Module: 2
Lecture: 3

OXYGEN AND NITROGEN

INTRODUCTION

Oxygen

Oxygen (O\textsubscript{2}) composed of two atoms of the element at (O) bind to form dioxygen, a very pale blue, odorless, tasteless diatomic gas. Diatomic oxygen gas constitutes 20.8% of the volume of air. It is necessary to sustain global life.

Oxygen is the highly reactive nonmetallic element that readily forms compounds or oxides with almost all other elements. Oxygen is a strong oxidizing agent and has the second-highest electronegativity after fluorine than of all the elements. By mass, after hydrogen and helium, oxygen is the third-most abundant element in the universe. Free oxygen is too chemically reactive to appear on Earth without the photosynthetic action of living organisms, which use the energy of sunlight to produce elemental oxygen from water. Elemental O\textsubscript{2} only began to accumulate in the atmosphere after the evolutionary appearance of these organisms, roughly 2.5 billion years ago.

As larger constituent by mass of water, oxygen comprises most of the mass of living organisms. Elemental oxygen is produced by cyanobacteria, algae and plants, and is used in cellular respiration for all complex life. Oxygen is toxic to anaerobic organisms, which were the dominant form of early life on Earth until O\textsubscript{2} began to accumulate in the atmosphere.

Oxygen was independently discovered by Carl Wilhelm Scheele and Joseph Priestley in 1773 and 1774 respectively, but work was first published by Priestley. Antoine Lavoisier named as oxygen in 1777, whose experiments with oxygen helped to discredit the then-popular phlogiston theory of combustion and corrosion.

Oxygen is produced industrially by fractional distillation of liquefied air, use of zeolites with pressure-cycling to concentrate oxygen from air, electrolysis of water and other means.
Nitrogen

Nitrogen (N\textsubscript{2}) is a colorless, odorless, tasteless, and mostly inert diatomic gas at standard conditions, constituting 78.09% by volume of Earth’s atmosphere. Nitrogen occurs in all living organisms, primarily in amino acids, proteins and in the nucleic acids (DNA and RNA). The human body contains about 3% by weight of nitrogen, the fourth most abundant element after oxygen, carbon, and hydrogen.

Nitrogen was discovered by Daniel Rutherford in 1772, who called it noxious air or fixed air. He also explains that nitrogen does not support combustion. At the same time by Carl Wilhelm Scheele, Henry Cavendish, and Joseph Priestley, referred it as burnt air or phlogisticated air. Antoine Lavoisier referred nitrogen as inert gas and as “mephitic air” or azote, in which animals died and flames were extinguished. English word nitrogen entered the language in 1794.

The extremely strong bond in elemental nitrogen causing difficulty for both organisms and industry in breaking the bond to convert the nitrogen into useful compounds, but large amounts of useful energy released when the compounds burn, explode, or decay back into nitrogen gas.

Analysis of Air

Air mainly consist of two gases oxygen and nitrogen, which are practically considered to constitute 1/5 and 4/5 of air by volume respectively. The list of various gases present in air by weight percent is as under

<table>
<thead>
<tr>
<th>Name of the gas</th>
<th>% by weight in air</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>20.99</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>78.01</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>0.03 - 0.07</td>
</tr>
<tr>
<td>Argon</td>
<td>0.94</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>0.01</td>
</tr>
<tr>
<td>Neon</td>
<td>0.0015</td>
</tr>
<tr>
<td>Helium and Krypton</td>
<td>0.01 - 0.02</td>
</tr>
</tbody>
</table>

Except CO\textsubscript{2} the concentration of all the gases listed above are present in air are constant. However water vapours and traces of ozone and iodine are present in air in variable amounts. Also, composition of air also depends on altitude and distance to sea, in neighbourhood of industry, built up urban areas, nearby volcanic phenomena. Other gases such as CO, H\textsubscript{2}S and NO\textsubscript{2} are also present in air.

Kinetics and theory of gases

According to kinetic theory a gas consists of swiftly moving molecules moving in a haphazard manner. During the movement some molecules collide with one another, some others move away from one another, these phenomena leaving an
average distance between the molecules. At lower pressure the average distance is large, and at high pressure the molecules are brought near to one another.

In all the three state of matter, molecules have two tendencies i.e. Attraction tendency and Repulsive tendency. The repulsive tendency is most predominant in gases, and least prominent in solids. While in most of liquids the attractive tendency in molecules is more than the repulsive tendency, so that the molecules remain together, but the attracting tendency is still less than in comparison of solids there so liquid is in fluid state. In the gases as the temperature raises the repulsion tendency increases, and pressure remaining constant the average distance between molecules increases i.e. the volume increases. Hence with fall of temperature the distance diminishes and, the molecules come closer together. Thus it becomes apparent that the average distance of molecules will progressively diminish with fall of temperature, and rise of pressure. Change of average distance of gas is quantitatively expressed by PV/T = constant

**Critical temperature**

When by decreasing the distance the molecules of a gas are brought close together the gas assumes the liquid form provided the repulsive tendency has been diminished beyond a certain point known as critical temperature which is different for different gases.

Critical temperature is the temperature below which any gas can be liquefied by increasing the pressure. Above the critical temperature any gas cannot be liquefied by compression.

**Critical pressure**

Above critical temperature the gas will never liquefy under any pressure. The minimum pressure under which gas liquefies at the critical temperature is called as critical pressure.

Therefore air should be cooled at very high pressure and low temperature for cooling purpose. The liquid form is obtained when the kinetic energy and the potential energy of the substance is approximately equal.
The critical temperature and critical pressure of some gases are as follows.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Gases</th>
<th>Critical temperature (°C)</th>
<th>Critical pressure (atm.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Ethylene</td>
<td>+9.5</td>
<td>50.65</td>
</tr>
<tr>
<td>2.</td>
<td>Methane</td>
<td>-82.85</td>
<td>45.6</td>
</tr>
<tr>
<td>3.</td>
<td>Nitrogen</td>
<td>-147.13</td>
<td>33.49</td>
</tr>
<tr>
<td>4.</td>
<td>Hydrogen</td>
<td>-239.9</td>
<td>12.8</td>
</tr>
<tr>
<td>5.</td>
<td>Oxygen</td>
<td>-118.75</td>
<td>49.7</td>
</tr>
<tr>
<td>6.</td>
<td>Acetylene</td>
<td>+35.5</td>
<td>61.55</td>
</tr>
<tr>
<td>7.</td>
<td>Ammonia</td>
<td>+132.5</td>
<td>112.3</td>
</tr>
<tr>
<td>8.</td>
<td>Carbon monoxide</td>
<td>-138.7</td>
<td>34.6</td>
</tr>
<tr>
<td>9.</td>
<td>Carbon dioxide</td>
<td>+31.3</td>
<td>72.9</td>
</tr>
</tbody>
</table>

**Liquefaction of air by Joule - Thomson effect**

CO₂ free air is compressed to 200atm and is cooled by water. The condensed water is removed by passing through activated alumina. Then air is passed through inner coil of heat exchangers. The valve with nozzle is provided at the end of the inner coil. Then gas is allowed to suddenly expand by opening the valve, which result in decrease of temperature of air. After expanding the cold air goes out through the outer coil, is then recompressed to 200atm pressure, cooled by water and then again allowed to transverse the inner coil. The temperature of the
incoming air further falls due to the presence of cold air in the outer coil. Now as the cooled air suddenly expands through the nozzle, the air suffers cooling, the temperature becomes lower than in the first operation. The colder air now passes through the outer coil producing an atmosphere of lower temperature. Hence when the cooled compressed air passes repeatedly through the inner coil and subsequently undergoes Joule-Thomson effect, the temperature of the air further drops. In this way progressive cooling takes place until the temperature of air falls below the critical temperature of oxygen and nitrogen. When this happens air undergoes liquefaction in the inner coil, so on opening the valve liquid air falls in the container. A part of liquid air evaporates, through the outer coil, maintaining the low temperature below the critical temperature.

**MANUFACTURE**

Oxygen in pure condition is obtained as a byproduct in the manufacture of H₂ by electrolytic process is described in Module: 2, Lecture: 4. Oxygen and nitrogen are usually separated by rectification of liquid air.

**Linde's process (O₂ and N₂)**

The first rectification of N₂ and O₂ using Joule Thomson effect was carried out by Linde in 1906. After six year Claude rectified them by combined effect of external work and internal work in cooling the air to liquefaction point.

**Raw materials**

- Basis: 1000kg Oxygen (95%)
- Air = 3600Nm³
- Steam = 1750kg
- Cooling water = 5000kg
- Electricity = 450-480KWH

**Manufacture**

- Block diagram of manufacturing process
- Process equipment
- Animation
The distillation tower is specially designed bubble cap tray double columns arranged one above another. The two distillation columns are having intermediate distillation dome for effective separation of liquid enriched with O₂. The column feed is liquefied air at 200atm pressure introduced at the bottom of the column. Since the boiling point of O₂ (-183°C) and N₂ (-195°C) are very low, column does not require any external heating. Distillation take place only due to release of vacuum. Thus a number of recycling from lower column to upper column and lower column to dome is required. The construction of dome includes number of internal pipes so that distillate of the lower column collides to the roof and is returned back to the column as reflux. The compressed air which arrives from the first section of the plant which acts as the heating fluid in the heater at the base of the enrichment column. The same air, always contained within a tube, passes out from the lower column of the tower only to reenter it higher up after the pressure to which it is subjected is reduced by means of a valve, resulting in the lowering of its temperature. Nitrogen with a small oxygen impurity collects at the top of the enrichment column, and after expansion to atmospheric pressure; this nitrogen is sent to back as the reflux in the rectification column situated above. The liquid which collects in the heater at the base of the enrichment column is fed, after expansion to atmospheric pressure onto a suitable plate of the rectification column. Only after number of recycling, liquid with 82% concentration of O₂ is taken in outer part of dome. This liquid goes to further rectification in upper column where it is refluxed with N₂ rich liquid coming from lower column. The final separation in the
upper column takes place which has less number of trays. Gaseous $N_2$ is the top product of the column and the bottom product is liquid $O_2$.

**Claude process**

In Claude process, progressive cooling of compressed air is done by external work and Joule - Thomson effect. 70% of air is cooled by external work and 30% by Joule - Thomson effect.

**Two variants of Claude process**

**Molecular sieve variant**

Cooling of air is brought about primarily by expansion with the performance of work. Therefore, there is no need to equip the plant with cycles that use refrigerants or make use of very high pressures which are employed when free expansion is used, in order to produce cooling.

**Evaporation to diffusion**

Cooling of the air can be adopted such as causing liquids which can evaporate to diffuse air. It is then safe to reabsorb them when necessary.

**Kinetics and thermodynamics**

Liquefied air is subjected to rectification to separate the oxygen and nitrogen components present in it. In liquid state both are miscible in all ratios and they do not form azeotropic mixtures; so they could not separate by boiling the solution.

**Operation of a rectification column**

Figure: Section of a plate rectification column
Rectification is carried out in a ‘plate column’, which is a tall cylindrical structure inside which repeated condensations and evaporations take place on plates, which lead to a continuous change in the composition of the binary system throughout the length of the column. This is continued until one of its pure components exists at the top of the column and the other at the bottom of the column.

For better understanding of rectification of binary mixture a small section of column is shown in figure which is formed by three plates: an intermediate plate $P_n$, and two collateral plates $P_{n-1}$ and $P_{n+1}$ which are arranged below and above the plate $P_n$ respectively.

- $V_1$, $V$, and $V_2$ be the vapours which, as they pass toward the top of the column, leave the plates $P_{n-1}$, $P_n$, and $P_{n+1}$ respectively
- $L_1$, $L$, and $L_2$ be the liquids which, as they pass down the column, descend from the plates $P_{n-1}$, $P_n$, and $P_{n+1}$ respectively
- $T_{n+1}$, $T_n$ and $T_{n-1}$ be the temperatures of the plates $P_{n-1}$, $P_n$, and $P_{n+1}$ respectively

The rectification of liquid mixture is exclusively on the basis of heat exchange of the different fraction present in liquid form as well as vapour form. As shown in the diagram plate $P_n$ is considered as the reference plate having temperature $T_n$ and liquid composition $L$, vapour composition $V$. As pressure is released the more volatile component i.e. $N_2$ is evaporated out partly and goes to the upper plate $P_{n+1}$. The composition of liquid $L_2$ is having less concentration of $N_2$ at temperature $T_{n-1}$. Similarly liquid below the reference plate is $P_{n-1}$ has higher concentration of $O_2$ and vapour $V_1$ having higher composition of $O_2$ at temperature $T_{n+1}$.

Thus the separation of more volatile component $N_2$ in vapour form and low volatile component $O_2$ in the liquid form is achieved.

Finally:

- The liquids which fall down from the plates toward the heater in the base of the column ($L_2$, $L$, $L_1$) become progressively richer in the less volatile component (oxygen)
- The vapours which rise toward the top of the column ($V_1$, $V$, $V_2$) gradually become enriched in the more volatile component (nitrogen)

Subsequently, in a column fitted with a suitable number of plates, $O_2$ is obtained in pure state at the base of the column and the $N_2$ is obtained in a practically pure state at the top of the column.

For, perfect operation of a rectification column always requires that:

- The liquid should always be introduced onto a plate which supports a liquid of the same composition as that of the feedstock liquid
Part of the distillate from the top of the column is recycled in the form of a 'reflux' with the aim of repeated washing on all of the plates which refine the vapours moving towards the top of the column.

**Condensation medium**

The separation of liquid air into nitrogen and oxygen is not as simple as the fractionation of any other binary mixture. Because the separation is carried out at very low temperature around -200°C. It is difficult to find a suitable medium for the refluxing of a liquid air distillate at this temperature. The only possible media for the condensation of the reflux would be liquid helium or liquid hydrogen, the use of which is clearly unacceptable on both economic and operational grounds.

**Engineering aspects**

**Two-section fractionating tower**

Designing a fractionating tower consisting of two columns which are arranged one above the other is the economically acceptable solution. The upper column is about twice the height of the lower column, and both of them are fitted with plates spaced at intervals. The average numerical ratio of the repartitioning between the two columns is 42:25.

The upper column has all the requisites of a rectification column, while the lower column functions as a simple enrichment column. As a bottom reboiler, the lower column has a boiler with a curved base. There is no condenser at the top of the rectification column, and it is closed by means of a gently curved cover with an outlet aperture.

Fundamentally, one is concerned with two columns, one being situated above the other, working at different pressures

- Lower column operating at 6atm
- Upper column operates only slightly above atmospheric pressure

The heat exchanger provided between the two columns acts as a condenser with respect to the lower column and a boiler with respect to the upper column precisely as a result of the two different pressures which appertain in the two compartments.

More precisely: the upper column is supplied with a feedstock of a composition which is proportionate with that of the liquid situated on the plate where the feedstock is let in, and receives a suitable reflux at the top, while the lower column is fed almost normally but is not refluxed, and instead of leading to practically pure components, it produces a liquid which is enriched in the oxygen at the bottom and in the nitrogen at the top of the column.
The shape of the plates differs according to the type of plant in which they operate.

**Linde method**

![Linde's type plate](image1)

Every plate is made up from two metal plates which are separated from one another by a certain spacing and perforated with very small apertures in the lower plate and quite large holes in the upper plate.

**Claude method**

![Claude's type plate](image2)

The column plants using claude’s method is strips of thin steel plate wound into a spiral with separation of the order of tenth of a millimeter between the spirals.

On account of the capillarity due to the small apertures in the lower half of the Linde plates and the small cavities between the spirals of the Claude plates, the
down-flows of the liquids are retarded, thereby favouring perfect contact between
the descending liquids and the rising vapours. Material of constriction should be
chosen in such a way that can resist very low temperature.

**PROPERTIES**

**Oxygen**

- Molecular formula : \( \text{O}_2 \)
- Molecular weight : 32gm/mole
- Appearance : Colourless gas
- Odour : Odourless
- Boiling point : -182.95°С
- Melting point : -218.79°С
- Density : 1.429gm/L (0°С, 101.325kPa)
- Solubility : Sparingly soluble in water

**Nitrogen**

- Molecular formula : \( \text{N}_2 \)
- Molecular weight : 28gm/mole
- Appearance : Colourless gas
- Odour : Odourless gas
- Boiling point : -195.79°С
- Melting point : -210°С
- Density : 1.251gm/L (0°С, 101.325kPa)
- Solubility : Slightly soluble in water

**USES**

**Oxygen**

- It is used to produce oxyacetylene flame to cutting and welding the metals
- Used in L. D. process for steel production
- Used for artificial respiration in case of patients
- Used for mountain climbers and high attitude aero planes flights

**Nitrogen**

- Used in manufacture of synthetic ammonia, nitric acid
- Used in manufacture organic nitrates like propellants and explosives,
- Synthetically produced nitrates are key ingredients of industrial fertilizers
- Used in producing nitrogen oxide.
- Applied to create inert atmosphere.