

Topic : THERMODYNAMICS

Thermodynamics is the study of the relationship between heat and other forms of energy involved in a chemical or physical process. Thermodynamics is normally described in terms of three laws.

The first law of thermodynamics : states that energy is neither created nor destroyed; it is only transferred between the system and its surroundings. It is essentially the law of conservation of energy applied to thermodynamic systems.

To state the law you need to understand what the internal energy of a system is.

A system is the part of the universe chosen for study, and it can be as large as all the oceans on earth or as small as the content of a beaker. Everything in the system's environment constitute its surroundings. The surroundings are that part of the universe outside the system with which the systems interact.

An Open System : freely exchanges energy and matter with its surroundings. Example, a beaker of hot coffee transfers energy to the surroundings - it loses heat as it cools. Matter is transferred in the form of water vapor.

Closed system : can exchange energy, but not matter, with its surroundings. eg A flask of hot coffee transfers energy (heat) to surroundings as it cools. Because the flask is stoppered, no matter (water vapor) escapes and no matter is transferred.

An Isolated System : does not interact with its surroundings. Example hot coffee in an insulated system container, no vapor escaped and for a time at least, little heat is transferred to the surroundings. Eventually, the coffee in the container cools to room temperature.

Internal Energy : The internal energy, U , is the sum of kinetic potential energies of the particles making up the system. Energy is the capacity to do work.

The kinetic energy : The energy of a moving object is called kinetic energy. Kinetic energy includes the energy of motion of electrons, nuclei and molecules. The kinetic energy (E_k) of an object is given by

on its mass (m) and velocity (v)

$$E_k = \frac{1}{2}mv^2$$

The unit of kinetic energy is $\text{kg m}^2\text{s}^{-2}$, which is the SI unit of energy the joule (J) that is $1\text{J} = 1\text{kg m}^2\text{s}^{-2}$

Potential Energy : This is the energy that a system possess by virtue of its position or composition. It is an energy associated with force of attraction or repulsion between objects. The potential energy results from the chemical bonding of atoms and from the chemical attractions between molecules.

Internal Energy is a state function. That is, it is a property of a system that depends only on its present state, which is completely determined by variables such as temperature and pressure. Thermodynamic State of System is defined by a set of conditions that completely specifies all the properties of the system. This set commonly includes the temperature, pressure, composition (identity and number of moles of each compound) and physical state (liquid, gas or solid) of each part of the system.

A change in a state function describes a difference between the two states. It is independent of the process or pathway by which the change occurs. For instance, consider a sample of one mole of pure liquid water at 30°C and 1 atm pressure. If at later time, the temperature of the liquid is 22°C at the same pressure, then it is in a different thermodynamic state. We can tell that the net temperature change is -8°C , it does not matter whether the cooling took place direct from 30°C to 22°C or any other conceivable path was followed from the initial state to the final state. The most important use of state functions in thermodynamics is to describe changes.

1 mol of water at 0°C and 1 atm pressure has a definite quantity of energy. When a system changes from one state to another, its internal energy changes from one definite value to another. You can calculate the change in internal energy, ΔU , from the initial value of the internal energy, U_i , and the final value of the internal energy U_f

$$\Delta U = U_f - U_i$$

According to the law of conservation of energy the total energy remains constant. Energy is neither created nor

destroyed. We are interested in changes for a thermodynamic system. These changes of energy are noted in two forms; heat and work.

Heat! Is energy transferred between a system and its surroundings as a result of temperature difference. Energy that passes from a warmer body (with higher temperature) to a colder body (with lower temperature) is transferred as heat. At the molecular level, molecules of the warmer body, through collisions, loose kinetic energy to those of the colder body. Heat like work describes energy in transit between a system and its surroundings. During the process of melting, for example, the temperature remains constant as a thermal energy transfer (heat) is used to overcome the forces holding the solid together. Once a solid has melted completely further heat flow will raise the temperature of the resulting liquid. Historically, the quantity of heat required to change the temperature of one gram of water by one degree Celsius has been called calorie (cal). The calorie is a small unit of energy and the unit kilocalorie (kcal) has also been widely used. The SI units for heat is simply the basic SI energy unit, the joule (J).

$$1 \text{ cal} = 4.184 \text{ J}$$

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Heat capacity

The quantity of heat required to change the temperature of a system by one degree is called the heat capacity of the system. Heat capacity is represented by the symbol C . To obtain the heat capacity of a system, for example, a reaction vessel, we deliver known quantity of heat q , and measure the temperature change ΔT , heat capacity, C is then calculated as

$$C = \frac{q}{\Delta T}$$

$$q = C \Delta T$$

eq ①

The molar heat capacity at constant pressure (symbol (C_m)) is the quantity of heat required to raise the temperature of one mole of substance by one degree under the condition of constant pressure. Specific heat capacity (symbol C_p): Sometimes called the specific heat is the quantity of heat required to change the temperature

of one gram of a substance by one degree at constant pressure
Here are the values for water at 25°C
For water at 25°C : $C_p, m = \frac{75.326}{\text{mol}} \text{ J}$, $C_p = \frac{4.1813}{\text{g}^{\circ}\text{C}}$

$$C = nC_p m \text{ and } m C_p$$

Furthermore, for a sample, containing a known amount (n) or mass (m) of a single (pure) substance at constant pressure, heat capacity of the sample is

$$C = nC_p m = m C_p \text{. Therefore equation (1) takes the following form}$$

$$Q = C_p \Delta T = nC_p m \Delta T = m C_p \Delta T$$

Example — How much heat is required to raise the temperature of 100.0 mL of water (approximately 100.0 g) from room temperature, typically 21.0°C , to body temperature, typically 37°C ? (Assume that the heat capacity of water is throughout this temperature range)

Analyze : To answer this question, we begin by multiplying the specific heat capacity by the mass of water to obtain the heat capacity of the system. To find the amount of heat required to produce the desired temperature change we multiply the heat capacity by the temperature difference.

Solve : The specific heat capacity is the heat capacity of $\frac{100}{1000 \text{ g}}$ of water $\frac{4.181}{\text{g water}^{\circ}\text{C}}$ 4

The heat capacity of the system is $100.0 \text{ g water} \times \frac{4.181}{\text{g water}^{\circ}\text{C}} = 418 \text{ J}/^{\circ}\text{C}$

The required temperature change in the system is $(37.0 - 21.0)^{\circ}\text{C} = 16.0^{\circ}\text{C}$

The heat required to produce this temp change is

$$418 \text{ J}/^{\circ}\text{C} + 16.0^{\circ}\text{C} = 6.69 \times 10^3 \text{ J}$$

The temperature change is expressed as $\Delta T = T_f - T_i$, where T_f is the final temperature and T_i is the initial temperature. When the temperature of a system increases ($T_f > T_i$), ΔT and Q are positive. A positive value of Q signifies that heat is absorbed or gained by the system. When the temperature of a system decreases ($T_f < T_i$), ΔT and Q are negative. A negative value of Q signifies that heat is evolved or lost by the system.

work: is the energy exchange that result when a force F moves an object through a distance

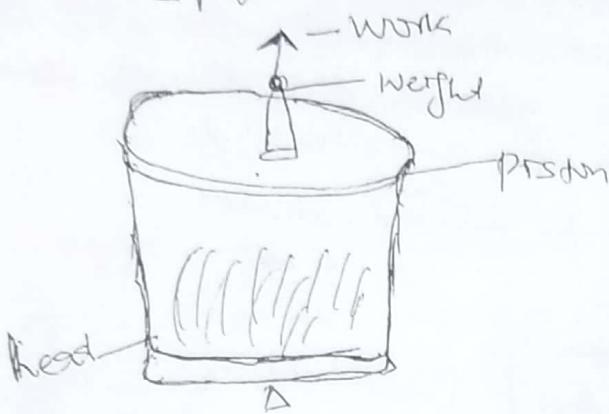
$$W = F \times d$$

$$F = ma$$

$$W = -P\Delta V$$

$$W = \Delta PV$$

(W = work, F = force, d = distance, m = mass)
 a = acceleration)



Exchanges of heat and work with surrounding

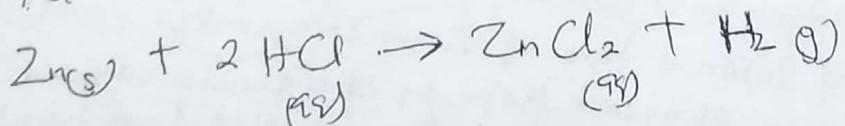
A gas is enclosed in a vessel with a piston. Heat flows into the vessel from the surroundings, which are at a higher temperature. As the temperature of gas increases, the gas expands lifting the weight (doing work).

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Example
When 1.00 mol Zn reacts with excess hydrochloric acid, 1.00 mol H₂ is produced. At 25°C and 1.00 atm (1.01×10^5 Pa), this amounts of H₂ (24.5×10^{-3} m³). The work done by the chemical system in pushing back to the atmosphere is

$$W = -P\Delta V = (1.01 \times 10^5 \text{ Pa}) \times (24.5 \times 10^{-3} \text{ m}^3)$$

$$W = -2.47 \times 10^3 \text{ J} \text{ or } -2.47 \text{ kJ}$$



Internal energy of a system can thus be expressed as ~~W~~ $U = q + W$

Change in internal energy becomes $\Delta U = q + W$

Enthalpy and enthalpy change

The quantity of heat transferred into or out of a system as it undergoes a chemical or physical change at constant pressure, q_p , is defined as the enthalpy change, ΔH of the process.

We define enthalpy H , precisely as quantity $U + PV$, because U and V are state functions, H is also a state function. This means that for a given temperature and pressure, a given amount of a substance has a definite enthalpy, therefore, if you know the enthalpies of substances, you can calculate the change enthalpy, ΔH , from a reaction.

ΔH is found enthalpy H_f minus the ^{initial} enthalpy H_i

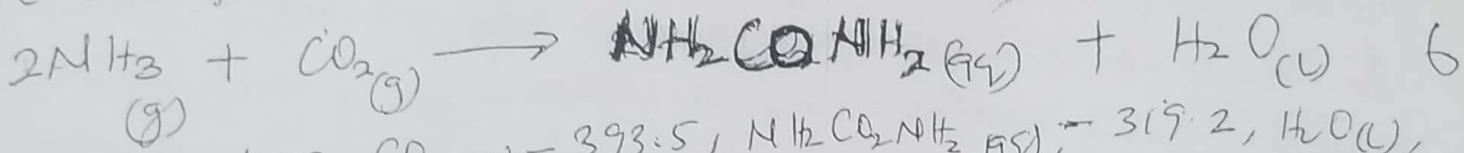
$$\Delta H = H_f - H_i$$

$$\Delta H = q_p$$

Standard enthalpy for a reaction is

$$\Delta H^\circ = \sum n \Delta H^\circ_f (\text{Products}) - \sum m \Delta H^\circ_f (\text{Reactants})$$

The following are standard enthalpies of formation at 25°C for the substances indicated. Suppose you would like to know how much heat is absorbed or evolved in the reaction between NH_3 and CO_2 to produce urea and water.



$$\text{NH}_3(g) - 45.9, \text{CO}_2(g) - 393.5, \text{NH}_2\text{CONH}_2(g) - 319.2, \text{H}_2\text{O}(l),$$

- 285.8 substituting into the previous equation yields

$$\Delta H^\circ = [(-319.2 - 285.8) - (2 \times 45.9 - 393.5)] \text{ kJ} = -119$$

$$\Delta H^\circ = -119.7 \text{ kJ}$$

The minus sign in the value of ΔH° , shows that heat is evolved and the reaction is exothermic.

Second Law of thermodynamics and Entropy

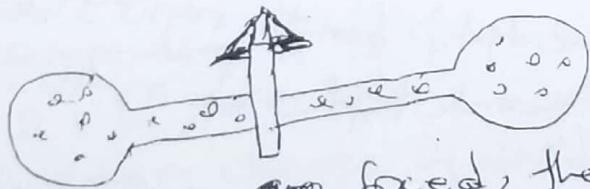
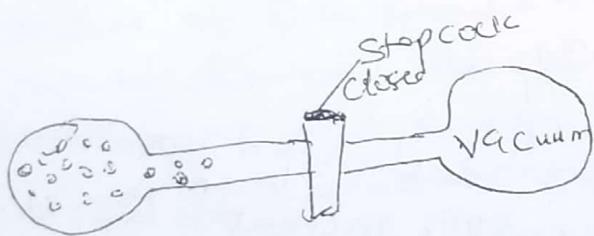
Second law of thermodynamics deals with the direction taken by spontaneous process. The Second law of thermodynamics establishes the concept of entropy as a physical property of a thermodynamic system. The second law of thermodynamics states that heat transfer occurs spontaneously only from high to low temperature bodies.

Entropy S , is a thermodynamic quantity that is a measure of how dispersed the energy of a system is among different possible ways

Net System can contain energy. When the energy of a thermodynamic system is ~~more~~ concentrated in a relatively few energy states, the entropy is low. When that same energy, however, is dispersed or spread out over a great many energy states, the entropy of the system is high. Entropy (energy dispersed) of a system plus its surroundings increases in a spontaneous process. A spontaneous process is a physical or chemical change that occurs by itself. Examples of spontaneous processes include: A ball at the top of a hill rolls down, heat flows from a hot object to a cold one.

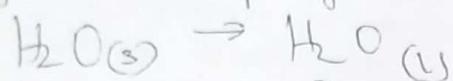
Imagine a flask containing a gas connected to an evacuated flask by a valve or stopcock. When the valve is opened, gas in the first flask flows into the space of the evacuated flask. In this case, the kinetic energy of the gas molecules spreads out or disperses over the volume of both flasks. The entropy of this system (both flasks) increases in this spontaneous process. In this case, we assume that surroundings do not participate in the overall change (there is no entropy change in the surroundings). The entropy change occurs entirely within the system. The SI unit of entropy is Joules per Kelvin (J/K). Entropy, like enthalpy is a state function, the quantity of entropy in a given amount of substance depends only on variables, such as temperature and pressure, that determine the state of the substance.

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If the variables are fixed, the quantity of entropy is fixed. For example, 1 mol of ice at $0^\circ C$ and 1 atm pressure has an entropy that has been determined experimentally as $41 J/K$.

Entropy is the entropy of liquid higher than that of solid water. In ice crystal, water molecule occurs in regular forced positions. Other wise restricted in their motions, and therefore in the liquid state, water molecules can rotate as well as vibrate internally and can move around somewhat (though not as freely as most can move in the gaseous state). Thus entropy of liquid water is expected to be higher than that of ice, the entropy is due to the entropy change, ΔS , for a process similar to the way calculate ΔH , if S_i is the initial entropy and S_f is the final entropy, the change in entropy is $\Delta S = S_f - S_i$. From melting of ice to liquid water.



$$\Delta S = (63 - 41) \text{ J/K} = 22 \text{ J/K}$$

When 1 mol of ice melts at 0°C , the water increases in entropy 22 J/K . The entropy increases as you expect, because the one of water becomes more dispersed when it melts.

Heat flow is also a flow of entropy, because it is a flow of energy either into the flask or outside of it. In general, the entropy change associated with heat flow q at an absolute temperature T can be shown to equal q/T . The net change of entropy created during the spontaneous chemical reaction that occurs plus the entropy change that is associated with heat flow (heat flow)

$$\Delta S = \text{Entropy Created} + \frac{q}{T}$$

The quantity of entropy created during a spontaneous process is a positive quantity; the entropy increases as it is created. If we delete "entropy created" from the right side of the equation ΔS , we know that the left side is then greater than the right side.

$$\Delta S > \frac{q}{T}$$

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Under essentially equilibrium conditions, no significant amount of entropy is created. The entropy change results entirely from absorption of heat. Therefore

$$\Delta S = \frac{q}{T} \text{ (equilibrium process)}$$

Recall that heat of reaction at constant pressure, q_p equals the enthalpy change ΔH . The Second Law of thermodynamics for a spontaneous reaction at constant temperature and pressure becomes

$$\Delta S > \frac{q_p}{T} = \frac{\Delta H}{T} \text{ (Spontaneous reaction)} \quad \text{Constant T \& P}$$

ΔS is greater than $\Delta H/T$ for a spontaneous reaction at constant temperature and pressure.

Subtract from $\Delta H/T$, you will get a negative quantity that:

$$\frac{\Delta H}{T} - \Delta S < 0 \text{ (Spontaneous reaction at constant T and P)}$$

$$\Delta H - T\Delta S < 0 \text{ (Spontaneous reaction at constant T \& P)}$$

If $\Delta H - T\Delta S$ is negative, you will predict a spontaneous reaction.

If $\Delta H - T\Delta S$ is positive, you will predict a non-spontaneous

reaction written but spontaneous in the opposite direction.

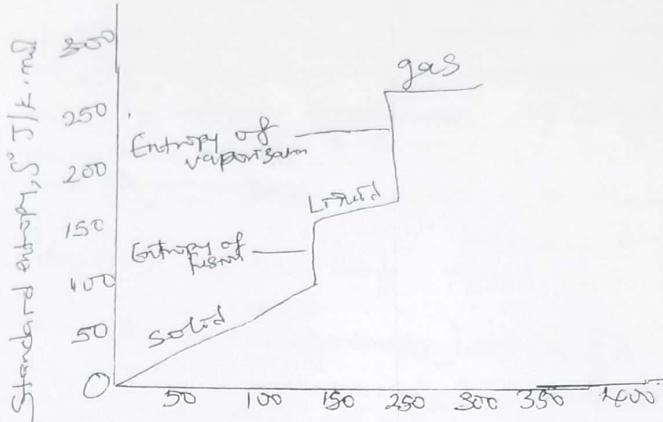
If $\Delta H - T\Delta S$ is zero, the reaction is at equilibrium.

Third Law of Thermodynamics

The third law of thermodynamics states that a substance that is perfectly crystalline at 0 K has an entropy of zero. A perfectly crystalline at 0 K should have perfect order. When the temperature is raised, however, the substance increases in entropy as it absorbs heat and energy disperses through it. You can determine the entropy of a substance from near 0 K to 298 K. Recall that the entropy change ΔS that occurs when heat is absorbed at a temperature T is q/T . Suppose you heat the substance from near 0.0 K to 2.0 K and the heat absorbed is 0.19 J/K. Find the entropy change by dividing heat absorbed by average absolute temp [$\frac{1}{2}(0.0 + 2.0)K = 1.0K$]. Therefore, $\Delta S = \frac{0.19J}{1.0K} = 0.19J/K$. This gives the entropy of substance at 2.0 K $= 0.19J/K$. Heat the substance from 2.0 K to 4.0 K and this

$0.88 \text{ J of heat is absorbed. The average temperature is } \frac{2.0 + 4}{3} \text{ OK}$, and entropy change is $0.88 \text{ J}/3.0 \text{ K} = 0.29 \text{ J/K}$. The entropy of the substance at 4 OK is $(0.19 + 0.29) \text{ J/K} = 0.48 \text{ J/K}$.

Proceeding in this way, you can eventually get the entropy at 298 K.



Note that the entropy increases gradually as the temperature increases. But when there is a phase change (e.g. from solid to liquid), the entropy increases sharply. The entropy ~~increases~~ change for the phase transition is calculated from enthalpy or phase transition. The standard entropy of a substance also called its absolute entropy S° , is the entropy value for the standard state of the species (indicated by the superscript degree sign). For a solution, the standard state ~~is~~ is 1 M solution unlike standard enthalpies of formation ΔH_f° which by convention are zero.

The symbol S° is chosen for standard enthalpies to emphasize they originate from the third law.

You can find the standard change of entropy, ΔS° for a reaction by subtracting the standard of reactants from the standard enthalpies of products, similar to the way you obtain ΔH° .

$$\Delta S^\circ = \sum n S^\circ (\text{products}) - \sum m S^\circ (\text{reactant})$$

- Entropy usually increases in the following situations ☺
1. A reaction in which a molecule is broken into two or more smaller molecules.
 2. A reaction in which there is an increase in moles of gas (This may result from a molecule breaking up, in which case rules 1 & 2 are violated).
 3. A process in which a solid changes to liquid or gas or a liquid changes to a gases.

Free entropy free energy & Spontaneity

American physicist J. Willard Gibbs (1839-1903) introduced the concept of free energy, G , which is a thermodynamic quantity defined by the equation $G = H - TS$. This quantity gives a direct criterion for spontaneity of reaction. As a reaction proceeds at a given temperature and pressure, reactants form products & the enthalpy H & entropy S change. These change in H and S , denoted with ΔH and ΔS results in a change in free energy, ΔG given by the equation

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

Note that the change in free energy ΔG , equals the quantity $\Delta H - T\Delta S$ a criterion for spontaneity of a reaction. Thus, if you can show that ΔG for a reaction at a given temperature and pressure is negative, you can predict that the reaction will be spontaneous.

Standard Free energy Change

The standard states are as follows for pure liquids & solids, 1 atm pressure, for gases, 1 atm partial pressure, for solutions, 1 M concentration. The temperature is the temperature of interest, usually $25^\circ C$ ($298 K$). The standard free-energy change, ΔG° , is the free energy change that occurs when reactants in their standard states are converted to products in their standard states.

Calculation of standard free energy change, ΔG° from ΔH° and ΔS°

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

The standard free energy change is given by tables. If you know the free energy data from thermodynamic tables under non-standard conditions (ΔG), you can obtain it from the standard free energy change ΔG° using the following equation:

$$\Delta G = \Delta G^\circ + RT \ln Q$$

Here Q is the thermodynamic form of the reaction quotient, it has the same general appearance as the thermodynamic equilibrium constant K , but the concentrations and partial pressures are those for a mixture at some instant, perhaps at the beginning of a reaction. You obtain ΔG from ΔG° by adding $RT \ln Q$ where $\ln Q$ is the natural logarithm of Q ($\ln Q = 2.303 \log Q$)

Note that ΔG is the change of free energy that occurs when the reaction mixture has the composition expressed by Q . When chemical reaction approaches equilibrium, the free energy decreases and continues to decrease until equilibrium is reached. At equilibrium the free energy ceases to change, then $\Delta G = 0$. Also, the reaction quotient Q becomes equal to the equilibrium constant K . If you substitute $\Delta G = 0$ and $Q = K$ into the preceding equation, you get

$$0 = \Delta G^\circ + RT \ln K$$

This result is easily rearranged to give the basic equation relating the standard free-energy change to the equilibrium constant

$$\Delta G^\circ = -RT \ln K$$

Example : Find the value of the equilibrium constant K at $25^\circ C$ (298 K) for the reaction. $2NH_3(g) + O_2(g) \rightleftharpoons NH_2CONH_2(aq) + H_2O(l)$

The standard free energy change, ΔG° , at $25^\circ C$ equals -13.6 kJ

The standard free energy change, ΔG° , at $25^\circ C$ equals -13.6 kJ

This value of $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

Problem strategy : Rearrange the equation $\Delta G^\circ = -RT \ln K$ to give

$$\ln K = \frac{\Delta G^\circ}{-RT}, \quad \Delta G^\circ \text{ and } R \text{ must be in compatible units, } \Delta G^\circ \text{ in Joules and } R \text{ equal to } 8.31 \text{ J/(K.mol)}$$

Solution : Substituting numerical values into this equation

$$\ln K = \frac{-13.6 \times 10^3}{-8.31 \times 298} = 5.49 \quad \text{Hence, } K = e^{5.49} = 2.4 \times 10^2$$

ELECTROCHEMISTRY

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Electrochemistry deals with the chemical changes produced by electric current and with the production of electricity by chemical reactions. It is concerned with oxidation-reduction reaction.

Many metals are purified or are plated onto jewelry by electrochemical methods.

All electrochemical reactions involve the transfer of electrons and are therefore oxidation-reduction reaction.

Electrochemical processes require some method of introducing a stream of electrons into a reacting chemical system and some means of withdrawing electrons.

In most applications the reacting system is contained in a cell and an electric current enters or exits by electrodes.

Classification of cells into two types

1. Electrolytic cells are those in which electrical energy from an external source causes non-spontaneous chemical reaction to occur.
 2. Voltaic cells are those in which spontaneous chemical reaction produce electricity and supply it to an external circuit.
- A voltaic cell employs a spontaneous oxidation-reduction reaction as a source of energy. It is constructed to separate the reaction physically into two half-reactions, one involving oxidation & the other reduction, with electrons moving from the oxidation half-reaction through the external circuit to the reduction half-reaction.

Electrical Conduction

Electrical current represents transfer of charge. Charge can be conducted through metals and through pure liquid electrolytes (that is, molten salts) or solutions containing electrolytes. The former type of conduction is called metallic conduction. It involves the flow of electrons with no similar movement of the

atoms of the metals and no obvious changes in the metal. Ionic, electrolytic conduction is the conduction of electric current by the ions through a solution or a pure liquid. Positively charged ions migrate toward the negative electrode while negatively charged ions move toward the positively charged electrode. Both kinds of conductors, (one the metallic, occur in, electrochemical cells.

Electrodes: Electrodes are surfaces on which oxidation or reduction half-reactions occur. They may or may not participate in the reactions. Those that do not react are called inert electrodes. Regardless of the kind of cell, electrolytic or voltaic, the electrodes are identified as follows. The cathode is defined as the electrode at which reduction occurs as electrons are gained by some species. The anode is the electrode at which oxidation occurs as electrons are lost by some species.

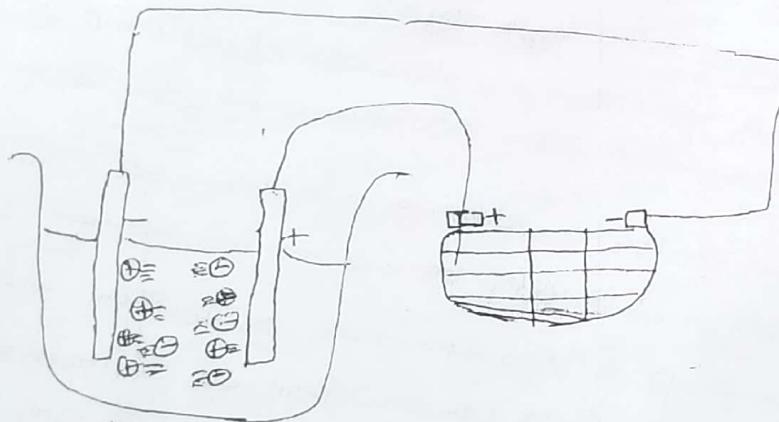


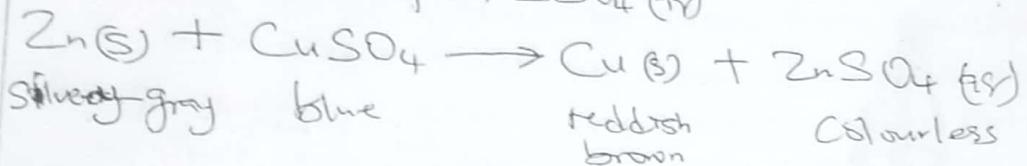
Fig 1 - The motion of ions through a solution is an electric current. This accounts for ionic (electrolytic) conduction. Positively charged ions migrate toward the negative electrode and negatively charged ions migrate toward the positive electrode.

In an oxidation-reduction reaction, the oxidation states of atoms in the reactants change. The changes in oxidation states are imagined to occur as ^{result} ~~the~~ of electron transfer from one reactant to another.

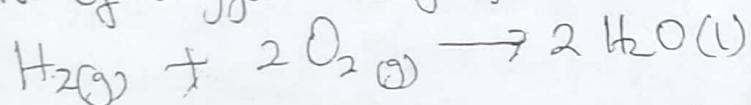
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In an oxidation-reduction reaction, the oxidation states are imagined to occur as the result of electron transfer from one reactant to another.

A classic example is the reaction of zinc metal, $Zn(s)$, with aqueous copper sulfate, $CuSO_4(aq)$, to form solid copper, $Cu(s)$, in aqueous zinc sulfate, $ZnSO_4(aq)$.



This reaction is often demonstrated by placing a zinc rod bearing a reddish-brown deposit of copper and the blue of the solution fades. At the molecular level, Cu^{2+} ions in the solution are reduced to form Cu atoms that deposit onto the surface of the zinc rod. At the same time, 2n atoms from the zinc rod are oxidized to produce 2n^{2+} ions that enter into the solution. The simultaneous oxidation of 2n to 2n^{2+} and reduction of Cu^{2+} to Cu involves the transfer of two electrons from Zn to Cu^{2+} . Another example of an oxidation-reduction reaction is the combination of oxygen and hydrogen to form water.



$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$

In this reaction, H atoms of molecular hydrogen are oxidized (from 0 to 1) and O atoms of molecular oxygen are reduced (from 0 to -2) under appropriate conditions, the electron transfer process in these chemical reactions and many others can be used to our advantage, for example, to run an electric motor or operate a Phare, or Infrate another chemical.

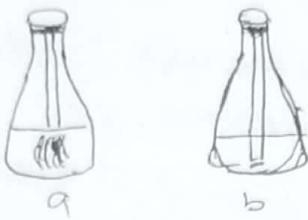
Electrode Potentials and their measurement

Electrode potentials and their measurement

The Criteria for Spontaneous change apply to reaction all type precipitation, acid-base, and oxidation-reduction (redox). We can devise an additional useful Criteria for redox reaction occurs between $\text{Cu}(\text{s})$ and $\text{Ag}^+(\text{aq})$ but not between $\text{Cu}(\text{s})$ and

$Zn^{2+}(aq)$

Sparingly, we see that silver ions are reduced to silver atoms on a copper surface, whereas zinc ions are not reduced to zinc atoms on a copper surface. This causes that Ag^+ is more readily reduced than is Zn^{2+} .



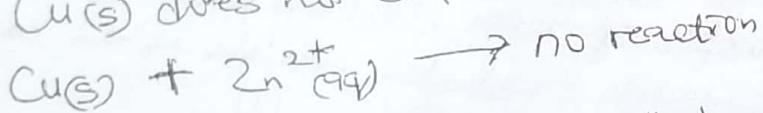
Behaviour of $Ag^+(aq)$ and $Zn^{2+}(aq)$ in the presence of copper

(i) Copper metal displaces silver ions from colourless $AgNO_3(aq)$ as a deposit of silver metal, the copper enters the solution as blue

$Cu(s)$



(ii) $Cu(s)$ does not displace colourless Zn^{2+} from $Zn(NO_3)_2(aq)$



A strip of metal, M, is called an electrode. An electrode immersed in a solution containing ions of the same metal, M^{n+} , is called a half-cell. Two kinds of interactions are possible between metal atoms on the electrode and metal ions in the solution.

1. A metal ion M^{n+} from solution may collide with the electrode and gain n electrons from it, and be converted to a metal atom M. The ion is reduced.

2. A metal atom M on the surface may lose n electrons to the electrode and enter the solution as ion M^{n+} . The metal atom is oxidized.

An equilibrium is quickly established between the metal and the solution, which can be represented as

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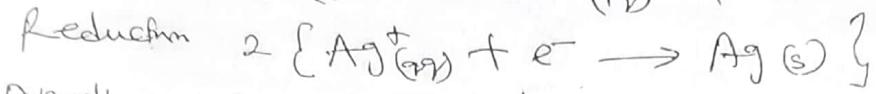


However, any changes produced at the electrode or in solution as a consequence of this equilibrium are too slight to measure. Instead measurements must be based on a combination of two different half-cells. Specifically, we must measure the tendency for electrons to flow from the electrode of one half-cell to the electrode of the other. Electrodes are classified according to whether oxidation or reduction takes place there. If oxidation takes place, the electrode is called the anode; if reduction takes place, the electrode is called the cathode.

Fig 3. depicts a combination of two half-cells, one with a Cu electrode in contact with $\text{Cu}^{2+}_{(\text{aq})}$, and the other with an Ag electrode in contact with $\text{Ag}^+_{(\text{aq})}$. These two electrodes are joined by wires to an electric circuit, the two solutions joined by a salt bridge. The salt bridge must also be connected electrically. However, because it is carried through solutions by the migration of ions, a wire cannot be used for this connection. The salt bridge must be indirect contact through a porous barrier or joined by a third solution in a U-tube called a salt-bridge. The properly connected combination of two half-cells is called an electrochemical cell. The properly connected combination of two half-cells is called an electrochemical cell.

Now, we will consider the changes that occur in electrochemical cell in fig 3. As the arrows suggest, Cu atoms release electrons at the anode and enter the $\text{Cu}(\text{H}_2\text{O})_6^{2+}_{(\text{aq})}$ as Cu^{2+} ions. Electrons lost by the Cu atoms pass through the wire and the voltmeter to the cathode, where they are gained by Ag⁺ ions from the $\text{AgNO}_3_{(\text{aq})}$ producing a deposit of metallic silver. simultaneously, anions (NO_3^-) from the salt bridge migrate into the copper half cell and neutralise the positive charge of the excess Cu^{2+} ions; cations (K^+) migrate into the silver half cell and neutralise negative charge of the excess NO_3^- ions. Each copper atom loses two electrons

to produce $\text{Ag}(\text{s})$, consequently, two silver atoms^(S) are produced for every Cu^{2+} ion formed. The overall reaction that occurs in an electrochemical cell spontaneously produces electric current.



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