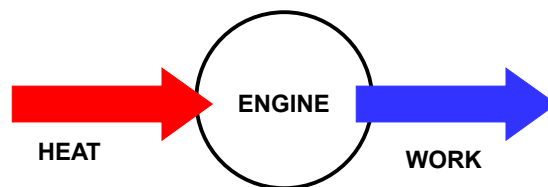
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Thermodynamics



- ❑ The study of heat and work and the transformation of one into the other
- ❑ Thermodynamics deals with devices which use heat to do **work** --- e.g., a steam engine.



$$\text{Efficiency} = \frac{\text{work out}}{\text{heat in}}$$

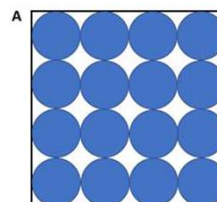
The laws of thermodynamics place limits on the efficiency of engines, observations of energy exchanges between macroscopic systems

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☐ Thermodynamics



The laws of thermodynamics are deceptively simple to state, but they are far-reaching in their consequences.

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In words

0. Two bodies in thermal equilibrium are at same T

1. **Energy can never be created or destroyed.**

$$\Delta E = q + w$$

2. **The total entropy of the UNIVERSE (= system plus surroundings) MUST INCREASE in every spontaneous process.**

$$\Delta S_{\text{TOTAL}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$$

3. The entropy (S) of a pure, perfectly crystalline compound at T = 0 K is ZERO. (no disorder)

$$S_{T=0} = 0 \text{ (perfect xll)}$$

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Thermodynamics



Thermodynamics answers the following question:

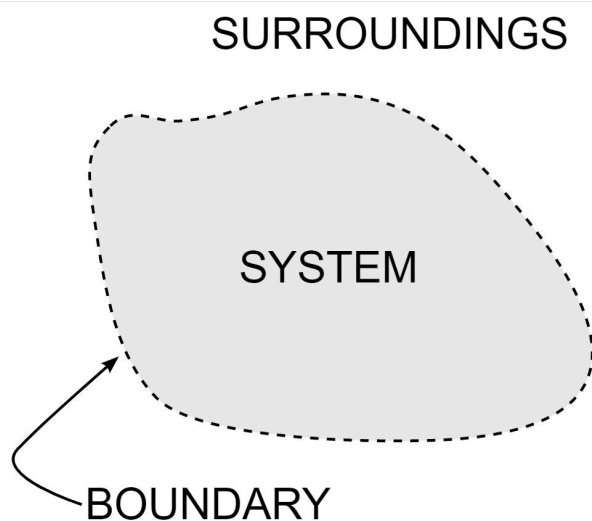
- ❑ For any reaction - defined by a set of reactants and products set in exactly defined conditions (temperature, pressure, concentration, etc.) → will that reaction go forward spontaneously or not??
- ❑ It can address ANY chemical reaction, if thermodynamics says NO, rest assured the reaction will not proceed, if thermodynamics says yes, then we can progress to the next question → how fast? (that is kinetics)

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Origin



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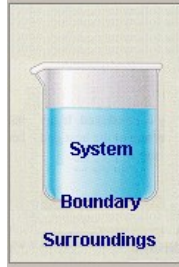
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Origin



- ❑ A thermodynamic system, or simply **system**, is defined as a **quantity of matter or a region in space chosen for study**. The region outside the system is called the **surroundings**. The real or imaginary surface that separates the system from its surroundings is called the **boundary**. The boundary of a system may be fixed or movable



- ❑ Systems may be considered to be **closed** or **open**, depending on whether a fixed mass or a fixed volume in space is chosen for study

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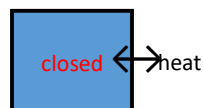
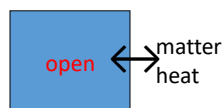
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Systems



- Open system → when matter and heat CAN cross the boundary
- Closed system → when matter CANNOT cross the boundary
- Isolated → Boundary seals matter and heat from exchange with another system



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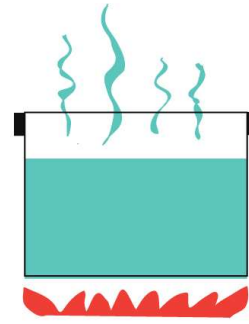
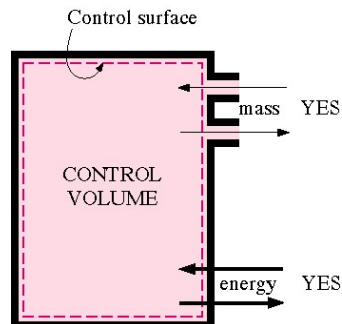
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Systems, examples



- ❑ An **open system** has mass as well as energy crossing the boundary, called a control surface
- ❑ Examples of open systems are **pumps, compressors, turbines, valves, and heat exchangers**



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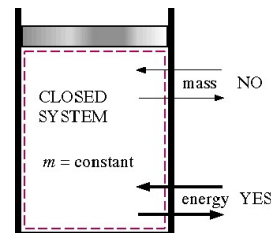
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Systems



- ❑ A **closed system** consists of a fixed amount of mass and no mass may cross the system boundary. The closed system boundary may move.
- ❑ Examples of **closed systems** are **closed saucepan, sealed tanks and piston cylinder devices** (note the volume does not have to be fixed). However, energy in the form of heat and work may cross the boundaries of a closed system.



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Systems



- ❑ An **isolated system** is a general system of fixed mass where no heat or work may cross the boundaries.
- ❑ An isolated system is a closed system with no energy crossing the boundaries and is normally a collection of a main system and its surroundings that are exchanging mass and energy among themselves and no other system.



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Intensive and extensive properties



- ❑ Thermodynamic properties can be divided into 2 general classes such as intensive and extensive properties
- ❑ **Intensive property**, is a physical property of a system that does not depend on the system size or the amount of material in the system. **Examples:** *pressure, hardness, temperature*
- ❑ **Extensive property** of a system does depend on the system size or the amount of material in the system. **Examples:** *volume, mass*

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- ❑ An intensive property is a bulk property, meaning that it is a physical property of a system that does not depend on the system size or the amount of material in the system.
- ❑ Examples of intensive properties include **temperature, T; refractive index, n; density, ρ ; and hardness of an object, n**
- ❑ When a diamond is cut, the pieces maintain their intrinsic hardness, so hardness is independent of the size of the system, for larger samples

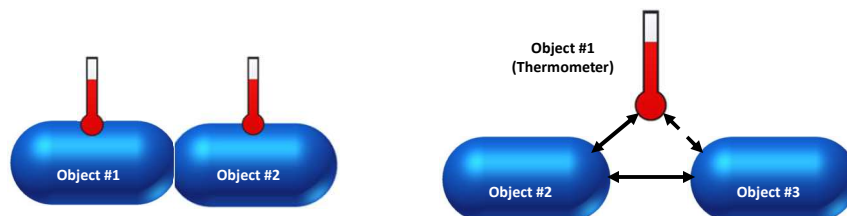
Laws, recap

- ❑ **The Zeroth Law** deals with **thermal equilibrium** and provides a means for measuring temperatures
- ❑ **The First Law** deals with the **conservation of energy** and introduces the concept of **internal energy**
- ❑ **The Second Law** of thermodynamics provides with the guidelines on the **conversion of internal energy of matter into work**. It also **introduces the concept of entropy**.
- ❑ **The Third Law** of thermodynamics defines **the absolute zero of entropy**. **The entropy of a pure crystalline substance at absolute zero temperature is zero.** (entropy of a system approaches a constant value as the temperature approaches absolute zero)

Thermodynamic Equilibrium



- ☐ Thermal equilibrium is obtained when touching objects within a system reach the same temperature
- ☐ When thermal equilibrium is reached, **the system loses its ability to do work**
- ☐ **Zeroth Law of Thermodynamics: If two systems are separately found to be in thermal equilibrium with a third system, the first two systems are in thermal equilibrium with each other**



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- ☐ The thermometer may be the most well-known example of the zeroth law in action.
- ☐ For example, say the thermostat in your room reads 23 degrees C.
- ☐ This means that the thermostat is in thermal equilibrium with your room.
- ☐ However, because of the zeroth law of the thermodynamics, you can assume that both the room and other objects in the room (say, a clock hanging in the wall) are also at 23 degrees C.



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Energy



- ❑ The **internal energy, E** , of a system is the **sum of all the kinetic and potential energies of the components** of the system
- ❑ **Energy is converted to work**, energy in the form of heat moves from one place to another, or energy is stored up in the constituent chemicals
- ❑ **Change in internal energy, denoted ΔE** , is the difference between E_{final} and E_{initial}

$$E = \Delta E_{\text{final}} - E_{\text{initial}}$$

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Energy

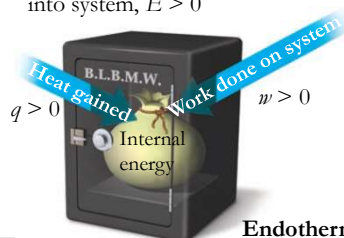


When a system undergoes any chemical or physical change, the accompanying change in internal energy, **ΔU , is the sum of the heat added to or liberated from the system, q , and the work done on or by the system, w .**

$$\Delta U = Q - W$$

First law of thermodynamics

Energy deposited into system, $E > 0$



System is interior of vault

$$\Delta U = Q - P\Delta V$$

Energy withdrawn from system, $E < 0$



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Essential terms of thermodynamics



Essential terms

- ☐ **Enthalpy (H)** – Heat content of a system under a given pressure
- ☐ **Entropy (S)** – The energy of disorderness, not available for work in a thermodynamic process of a system
- ☐ **Free energy change (ΔG)** – Overall free energy difference between the reactant and the product

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Enthalpy



- ☐ It also refers to the **difference in bond energies** between the reactant and product.
- ☐ **In short enthalpy is 'the heat absorbed (or released) by a chemical reaction'.**

$$H = E + PV$$

H = enthalpy

E = energy of the system

PV = pressure in atm times volume in liters

We will define the **enthalpy change**, ΔH , of a system as being equal to its heat output at constant pressure


$$\Delta U = Q - P\Delta V$$

$$\Delta H = Q \text{ at constant pressure}$$

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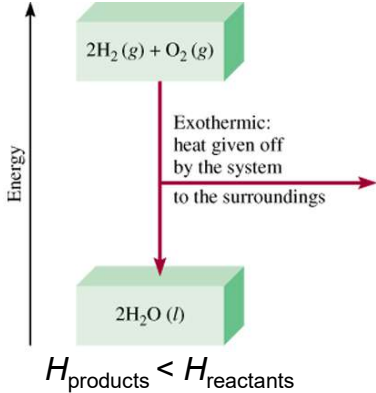
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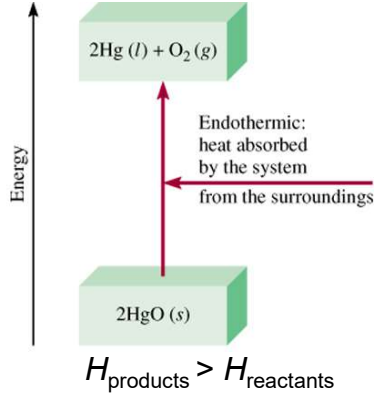
Enthalpy (H) is used to quantify the heat flow into (or out of) a system in a process that occurs at constant pressure

$$\Delta H = H(\text{products}) - H(\text{reactants})$$

ΔH = heat given off or absorbed during a reaction **at constant pressure**




$H_{\text{products}} < H_{\text{reactants}}$
 $\Delta H < 0$




$H_{\text{products}} > H_{\text{reactants}}$
 $\Delta H > 0$

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2nd Law of Thermodynamics

- ☐ Entropy is disorderness
- ☐ A system tends to go from order to disorder



Order



Disorder

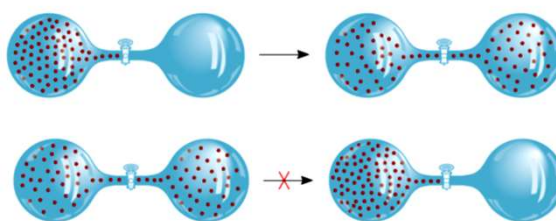
- ☐ Firewood has low entropy (molecules in order) when stacked and high entropy when burning (molecules in disorder)

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Entropy



- ❑ The second law of thermodynamics states that the **entropy** of any closed system, not in thermal equilibrium, will almost **always increases**
- ❑ Entropy is a thermodynamic property, it is the measure of energy (not used to perform work) but is dependent on temperature as well as volume
- ❑ Entropy is directly proportional to **spontaneity**



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Entropy



- ❑ The significance of entropy is that when a **spontaneous change occurs** in a system, it will always be found that if the total entropy change for everything involved is calculated, a **positive value** will be obtained.
- ❑ $\Delta S = S_{\text{final}} - S_{\text{initial}}$ or $\Delta S = S (\text{products}) - S (\text{reactants})$
- ❑ ΔS is change in entropy
 S_{final} and S_{initial} are the final and initial entropies, respectively

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Entropy



- ❑ Comparison of entropies: Gases > liquids > solids (bromine gas has greater entropy than when in liquid state)
- ❑ Entropy is greater for larger atoms (as we move down in groups in periodic table) and molecules with larger number of atoms
- ❑ Entropy is a measure of the number of ways particles as well as energy can be arranged
- ❑ **The change in entropy (ΔS) is equal to the heat transfer (ΔQ) divided by the temperature (T).**

$$\Delta S = (\Delta Q) / T$$

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surr} > 0$$

For a spontaneous process

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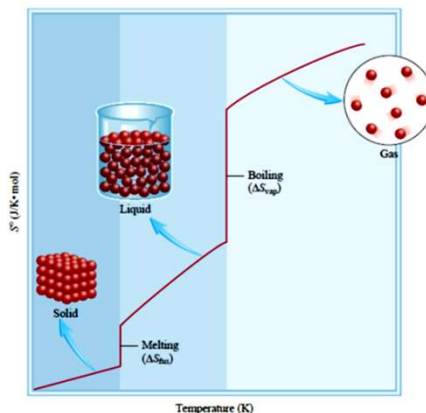
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Absolute Entropy of a Substance



The third law of thermodynamics, which states that the entropy of a *pure substance* in its thermodynamically most stable form is zero at the absolute zero of temperature, independent of pressure.



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Free energy



- ❑ Free energy is used to determine how systems change and how **much work they can produce**.
- ❑ The changes in free energy, **ΔF or ΔG** , are useful in determining the **direction of spontaneous change** and **evaluating the maximum work that can be obtained** from reactions.
- ❑ Expressed in two forms: the **Helmholtz free energy F and the Gibbs free energy G** .
- ❑ Free energy is an **extensive property**, meaning that its magnitude depends on the amount of a substance in a given thermodynamic state.

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Free energy



- ❑ **Gibbs free energy** is a measure of the **amount of energy available to do work** in an **isothermal and isobaric (constant temperature and pressure)** thermodynamic system
- ❑ The Gibbs free energy change at temperature T is expressed as,

$$\Delta G = \Delta H - T\Delta S$$
- ❑ In **terms of standard states**, when reactants and products at 1 M concentrations (or 1 atmosphere pressure), the free energy change is expressed as,

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$
- ❑ The Helmholtz free energy F is defined by **$F = U - TS$**

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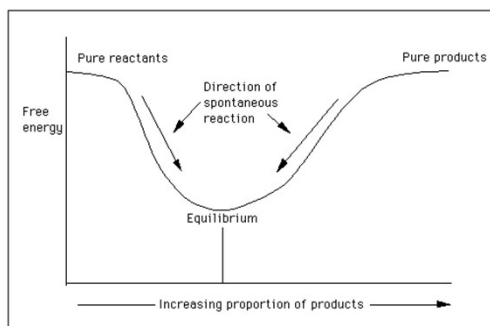
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Free energy



Given a constant temperature and pressure, **the direction of any spontaneous change is towards a lower Gibbs free energy**



The graphic shows that during a reaction, the amount of free energy decreases until the reaction is at equilibrium. If the reaction goes towards completion, the free energy minimum occurs very close to the pure products part of the curve. In other words, the curve moves depending on the conditions of the reaction

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Gibbs – Helmholtz equation



$$\left(\frac{\partial \left(\frac{G}{T} \right)}{\partial T} \right)_p = -\frac{H}{T^2},$$

The Gibbs–Helmholtz equation is a thermodynamic equation used for calculating **changes in the Gibbs energy of a system as a function of temperature**

where H is the enthalpy, T the absolute temperature and G the Gibbs free energy of the system, all at constant pressure p.

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Gibbs – Helmholtz equation



$$G = H - TS, H = U + PV$$

$$dG = dH - TdS - SdT$$

$$dH = dU + VdP + PdV$$

$$dG = dU + VdP + PdV - TdS - SdT$$

$$\text{we know } dU = TdS - PdV$$

$$dG = TdS - PdV + VdP + PdV - TdS - SdT$$

$$\text{So } dG = -SdT + VdP$$

$$dU = dQ - dW.$$

$$dW = PdV,$$

$$dQ = TdS.$$

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$$dG = TdS - PdV + VdP + PdV - TdS - SdT$$

$$\text{So } dG = -SdT + VdP$$

$$\left(\frac{\partial G}{\partial T} \right)_P = -S$$

$$\left(\frac{\partial G}{\partial P} \right)_T = V$$

Hence;

$$\left[\frac{\partial(\Delta G)}{\partial T} \right]_P = -\Delta S \quad (4)$$

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The Gibbs-Helmholtz Equation

Derivation of the Gibbs-Helmholtz Equation

The Gibbs-Helmholtz equation provides information about the temperature dependence of the Gibbs free energy.

The derivation of the Gibbs-Helmholtz equation begins with the fundamental equation for the Gibbs free energy G ,

$$dG = -SdT + VdP. \quad (1)$$

Using the relationships for an exact differential, we have that

$$\left(\frac{\partial G}{\partial T}\right)_P = -S. \quad (2)$$

Substituting this result for $-S$ into the equation defining the Gibbs free energy, $G = H - TS$, yields

$$G = H + T\left(\frac{\partial G}{\partial T}\right)_P. \quad (3)$$

Dividing both sides of Eq. (3) by T leads to the result

$$\frac{G}{T} = \frac{H}{T} + \left(\frac{\partial G}{\partial T}\right)_P. \quad (4)$$

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The Gibbs-Helmholtz equation involves the partial derivative with respect to temperature (at constant pressure) of the quantity on the left side of Eq. (4), G/T . Taking the partial derivative gives

$$\frac{G}{T} = \frac{H}{T} + \left(\frac{\partial G}{\partial T}\right)_P, \quad \left(\frac{\partial(G/T)}{\partial T}\right)_P = -\frac{G}{T^2} + \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_P. \quad (5)$$

Note that in Eq. (5), since G is a function of temperature, $G = G(T)$, the product rule was employed in order to evaluate the derivative of G/T . Factoring $1/T$ out from the right side of Eq. (5) yields

$$\left(\frac{\partial(G/T)}{\partial T}\right)_P = \frac{1}{T}\left[-\frac{G}{T} + \left(\frac{\partial G}{\partial T}\right)_P\right]. \quad (6)$$

Substituting the relation for G/T from Eq. (4) gives the result

$$\begin{aligned} \left(\frac{\partial(G/T)}{\partial T}\right)_P &= \frac{1}{T}\left[-\frac{G}{T} + \left(\frac{\partial G}{\partial T}\right)_P\right] \\ &= \frac{1}{T}\left[-\left[\frac{H}{T} + \left(\frac{\partial G}{\partial T}\right)_P\right] + \left(\frac{\partial G}{\partial T}\right)_P\right] \\ \left(\frac{\partial(G/T)}{\partial T}\right)_P &= -\frac{H}{T^2}. \end{aligned} \quad (7)$$

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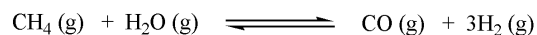
- ☐ The equation states that the change in the **G/T ratio at constant pressure as a result of an infinitesimally small change in temperature is a factor H/T^2 .**
- ☐ The main difference between Gibbs and Helmholtz free energy is that **Gibbs free energy is defined under constant pressure, while Helmholtz free energy is defined under constant volume.**
- ☐ The **Gibbs free energy is often used** since it considers a **constant pressure condition.**
- ☐ The **Helmholtz free energy is not much used because it considers a constant volume condition.**

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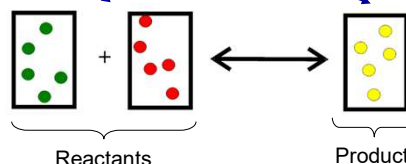
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Chemical Equilibrium



- ☐ Reactants are constantly forming products and vice-versa
- ☐ At the beginning of the reaction, the rate that the reactants are changing into the products is higher than the rate that the products are changing into the reactants.
- ☐ **When the net change of the products and reactants is zero the reaction has reached equilibrium**
- ☐ This state results when the forward reaction proceeds at the same rate as the reverse reaction. The reaction rates of the forward and backward reactions are generally not zero, but they are equal.



At equilibrium the amount of reactants and products are constant, but not necessarily equal.

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Chemical Equilibrium



Equilibrium Constant

- 1.) The relative concentration of products and reactants at equilibrium is a constant.
- 2.) Equilibrium constant (K):
 - For a general chemical reaction



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

Where:

- small superscript letters are the stoichiometry coefficients
- [A] concentration chemical species A relative to standard state

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Free energy



- ☐ For a reaction to be spontaneous
- ☐ The overall free energy at any concentration of reactant and product is:

$$\Delta G = \Delta G^\circ + RT \ln [\text{product}]/[\text{reactant}]$$

Where R (gas constant)= $8.314 \text{ Jmol}^{-1}\text{K}^{-1}$ and
 T (temperature) = in $^\circ\text{K}$

At equilibrium,

$$\Delta G^\circ + RT \ln [\text{product}]/[\text{reactant}] = 0$$

$$\begin{aligned} \Delta G^\circ &= -RT \ln K_{eq} \\ &= -2.303 RT \log K_{eq} \end{aligned}$$

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Free energy



$$\Delta G^{\circ} = \sum \Delta G_{f, \text{products}}^{\circ} - \sum \Delta G_{f, \text{reactants}}^{\circ}$$

□ $G^{\circ}(\text{reactant}) > G^{\circ}(\text{product})$ then,
reaction is spontaneous since $\Delta G^{\circ} < 0$.
 i.e. **negative** and $K_{eq} > 1$

□ $G^{\circ}(\text{reactant}) < G^{\circ}(\text{product})$ then,
reaction is non-spontaneous since $\Delta G^{\circ} > 0$
 i.e. **positive** and $K_{eq} < 1$

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Table 1. Sign of Gibbs Free Energy

ΔG	Reaction Behavior
Negative	Proceeds spontaneously to the right
Zero	Is at equilibrium
Positive	Will not proceed

1. If ΔG is **negative**, the forward reaction is spontaneous.
2. If ΔG is **0**, the system is at equilibrium.
3. If ΔG is **positive**, the reaction is spontaneous in the reverse direction.

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Thank you all for your attention

Information presented here were collected from various sources – textbooks, articles, manuscripts, internet and newsletters. All the researchers and authors of the above mentioned sources are greatly acknowledged.