Experimental System and Diagnostics

2.1 The experimental set-up

2.1.1 Introduction

A schematic diagram of our basic experimental plasma chemical reactor system for synthesis of nanoparticles is shown below, in figure 2.1. The plasma jet is
produced by a segmented plasma torch, which after passing through a reactant injection section and a converging nozzle, expands supersonically into a vacuum chamber maintained at a lower pressure than the plasma production region. Gaseous precursors are injected directly into the injection section. Solid and liquid precursors are first vaporized in a tubular furnace and swept into the injection section with some additional gases. Particles are seen forming immediately, which then deposit on all exposed parts inside the chamber, including a substrate usually kept at a distance of 120 mm from the torch nozzle. Samples are later collected and sent for different material characterization. Figure 2.2 shows a photograph of the complete experimental set-up. The different sub-systems of our experimental set-up are explained below.

Figure 2.2: A photograph of our complete experimental system showing (A) Segmented plasma torch assisted reactor (B) Vacuum chamber (C) Power supply (D) Water storage tank for cooling system (E) Tubular furnace (F) Vacuum pumps and (G) Gas cylinders.
2.1.2 Segmented plasma torch

One of the most integral parts of the experimental system is the segmented plasma torch. A schematic of the plasma torch is given in figure 2.3. It consists of four floating ring segments, each 10 mm thick, having 90 mm outer diameter, 10 mm inner diameter passage for plasma, and fabricated from copper/brass. All segments are insulated from each other through 2 mm thick Teflon rings, which also sustains vacuum inside the torch channel. The cathode is made of thoriated tungsten in the form of a rod embedded in the top most copper/brass segmented ring. This ring also

Figure 2.3: Schematic diagram showing the segmented plasma torch, injection section and the converging nozzle.

has the provision for discharge gas injection tangentially, which leads to the vortex stabilization of the discharge inside the plasma torch. The bottom most segment serves
as the anode (six segments in total). Some of the floating rings also have provision for
gas injection which can be utilized for injection of additional gases. All torch
segments are intensely water cooled by approximately 8 lpm water flowing through
individual components. The water cooled walls of the central holes of the floating
rings offers additional stabilization of the plasma arc.

The plasma torch is connected to a mating flange which is placed just over the
neck section to a bottom chamber. The interior of the neck section forms the injection
section which is an annular region of diameter 15 mm and length 25 mm, and also
holds the converging nozzle, inlet diameter 10mm, outlet diameter 5 mm and length
50 mm. The neck section has four small ports of inner diameter 2 mm which opens
into the injection section. One each of these small ports is used for measuring pressure
via a mercury manometer, for collection of light from plasma for optical emission

Figure 2.4: Photograph of the segmented plasma torch.

spectroscopy (OES) studies, for injection of precursors in gaseous form and for
injection of precursor vapor from the tubular furnace. The mating flange, the neck
section and the converging nozzle are all made of copper and all water cooled. The converging nozzle opens into the vacuum chamber. A photograph of our segmented plasma torch is given in figure 2.4.

2.1.3 Vacuum chamber

The vacuum chamber is a double walled, water cooled, vertical cylindrical chamber fabricated out of non-magnetic stainless steel having diameter 300 mm and height 300 mm, as shown in figure 2.5. The torch with the mating flange and the neck section is connected at the top flange of this chamber. The converging nozzle in the injection section opens out into this chamber. The chamber is provided with four large side ports. One of them is used for accessing the interior of the chamber for placing/removing substrate, sample collection, cleaning etc. while the remaining three is used for viewing the plasma, optical diagnostics etc. It also has two small ports for

Figure 2.5: A photograph showing the segmented plasma torch mounted on the vacuum chamber and the tubular furnace used for vaporizing solid and liquid precursors.
connecting the pressure gauges. The vacuum pumps are connected through a port located at the bottom flange. Substrates for collecting the sample are placed on a water cooled substrate holder whose height can be manipulated from outside.

2.1.4 Power supply

To power the plasma torch, we have used a Memco (Miraj Electrical & Mechanical Co. Pvt. Ltd., Mumbai, MTW A6 400) made, full wave DC, thyristorised welding power supply, with maximum open circuit voltage of 150 volt and current 400 Amperes. A Memco make Plasma /TIG welding Console was also used to ignite the plasma, which is basically a high frequency (HF) igniter. The cathode and anode are directly connected to the power supply through water-cooled copper cables. The output of the HF igniter is connected to the first ring through a water-cooled cable with a 0.8-ohm resistance and an electrical contactor.

Later, we have also procured and used a custom built power supply, made by Technocrat Plasma, Thane (shown in figure 2.6). The new power supply was also a full wave DC, thyristorised welding power supply but this had a higher power rating of 80 kW, with maximum open circuit voltage of 200 volt and current 400 Amperes. Here, the high frequency (HF) igniter is in-built inside the body of the power supply. A schematic of the circuit diagram of our plasma torch is given in figure 2.7. For production of plasma, high voltage high frequency pulses are applied between the cathode and the first ring, which initiates a pilot arc between them. The discharge current flows through the 0.8 ohm resistance and a potential is dropped across it, which lowers the potential of the first ring. Due to the potential difference between the
first ring and the anode, the arc is transferred to the later and produces a stabilized, axis symmetric plasma flame coming out from the opening of the anode ring segment.

Figure 2.6: A photograph of the 80 kW power supply made by Technocrat Plasma, Thane.

Figure 2.7: Circuit diagram of the plasma torch.

2.1.5 Water cooling system
Because of the extreme heat generated by the plasma beam, all the components of the plasma torch and the vacuum chamber have to be intensely water cooled. For this, we use a closed loop water circulating system having fourteen numbers of water lines. The water is stored in an SS storage tank (shown in figure 2.2) of capacity 1500 liters from which a Kirloskar made centrifugal water pump (KDS 33517, 200 liters/minute, 2.2 HP), pumps the water into the fourteen lines. The water after passing through the reactor components flows back to the storage tank through a common water header. The flow rate in each water line can be monitored by rotameters attached to each line and the flow rate can be controlled individually from 0 to 10 litres per minute. Out of the fourteen water lines, six of them are used for cooling the torch segments and one each for the mating flange, vacuum chamber and the substrate holder and two lines for the neck section.

2.1.6 Tubular furnace

The precursors in gaseous state can be injected directly into the injection section through one of the ports attached to the injection section. But precursors in the solid and liquid state have to be injected in their vapor state as our reactor does not have the provision for solid and liquid phase injection. Therefore, for vaporizing the liquid and solid precursors, we use a tubular furnace, which consist of a stainless steel cylinder of length 300 mm and diameter 75 mm (shown in figure 2.5), surrounded by a heating coil temperature of which may be raised to 400 °C. The surface temperature of the tube can be measured with a thermocouple and programmed with a temperature controller. The precursor is kept inside the cylinder in a crucible and their vapors are swept into the injection section of the reactor by gases like hydrogen, argon etc. The SS cylinder is connected to the injection section by SS pipes through a valve. This
pipe is heated and kept at a constant temperature of 200 °C to prevent condensation of precursor vapors in the line.

### 2.1.7 Pumping system

![Image of vacuum pumps](image)

**Figure 2.8:** Photograph shows the roots vacuum pump (OKTA 500A, Pfeiffer Vacuum, Germany) backed by a rotary vacuum pump (FD-60, Hind High Vacuum Co. Pvt. Ltd., Bangalore).

In order to create vacuum in the chamber, we have used a roots vacuum pump backed by rotary vacuum pump. The roots pump (OKTA 500A, Pfeiffer Vacuum, Germany) had a capacity of 8000 liters per minute and the backing rotary pump (FD-60, Hind High Vacuum Co. Pvt. Ltd., Bangalore), 1500 liters per minute. The roots-rotary combination is shown in figure 2.8. This combination created a base pressure of
the order of $10^{-3}$ mbar. In working conditions, while injecting 20 lpm argon and few lpm of precursor gases like acetylene or carrier gases like hydrogen, the working pressure of around 20 mbar could be maintained in the vacuum chamber. We have also worked at higher chamber pressure in order to compare the results. For maintenance of high pressure, the chamber was connected directly to the rotary pump through capillary pipes. This arrangement gave working pressure of 350 and 600 mbar depending on the exact size of the capillary hole. A digital Pirani gauge was used to measure pressure in the sample collection chamber. Pressure at the injection section was measured with a mercury manometer, through one of the ports at the neck portion of the reactor.

2.1.8 Gases and reactants

For the production of plasma, ultra pure argon (99.999%, Assam Air Products Pvt. Ltd., Guahati, Assam) was used. For most of the experiments, the argon flow rate was maintained at 20 liters per minute. For the production of carbon nanoparticles, acetylene (IUPAC name ethylene, 99.9%, Vadilal Chemical Ltd., Ahmedabad, India) was injected directly into the injection section at the rate of 1.4 liters per minute. For the production of carbon encapsulated magnetic nanoparticles (CEMN), ferrocene ($\text{FeC}_10\text{H}_{10}$) from Spectrochem Pvt. Ltd., Mumbai, was heated in the tubular furnace and its vapor were carried by hydrogen (99.999%, Assam Air Products Pvt. Ltd., Gauhati, India) into the injection section. With the hydrogen flow rate of 1.2 liters per minute, the flow rate of ferrocene could be varied by controlling the temperature of the tubular furnace.

2.1.9 Optical emission spectrometer
We have used techniques of optical emission spectroscopy (OES) for plasma diagnostics. For the measurements we have used a CVI Laser Corporation (USA) make grating monochromator, DK 480. The specification of the monochromator is given in table 2.1 [1]. A computer controlled photo multiplier detection module AD110, was used in conjunction with the monochromator, which was mounted on the exit slit of the monochromator. Some of the features of the photomultiplier tube are given in table 2.2. A photograph of the complete spectrometer system is given in figure 2.9. The photomultiplier uses Gallium Arsenide, whose spectral response is given in figure 2.10.

Figure 2.9: Photograph shows the ½ meter monochromator (DK 480, CVI Laser corporation, USA), fiber cable for collecting light, photomultiplier tube and accessories used for OES studies of the plasma.
Table 2.1. Specification for the monochromator

<table>
<thead>
<tr>
<th>Specification</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength drive</td>
<td>Worm and wheel with microprocessor controlled, bi-directional</td>
</tr>
<tr>
<td>Focal length</td>
<td>480 mm</td>
</tr>
<tr>
<td>Grating</td>
<td>68×68 mm, 1200 groove/mm</td>
</tr>
<tr>
<td>Wavelength precision</td>
<td>0.01 nm</td>
</tr>
<tr>
<td>Wavelength accuracy</td>
<td>± 0.3 nm</td>
</tr>
<tr>
<td>Scan speed</td>
<td>1 to 1200 nm/minute</td>
</tr>
<tr>
<td>Maximum resolution</td>
<td>0.06 nm</td>
</tr>
<tr>
<td>Slits</td>
<td>Computer controlled, width 10 to 3000 µm, height 2 to 20 mm</td>
</tr>
</tbody>
</table>

Figure 2.10: Spectral response of the photomultiplier tube.
Table 2.2. Specification for the photomultiplier tube

<table>
<thead>
<tr>
<th>Specification</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength range</td>
<td>185 to 930 nm</td>
</tr>
<tr>
<td>Voltage range</td>
<td>0–1000 VDC</td>
</tr>
<tr>
<td>A/D resolution</td>
<td>12 Bit (Successive approximation)</td>
</tr>
<tr>
<td>D/A channel</td>
<td>1 (Programmable control of HV)</td>
</tr>
<tr>
<td>Input voltage</td>
<td>± 5 VDC</td>
</tr>
<tr>
<td>Max integration time per second</td>
<td>10 second</td>
</tr>
<tr>
<td>Minimum data speed</td>
<td>30 millisecond</td>
</tr>
<tr>
<td>A/D accuracy</td>
<td>0.015% of reading ± 1 bit</td>
</tr>
<tr>
<td>Amplification gain</td>
<td>X1, X2, X4, X8, X16</td>
</tr>
</tbody>
</table>

2.2 Nanoparticle characterization techniques

2.2.1 X-ray diffraction (XRD)

When electromagnetic radiation interacts with a crystalline structure whose lattice distance is about the same as the wavelength of the radiation, diffraction can occur. X-rays have wavelengths in the range of typical inter-atomic distances (in order of angstroms) in crystalline solids. Therefore, X-rays can be diffracted from the periodic patterns of atoms of crystalline materials.

When several X-rays scattered from a crystalline solid overlaps in space simultaneously, either constructive or destructive interference occurs. Constructive interference occurs when the diffracted waves move in phase with one another, while destructive interference occurs when the waves are out of phase. X-ray diffraction is
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based on constructive interference of monochromatic X-rays. The condition necessary for constructive interference is given by Bragg’s law [2] which is,

\[ n\lambda = 2d \sin \theta \]  

where the integer \( n \) is the order of the diffracted beam, \( \lambda \) is the wavelength of the incident X-ray beam, \( d \) is the distance between adjacent planes of atoms (the d-spacing), and \( \theta \) is the angle of incidence of the X-ray beam. This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. Knowing \( \lambda \) and \( \theta \), we can calculate the d-spacings.

If the thickness of a crystal was infinite, we would see diffraction only at the Bragg’s angle. Therefore diffraction from bulk crystalline materials gives sharp peaks. But as the crystallites in a powder get smaller, the diffraction peaks get broader. The dependence of line broadening on the crystallite size can be explained as follows. Consider that the path difference between rays scattered in the first and second layer of a crystal is only a quarter of wavelength, then these two rays are not completely out of phase and so do not cancel each other completely. But the wave from the third layer has a path difference of half a wavelength and completely cancels the ray reflected from the first layer. Similarly, the second and fourth layer along with the third and fifth and so on would cancel each other. But in case of rays near the Bragg peaks, the path difference between the first two planes is just slightly less than an integral number of wavelengths, and so, the plane scattering a ray completely out of phase with the one scattered in the first layer lies deep within the crystal. So if the crystal is too small for this plane to exist, the intensity cannot be cancelled out completely and leads to the broadening of the peaks.
When the crystallites diffracting the X-rays are less than about 100 nm in size, appreciable broadening in the X-ray diffraction lines will occur. These crystallites may correspond to the actual size of the particles or may be some domains in the larger particle and may be a distinguishing and important feature. But in each case, the observed line broadening can be used to estimate the average size.

The average size of the particle \((D)\)/crystallite can be evaluated from Scherrer's equation [3], which is,

\[
D = \frac{K\lambda}{\beta \cos \theta}
\]

where \(K\) is a constant known as shape factor, \(\lambda\) is the wavelength of the X-ray, \(\beta\) is the full width at half maximum intensity of the peak and \(\theta\) is the diffraction angle.

X-ray diffractometers consist of three basic components: an X-ray tube, a sample holder, and an X-ray detector. X-rays are generated in a cathode ray tube by heating a filament which emits electrons. These electrons are accelerated towards a target by applying a voltage. The bombardment of the target material with electrons having sufficient energy dislodge inner shell electrons of the target material producing characteristic X-ray spectra, consisting of several components, the most common being \(K_a\) and \(K_\beta\). Monochromatic X-rays, needed for diffraction, are produced by filtering, by foils or crystal monochromators.

These X-rays are collimated and directed onto the sample. As the sample and detector rotates, the intensity of the reflected X-rays is recorded. When the geometry of the incident X-rays impinging the sample satisfies the Bragg's Equation, constructive interference occurs and a peak in the measured intensity occurs. The
geometry of an X-ray diffractometer is such that the sample rotates in the path of the
collimated X-ray beam at an angle $\theta$ while the X-ray detector is mounted on an arm to
collect the diffracted X-rays and rotates at an angle of $2\theta$.

For this work, we have used the X-ray diffractometer facility at Research and
Development Department, Oil India Limited, Duliajan, Assam. We used Philips PW
1710 X-ray diffractometer using a copper target as X-ray source for Cu$\text{K}\alpha$ radiation.
The entire XRD patterns were taken in the powder mode.

### 2.2.2 Electron microscopy

Electron microscopy is based on the principle of using electrons as the source
of illumination in place of light used in optical microscopy. The limit of resolution is
inversely proportional to the wavelength of the illuminating source [4]. Since an
electron has much less wavelength as compared to light, a microscope using electrons
has much higher resolution. The electron microscope consists of a long column, the
top most chambers of which is called the electron gun chamber, which has a V-shaped
filament. The column is maintained at high vacuum to avoid collision between air
particles and electrons. When high voltage is applied, thermoionic emission takes
place in the filament and electrons are ejected out. Some electron microscope uses
field emitters like quartz crystal for the electron gun. In electron microscope,
electromagnetic fields called condenser lens are used to condense the electron beam
into a small pencil of ray, and acts like the lenses in optical microscope. The de
Broglie wavelength of the electron beam is inversely proportional to the voltage
applied and hence, higher the voltage applied, smaller will be the wavelength and
higher the resolution.
2.2.2.1 Transmission electron microscope (TEM)

In transmission electron microscope (TEM), the electron beam passes through the specimen and when it emerges from the specimen, the electron beam carries information about the structure of the specimen that is magnified by the objective lens system of the microscope. The spatial variation in this information which forms the image is viewed by projecting the magnified electron image onto a fluorescent viewing screen coated with a phosphor. TEM offers very high magnification ranging from 50 to $10^6$, with resolution as high as 0.1 nm [5], giving the ability to visualize atoms and molecules. The higher is the operating voltage, the smaller is the electron wavelength and hence, higher the resolution. TEM is also capable of obtaining the diffraction patterns of the samples for phase identification as well as perform local chemical analysis with X-ray spectrophotometry. For TEM, the samples may not be conducting and so, studies can be performed on metallic, ceramic, plastic, biological and other surfaces. TEM is also the best direct method for the actual size determination of the particles in nanometer level. In a single field of view, the sizes of a large number of particles can be determined from which the size distribution and the average particles size can be determined. But since the electron beam has to pass through the specimen, the specimen should be extremely thin (less than 100 nm) which is sometimes difficult to achieve.

Most of the TEM and HRTEM analyses of our samples were done at Central Salt and Marine Chemicals Research Institute (CSMCRI), Bhavnagar, Gujarat. Few images were also taken at Sophisticated Analytical Instrumentation Facility (SAIF), North Eastern Hill University (NEHU), Shillong, Meghalaya and UGC-DAE Consortium for Scientific Research (CSR), Indore, Madhya Pradesh (MP). In all these
institutes, we have used JEOL JEM 2100 at 200 kV acceleration voltages and similar sample preparation procedure was followed. The samples were dispersed in ethanol, sonicated for around 5 minutes and loaded over a Lacey carbon coated copper TEM grid (300 mesh), dried and loaded to the TEM machine.

### 2.2.2.2 Scanning electron microscope (SEM)

In SEM, the electron beam does not pass through the sample; rather it interacts with the sample surface and results in reflection of low energy secondary electrons from it which takes part in image formation. Hence the thickness of the sample is immaterial for SEM. But for SEM, the samples must have a good electrical conductivity. Non-conducting samples are coated with metals like gold or platinum prior to examination. SEM does not have a very high resolution but SEM images have greater depth of field (curved surfaces are resolved properly) yielding a characteristic 3D appearance useful for understanding the surface structure of a sample. SEM photographs of our samples were taken at Central Salt and Marine Chemicals Research Institute (CSMCRI), Bhavnagar, Gujarat using LEO 1430 VP.

### 2.2.3 Raman spectroscopy

Raman spectroscopy is a spectroscopic technique based on inelastic scattering of monochromatic light, usually from a laser source in the visible, near infrared, or near ultraviolet range. Inelastic scattering means that the frequency of photons in monochromatic light changes upon interaction with a sample. Photons of the laser light are absorbed by the sample and then re-emitted. Frequency of the re-emitted photons is shifted up or down in comparison with original monochromatic frequency,
which is called the Raman Effect. This shift provides information about vibrational, rotational and other low frequency transitions in molecules. The intensity, frequency and width of Raman features are strongly dependent on composition, defects, short-range order, crystalline structure, and internal stress in the materials [6]. Therefore, it has been widely used to obtain detailed information about the structural properties of semiconductors, ceramics, catalysts, carbon based materials etc. Raman spectroscopy can be used to study solid, liquid and gaseous samples.

Raman spectroscopy has been intensively used to study the structural characteristics of carbon nanostructures. Raman spectrums of carbon based nanostructures usually consist of the D band, G band and 2D band [7]. The G (graphite) mode corresponds to planar vibrations of carbon atoms of graphene layers and is located at around 1580 cm$^{-1}$. The presence of G band is related to the existence of graphite like structures in the sample. The D (disordered) band appears at about 1350 cm$^{-1}$ and is a characteristic feature of amorphous carbon materials containing sp$^2$ graphitic islands and disordered samples of graphite. The intensity ratio of the D band to the G band ($I_D/I_G$) is related to the inverse of the crystallite size along the basal plane $L_a$ [8] and so, this ratio have been often used to compare the degree of crystallinity of the carbon samples. It has also been seen that in carbon nanostructures, the full width at half maxima of the G band (G-FWHM) decreases as $d_{002}$ of the carbon material approaches more towards that of graphite [9]. The 2D band is the second harmonic of the D band and has its peak around 2700 cm$^{-1}$. The 2D band commonly occurs in samples with high degree of graphitization while this feature disappears in samples containing large amounts of amorphous carbon [10] and the
peak of this band shifts towards higher wave number as the number of graphene layers increases in the sample [7].

Raman spectroscopy of our carbon nanoparticles samples were taken at Departamento de Física, Pontificia Universidad Católica de Chile, Santiago, Chile. The spectra were obtained with a LabRam 010 instrument from ISA using a 5.5 mW He – Ne laser (633 nm). The confocal microscope uses a back-scattering geometry, where the incident beam is linearly polarized and the spectral detection unpolarized. The spectra were taken under room conditions using a 100X objective (10 μm spot size) and an observed frequency resolution of 1 cm⁻¹. Raman spectra of our carbon encapsulated magnetic nanoparticles (CEMN) were taken at UGC-DAE Consortium for Scientific Research (CSR), Indore, MP, using Jobin Yvon Horiba LabRam with a He – Ne laser (633 nm).

2.2.4 Nitrogen adsorption measurements

Gas adsorption methods can probe the specific surface areas, surface irregularities and pore interiors of powdered materials even at the atomic level which is not possible by other techniques. Pores are cavities or channels in a solid body that are deeper than they are wide. The porosity of a sample is defined as the ratio of the pores and voids (space between the particles) to the volume occupied by the solid. Depending on the size of the pores, the IUPAC classifies pores as micropores (internal diameter less than 2 nm), mesopores (internal diameter between 2 and 50 nm) and macropores (internal diameter greater than 50 nm).

The amount (weight) $W$ of vapor adsorbed on a solid surface depends upon the absolute temperature $T$, the pressure $P$, and the interaction potential $E$ between the
vapor (adsorbate) and the surface (adsorbent). A plot of $W$ versus $P$, at constant $T$, is referred to as the adsorption isotherm of a particular vapor-solid interface. Since the interaction potential $E$ varies with the properties of the vapor and the solid and also changes with the extent of adsorption, we have five different types of adsorption isotherms as shown in figure 2.11 [11].

Figure 2.11: The five isotherm classification where $W$ is the weight adsorbed; $P$ is adsorbate saturated equilibrium pressure; $P_0$ is adsorbate saturated equilibrium vapor pressure.
The type I isotherms is characteristic of either a chemisorptions isotherm or physisorption on a material with micropores. The type II isotherm is most frequently encountered when adsorption occurs on nonporous or macroporous powders, with high energy of adsorption. Type III isotherm is encountered in materials with low energy of adsorption where the interaction between the adsorbent and adsorbed is lower than the adsorbed-adsorbed interaction. Thus, as adsorption proceeds, additional adsorption is facilitated. Type IV isotherms occur on adsorbents possessing mesopores and having high energy of adsorption. Type IV isotherms occur on adsorbents possessing mesopores and having low energy of adsorption.

Hysteresis loops occur on various types of isotherms specially type IV and V isotherms. The presence of hysteresis loops in the isotherms is attributed to capillary condensation of adsorbate in the pores of the adsorbent. Hysteresis loops are classified into four types, H1–H4 by an IUPAC committee [12] and are shown in figure 2.12. The H1 type hysteresis is characterized by nearly vertical and parallel adsorption and desorption branches and is found in samples with a narrow distribution of uniform pores. The H2 type hysteresis is characterized by sloping adsorption branch and nearly vertical desorption branch and is found in samples with wide distribution of pore sizes and shapes with possible interconnecting channels. The H3 types hysteresis have sloping adsorption and desorption branch and are found in samples with slit shaped pores. The H4 types hysteresis also have sloping adsorption and desorption branch and are found in microporous samples.

The specific surface area of nanostructures can be calculated from the nitrogen adsorption isotherms by using the Brunauer-Emmet-Teller (BET) theory [1]. The BET theory effectively enables an experimental determination of the numbers of molecules
required to form a monolayer in spite of the presence of multilayers at some sites. The BET theory assumes that the molecules in the uppermost layers are in dynamic equilibrium with the vapor. Therefore, the number of molecules in each layer will remain constant even though the actual location of the surface sites covered by one, two or more layers may vary. The BET equation can be written as,

\[
\frac{P}{V(P_0 - P)} = \frac{1}{CV_m} + \frac{C - 1}{CV_m} \times \frac{P}{P_0}
\]

where \( P \) is the adsorbate pressure, \( P_0 \) the saturation vapor pressure and the ratio \( P/P_0 \) the relative pressure, \( V \) the amount of gas adsorbed, \( V_m \) the monolayer capacity and \( C \) is the BET constant.

From the above equation, we see that the plot of \( \frac{P}{V(P_0 - P)} \) versus \( \frac{P}{P_0} \), usually plotted in the range \( 0.05 \leq P/P_0 \leq 0.35 \) as most monolayers are completed in this range.

Figure 2.12: The four different types of hysteresis loops.
range, gives a straight line of slope $\frac{c-1}{CV_m}$ and intercept $\frac{1}{CV_m}$. Therefore from this, the amount adsorbed in a monolayer and the BET constant can be calculated. Once the value of $C$ is taken as experimentally acceptable, the specific surface area of the adsorbent can be obtained from,

$$S_{BET} = V_m N_a \sigma$$

where $N_a$ is the Avagadro’s number and $\sigma$ is the cross sectional area of one molecule of adsorbate.

Pore size and pore-size distribution studies by adsorption generally make use of the Kelvin equation which relates the equilibrium vapor pressure of a curved surface to the equilibrium pressure of the same liquid on a plane surface. The Kelvin equation [11] is given by

$$\ln\left(\frac{P}{P_o}\right) = -\frac{2\gamma V}{r_k RT} \cos \theta$$

where $P$ is the equilibrium vapor pressure of the liquid contained in a pore of radius $r_k$ and $P_o$ is the equilibrium pressure of the same liquid exhibiting a plane surface. The terms $\gamma$ and $V$ are the surface tension and molar volume of the liquid, respectively, and $\theta$ is the contact angle with which the liquid meets the pore wall. In a pore, condensation will occur at a lower pressure compared to that on an open or plane surface. Thus, as the relative pressure is increased from zero, adsorption is first restricted to a thin layers on the walls and then, condensation will occur in pores of smaller radii and will progress into larger pores. Thus the radius of a pore ($r_p$) being condensed at a particular partial pressure is equal to the sum of the Kelvin radius ($r_k$) and the thickness of the film ($t$),
Chapter 2

The pore size distribution is evaluated using the Barrett-Joyner-Halenda (BJH) method considering the pores to be cylindrical. Applying the Kelvin equation to nitrogen at the temperature of -196 °C and a hemispherical meniscus with 0 contact angle, the Kelvin radius is given by,

\[ r_k = \frac{0.415}{\ln\left(\frac{p}{p_0}\right)} \]  

In order to get the thickness of the film as a function of the partial pressure, we use the Halsey empirical relation given by,

\[ t = 3.54 \left(\frac{5}{\log\left(\frac{p}{p_0}\right)}\right)^{1/3} \]

Now, since we have the volume of nitrogen adsorbed/desorbed as a function of the partial pressure from the isotherms, it is possible to obtain the pore volume as a function of the pore size and hence the pore size distribution of the material.

Before undergoing the nitrogen adsorption process, the solid sample is usually pretreated by applying some combination of heat, vacuum and/or flowing gas to remove adsorbed contaminants acquired from atmospheric exposure. The sample is then cooled, usually to cryogenic temperature, under vacuum and is then exposed to nitrogen gas at a series of precisely controlled pressures. With each increase in pressure, the number of gas molecules adsorbed on the surface increases. The pressure at which adsorption equilibrium occurs is measured and the quantity of gas adsorbed is calculated. The gas volume adsorbed at each pressure, at a constant temperature, defines an adsorption isotherm.
The \( \text{N}_2 \) adsorption-desorption isotherms of our samples were measured in a static volumetric adsorption system surface area analyzer, Micromeritics ASAP 2010 at Central Salt and Marine Chemicals Research Institute (CSMCRRI), Bhavnagar, Gujarat. The adsorption and desorption isotherms were measured at 77 K after heating the sample at 200 °C under vacuum (\( 6.5 \times 10^{-3} \) mbar) for 2 hours. From this, the specific surface area was calculated using the Brunauer–Emmett–Teller (BET) theory. These measurements also gave the average pore size and pore volume distribution (\( \text{cm}^3\text{g}^{-1} \)) using the Barrett–Joyner–Halenda (BJH) method and the Halsey equation for multilayer thickness.

2.2.5 Vibrating sample magnetometer (VSM)

A vibrating sample magnetometer (VSM) works on the principle of Faraday’s law of induction, which states that an electric field is produced by a changing magnetic field. A VSM consist of a variable electromagnet, a non-magnetic rod where the sample is mounted and which is connected to a vibration unit and a detection coil. The sample is placed in a variable magnetic field produced by the electromagnet. The sample gets magnetized, the larger the applied field, higher is the magnetization. The sample is vibrated with the aid of the vibrating unit causing its magnetic field to change. This change in magnetic field generates an electric field which is proportional to its magnetization and this electric field is detected by the detection coil. The magnetic field, \( H \) of the electromagnet is varied and the samples magnetization (magnetic moment), \( M \) is noted. The output result plots the magnetic moment (\( M \)) as a function of the applied field (\( H \)).
When an external magnetic field is applied to a ferromagnetic material it gets magnetized by aligning its atomic dipoles along the external magnetic field. Even when the external magnetic field is removed, it retains some of the magnetization. Once magnetized, it can only be demagnetized by applying heat or magnetic field in the opposite direction. This property of the ferromagnets leads to the formation of hysteresis loops when the magnetic moment $M$ is plotted as a function of the applied field $H$ (figure 2.13). The relationship between the externally applied field and the Magnetization is not linear for such materials. For a linearly increasing field $H$, the magnetization or magnetic moment, $M$ follows a curve up to a point beyond which the magnetic moment does not increase even if we increase the applied field. This point gives the saturation magnetization ($M_s$) of the sample. Now if the applied field is reduced monotonically, the magnetic moment also reduces following a similar curve.
but offset from the original curve by an amount called the remnant magnetization. Therefore the M-H relationship forms a hysteresis loop when plotted for all strengths of applied magnetic field. The coercivity ($H_c$) of the sample is half the width of the curve where magnetization is zero. The value of magnetization at the point where applied field is zero gives the remnant magnetization ($M_r$).

In this study, the magnetic properties of carbon encapsulated magnetic nanoparticle samples were studied by vibrating sample magnetometer (VSM) at room temperature (300 K) and 10 K. Room temperature measurements were done at Department of Physics, Indian Institute of Technology (IIT), Guahati, Assam, with Lake Shore Vibrating Sample Magnetometers Model 7410. Measurements at 10 K were done at UGC-DAE Consortium for Scientific Research (CSR), Indore, MP, by Physical Property Measurement System (PPMS-14T) form Quantum Design.

### 2.2.6 Mossbauer spectroscopy

Mossbauer is a spectroscopic technique based on the Mossbauer Effect which was discovered by Rudolf Mossbauer in 1957. Mossbauer spectroscopy probes tiny changes in the energy levels of an atomic nucleus. When a free nucleus emits or absorbs a gamma ray, it recoils to conserve the momentum. But when a nucleus in a solid crystal emits or absorbs a gamma ray, some quantized energy may be lost in the form of phonons (vibration in the crystal lattice). But in solids, the recoiling mass is effectively the mass of the whole system and if the energy of the gamma ray is small enough, the recoil of the nucleus is too low to be transmitted as phonons [13]. This gives rise to a recoil free event, which is the Mossbauer Effect. So, if the nuclei emitting and the absorbing the gamma rays are in a solid matrix, the emitted
absorbed gamma-ray have the same energy i.e. resonance. By moving the absorber and the emitter, placed in different solids, relative to each other the energy of the gamma rays can be scanned across the resonance energy via the first order Doppler shift.

During Mossbauer measurements, a collimated beam of gamma radiation from a source passes through the sample and a detector measures the intensity of the emerging beam. The atoms in the sample which absorbs the radiation must be of the same isotope as the atoms in the source emitting the radiation. When the emitting and the absorbing nuclei are in identical chemical environment, resonant absorption occurs with both materials at rest. However, if they are in different chemical environment, the nuclear energy levels shift in a few different ways. In such situation, resonance can be brought back by slightly changing the energy of the gamma ray. The energy of the gamma-ray can be changed in very small increment by moving the source back and forth to generate a Doppler effect. Where the modulated gamma-ray energy matches precisely the energy of a nuclear transition in the sample, the gamma-rays are resonantly absorbed and we see a dip. In a Mossbauer spectrum, the gamma ray intensity is plotted against the energy scale quoted in terms of source velocity. Depending on the chemical environment of the absorbing nuclei, the number, position and intensities of the dips vary and these are used to characterize the sample.

The energy levels in the absorbing nuclei can be modified by their environment in three different ways, the Isomer Shift, Quadrupole Splitting and Magnetic splitting also called hyperfine splitting or Zeeman splitting. Isomer shift is a relative measure which gives the shift in resonance energy of the nucleus. It arises due to the non-zero volume of the nucleus and the electron charge density due to s
electrons within it. This leads to Coulomb interaction altering the nuclear energy levels. Thus, any difference in the s-electron environment between the source and the absorber produces a shift in the resonance energy of transition. The whole spectrum is shifted in either a positive or negative direction depending upon the s-electron charge density. Isomer shift is independent of temperature. This shift is useful in determining valence states, ligand bonding states, electron shielding and the electron drawing power of electronegative groups. Quadrupole splitting is due to the interaction between the nuclear energy levels and the surrounding electric field gradient. Nuclei with non-spherical charge distributions produce a quadrupole moment. The interaction of the nucleus with an asymmetric electric field, produced by either asymmetric electronic charge distribution or ligand arrangement, splits the nuclear energy levels. Quadrupole splitting is measured as the separation between the dips and reflects the nature of the electric field at the nucleus. Magnetic splitting is due to the interaction between the nucleus and the surrounding magnetic field. In the presence of a magnetic field, the nuclear spin moment experiences a dipolar interaction with the magnetic field i.e. Zeeman splitting. The magnetic field splits the nuclear levels with a spin of I into \((2I+1)\) substates. The line positions are related to the splitting of the energy levels but the line intensities are related to the angle between the Mossbauer gamma-ray and the nuclear spin moment.

Mossbauer spectroscopic studies of carbon encapsulated magnetic nanoparticle samples were also done at UGC-DAE Consortium for Scientific Research (CSR), Indore, MP. Mossbauer spectra were measured in transmission geometry at room temperature \((T=300 \text{ K})\) in zero applied external magnetic field. A constant acceleration spectrometer was used with \(^{57}\text{Fe}\) radioactive source. The relative fraction
of each iron-containing phase was calculated as the ratio of the area of each phase’s sub-spectrum to the entire spectral area.

### 2.2.7 Quartz crystal microbalance (QCM)

Quartz crystals possess piezoelectric effect, which allows probing an acoustic resonance by electrical means. When an alternating current is applied between the electrodes of a properly cut crystal, a standing shear wave is generated, with Q factor as high as $10^6$. Such a narrow resonance leads to highly stable oscillators and a high accuracy in the determination of the resonance frequency. The Quartz Crystal Microbalance (QCM) makes use of this precision for sensing. A QCM measures the mass per unit area by measuring the change in frequency of a quartz crystal resonator. The resonance is disturbed by the addition or removal of a small mass at the surface of the acoustic resonator.

A typical quartz crystal microbalance (QCM) contains water cooling tubes, the retaining unit, frequency sensing equipment, an oscillation source, and a measurement and recording device. Commonly used equipment allows resolution down to 1 Hz on crystals with a fundamental resonant frequency in the 4 – 6 MHz range. The quartz crystal frequency of oscillation is partially dependent on the thickness of the crystal. With all the other influencing variables remain constant, a change in thickness correlates directly to a change in frequency. When a mass is deposited on the surface of the crystal, the thickness increases and consequently the frequency of oscillation decreases from the initial value. This frequency change can be quantified and correlated precisely to the mass change using Sauerbrey's equation [14]. It can easily measure mass densities down to a level below 1 μg/cm².
QCM can also be used under vacuum in the gas phase as gas sensors. It can be used to measure the amount of gases like hydrogen adsorbed on some adsorbent deposited on the quartz surface. QCM can also be used in liquid environment and is highly effective at determining the affinity of molecules to surfaces functionalized with recognition sites.

We have used a quartz crystal microbalance (QCM) system from MDC model SQM-160 for the hydrogen absorption measurements. The quartz crystals (that fitted in the QCM head) were AT cut from a single crystal, have a diameter of 1.4 cm and oscillate in a transverse shear motion with a resonant frequency between 5 and 6 MHz when bare. The QCM head was placed inside a small (less than 1000 cm$^3$ in volume) all stainless steel vacuum chamber pumped by a 50 litres per second turbo pump from Balzers. A gate valve was placed between the steel chamber and the turbo pump to isolate the chamber from the vacuum thus being able to pressurize with hydrogen gas through a leak valve. The base pressure of the chamber was $10.4 \times 10^{-7}$ mbar before hydrogen was admitted. High pressures (in the range of 1 to 1000 mbar) were measured with a capacitor manometer (Baratron from MKS Instruments).

The Sauerbrey’s equation relating the mass added ($\Delta m$) to the quartz crystal and the shift in its resonance frequency ($\Delta f$) is given by,

$$\Delta f = -\frac{2f_0^2}{A\sqrt{\rho\mu}} \Delta m$$

where $f_0$ is the resonant frequency, $\rho$ is the density, $\mu$ is the bulk modulus of the quartz crystal and $A$ the area covered by the mass. We define the constant $C_f$ as,

$$C_f = \frac{2f_0^2}{A\sqrt{\rho\mu}}$$
Therefore, we get,

$$\Delta f = -C_f \Delta m$$.....................................................2.11

In order to obtain the constant $C_f$ experimentally, we grew Pd films of different thicknesses and we plotted the Pd mass versus the shift in resonant frequency, obtaining a value of $C_f$ as,

$$C_f = 162 \text{ Hz/\mu g}$$..............................................2.12

Small amount of the carbon powder was dispersed in isopropyl alcohol. Drops of the solution were deposited on the gold plated side of the quartz crystals. Once the alcohol evaporates the carbon material remains adhered to the crystal. After this, the crystal with the carbon sample was heated up to 200°C at a rate of 5°C/min in air and kept at 200°C for 10 min. These studies were done at Departamento de Física, Pontificia Universidad Católica de Chile, Santiago, Chile.

### 2.2.8 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is a quantitative spectroscopic technique used for studying the electronic structure of atoms, molecules and solids. XPS was originally used for spectroscopy of atoms and molecules in the gas phase, exciting with monochromatic ultraviolet light. Later, it was developed by Kai Siegbahn and his research group for spectroscopic investigations of solids by excitation with soft X-rays and was named ESCA (electron spectroscopy for chemical analysis) [15]. In XPS, a monochromatic X-ray beam is irradiated at the sample which detaches electrons from the surface of the sample. Kinetic energy and number of electrons ejected from the sample is analyzed which gives direct information about the
electronic structure and chemical composition of the sample. It is to be noted that XPS in solid state is very surface sensitive, because only photoelectron from a thin surface layer are emitted losslessly with the so-called escape depth varying from 2 to 20 Å, depending on the kinetic energy of the photoelectrons.

The energy ($E_{\text{Photon}}$) of the incident photon (X-ray) with particular wavelength is known and since the kinetic energy ($E_{\text{Kinetic}}$) of the emitted electrons is measured, the electron binding energy ($E_{\text{Binding}}$) of each of the emitted electrons can be calculated from the following equation, which is essentially the conservation of energy equation,

$$E_{\text{Binding}} = E_{\text{Photon}} - (E_{\text{Kinetic}} + \Phi) \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots 2.13$$

where, $\Phi$ is the work function of the spectrometer which is an adjustable instrumental correction factor that accounts for the few eV of kinetic energy lost by the photoelectron as it enters the instrument's detector.

In a typical XPS spectrum, the number of electrons detected ($Y$-axis, ordinate) is plotted against the binding energy of the electrons detected ($X$-axis, abscissa). Each element produces a characteristic set of XPS peaks at characteristic binding energy values corresponding to the electron configuration of the electrons within the atoms and the number of electrons detected in each of the characteristic peaks is directly related to the amount of element within the XPS sampling volume. The ability to produce information about the local bonding environment of the electron makes XPS a unique and invaluable tool for understanding the chemistry of any surface.

The spectra of X-ray photoelectron spectroscopy for our carbon encapsulated magnetic nanoparticle samples were taken at UGC-DAE Consortium for Scientific
Dynamic light scattering (DLS) is an important technique used for determining the size distribution pattern of fine particles in solution. When light hits particles whose sizes are much less than the wavelength of the light (below 250 nm), the light gets scattered in all directions, which is Rayleigh scattering. When the particle size is roughly equivalent to the wavelength of the illuminating light, a complex function of maxima and minima with respect to angle is observed which can be explained by Mie theory. When monochromatic and coherent light source like laser is used, a time-dependent fluctuation in the scattering intensity is observed. This is because the small particles in solutions are undergoing Brownian motion, and so the distance between the scatterers in the solution is constantly changing with time. This scattered light then undergoes either constructive or destructive interference by the surrounding particles, and within this intensity fluctuation, information is contained about the time scale of movement of the scatterers. The smaller the particle, the faster the Brownian motion will be and so, the smaller particles cause the intensity to fluctuate more rapidly than the large ones.

In DLS experiments, a correlator generates a correlation function, \( G(\tau) \). For monodisperse particles in Brownian motion, the correlation function is an exponential decaying function of the correlator time delay \( \tau \) given by,

\[
G(\tau) = A[1 + B \exp(-2\Gamma\tau)]
\]
where $A$ is the baseline of the correlation function, and $B$ is the intercept of the correlation function.

The term $\Gamma$ is given by,

$$\Gamma = Dq^2$$

where $D$ is the translational diffusion coefficient and $q$ is the wave vector given by,

$$q = \frac{4\pi n}{\lambda} \sin \left( \frac{\theta}{2} \right)$$

where $n$ is refractive index of dispersant, $\lambda$ the wavelength of the laser, $\theta$ the scattering angle.

The hydrodynamic radius $R_h$ is related to the translational diffusion coefficient $D$ by the Stokes–Einstein equation given by,

$$R_h = \frac{k_BT}{3\eta D}$$

where, $k_B$ is the Boltzmann constant, $T$ the absolute temperature and $\eta$ the viscosity of the solvent.

It may be pointed out here that DLS measures the hydrodynamic radius of a particle which is the effective radius of an irregularly shaped particle that is used when describing the manner in which particles in suspension diffuse through the suspending medium.

A typical DLS system includes a laser used to provide a light source to illuminate the sample within a cell while a detector measures the intensity of the scattered light. An attenuator is used for adjusting the intensity of the scattered light.
entering the detector. The light then passes through the correlator which is a digital
signal processing board. The correlator generates the rate at which the light intensity is
varying. This correlator information is then passed to a computer, where a software
analyzes the data and gives the particle size information.

The effective size of our carbon encapsulated magnetic nanoparticle (CEMN)
samples were measured by DLS at Central Salt and Marine Chemicals Research
Institute (CSMCRI), Bhavnagar, Gujarat with Mastersizer 2000 from Malvern in the
wet analysis mode.

2.2.10 Thermo gravimetric analysis (TGA)

Thermo gravimetric analysis (TGA) is a technique in which the change in
weight of a sample is monitored as a function of temperature and/or time as the
sample is heated as per a controlled temperature program in a controlled atmosphere.
TGA can give information about the sample’s composition, thermal stability,
oxidative stability of materials, decomposition kinetics, volatile contents etc. TGA is
commonly used to determine selected characteristics of materials that exhibit either
mass loss or gain due to decomposition, oxidation, or loss of volatiles (such as
moisture). The essential components of TGA includes a crucible which holds the
sample, a furnace that can heat the sample to required temperature and an appropriate
balance that continuously monitors the weight of the sample. A purge gas controls the
sample environment. This gas may be air, an inert gas like argon or a reactive gas like
Oxygen that flows over the sample and exits through an exhaust. The sample is placed
inside the crucible, which is supported on an analytical balance located outside the
furnace chamber and heated according to a predetermined thermal cycle. The weight
along with sample temperature and the time elapsed is stored in a computer. The TGA curve plots the percent weight change on the Y-axis against the corresponding material temperature and time elapsed on the X-axis.

The thermo-gravimetric analysis of carbon encapsulated magnetic nanoparticle (CEMN) was recorded in the range of 35–700 °C at 5 °C/min in air to make an estimate of the carbon amount in these samples. This also was done at Central Salt and Marine Chemicals Research Institute (CSMCRI) with a Thermogravimetry (TGA/DSC) instrument from Mettler Toledo.

2.3. Plasma diagnostics

2.3.1 Optical emission spectroscopy

During the last few decades, a great deal of research has been undertaken in plasma physics, both in theory as well as in experiments. But to avoid confrontation between theory and experiment requires theory to do calculations in realistic configuration and circumstances, but it also requires that the properties of plasma be measured experimentally as completely as possible. For this reason much of the experimental plasma physics is devoted to devising, developing and proving techniques for diagnosing the properties of plasma: plasma diagnostic. The overall objective of plasma diagnostic is to deduce information about the state of the plasma from practical observations of physical processes and their effects [16]. Considering the underlying physical principles of the process that enable us to make measurements, plasma diagnostics can be categorized as magnetic measurements, plasma particle flux measurements, plasma refractive index, scattering of
electromagnetic waves, ion process, electromagnetic emission from free electrons and electromagnetic emission from bounds electrons.

2.3.2 Electromagnetic radiation from plasma

In plasma, electromagnetic radiations are emitted by free electrons as well as bound electrons. When a free electron is accelerated in a magnetic or electric field, radiation is emitted. Most plasmas are permeated by some background magnetic field and the resultant motion (gyration) of electrons give rise to emission called cyclotron radiation. Rapidly varying electric field can also accelerate electron. When such a field is due to an incident electromagnetic field like Laser, scattering occurs. Plasma is a refractive medium and when the refractive index is greater than 1, it is possible for an energetic electron to travel faster than the local electromagnetic wave phase velocity. When this happens, Cerenkov emission takes place.

Radiation can also occur when a free electron is accelerated in the electric field of a charged particle. Such radiations are called Bremsstralung. This can happen either as free-free transition when the final state of the electron is free or free-bound transition in which the electron is captured by the ion into a bound final state which is also called recombination radiation. Radiation from a free electron is continuous while radiation from a bound electron (in atoms) is discontinuous and in the form of a narrow spectral lines.

Electrons bound to an atom, molecule or an ion can also emit radiation when they collide with energetic free electrons or ions. Such emission can occur in the following ways.

a) Electron impact excitation
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A + e = A* + e \{A is a neutral atom, e is an electron\}

b) Electron impact dissociation

\[ AB + e = A^* + B + e \] \{AB is a compound\}

c) Ion impact process

\[ A^+ + e(+M) = A^*(+M) \] \{e(+M) is a neutral atom\}

All the above processes creates an excited species A*, which releases energy in the form of radiation when they decay to lower energy states. It is radiation from such species which is made use in optical emission spectroscopy.

Usually the most intense radiation emitted from the plasma originates in the transition from first excited state \(E_1\) to the ground state \(E_0\) of the atoms. As each particle have precisely defined energy level, each emit a characteristic spectral line of frequency,

\[ \nu = \frac{(E_1 - E_0)}{h} \] \ ......................... 2.18

And wavelength,

\[ \lambda = \frac{hc}{(E_1 - E_0)} \] \ ......................... 2.19

where \(h\) is Planck’s constant and \(c\) is the velocity of light.

### 2.3.3 Plasma models

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In order to predict the radiative behavior of any atomic species in plasma, we must know the expected population of its various possible states. Therefore, we develop theories of models upon which the interpretation of spectral intensities is based. Knowing the electron temperature, density, and chemical composition, the theory provides the basis upon which spectrum may be calculated.

The observed intensity of radiation depends on the followings [17]:

a) The probability of an electron to be in upper level of transition.

b) The atomic probability of transition from concerned upper level to lower level.

c) The probability of the photons thus produced escaping from the volume of the plasma without being absorbed.

If the effect of interaction of radiation with the plasma (process c) is considered separately from the other two processes, the mathematics becomes quite simplified. There are physically realizable circumstances where this effect may be neglected and such plasmas are called optically thin plasma. The calculation of transition probability (process b) is a matter of atomic quantum theory. The distribution of electrons among the various energy levels available to them (process a) is determined by collision with other particles and by radiative processes. In order to solve the problem of electron distribution among various states, plasma models are proposed.

2.3.3.1 Local thermodynamic equilibrium (LTE) model
In LTE model, it is assumed that the distribution of population densities of the electrons is determined exclusively by particle collision process and that the collision takes place with sufficient rapidity that the distribution responds instantaneously to any change in the plasma condition. In such circumstances, each process is accompanied by its reverse and this pair of process occurs at equal rates by the principle of detailed balanced and equilibrium is established. The population distribution is determined by the statistical mechanical law of equipartition among energy levels. Thus, although the plasma temperature and density may vary in space and time, the distribution of population densities at any instant and point in space depends entirely on local values of temperature, density, and chemical composition of the plasma.

2.3.3.2 The steady-state corona model

This model was initially proposed to explain some features of the spectrum of the solar corona. Nevertheless, this model has been found useful in discussing low density laboratory plasmas. The balance in corona model is between collisional ionization (and excitation) and radiative recombination (and spontaneous decay). Again in this model, the plasma is considered to be optically thin, with very low electron density and for atom density sufficiently low to ensure that atom-atom collisions are negligible. It is also assumed that changes in population densities of the energy levels caused by variation in the electron temperature or density take place at a rate that is slow in comparison with the intrinsic rate of relaxation of the atomic process.

2.3.4 Equations governing LTE
If the free electrons are distributed among the various energy levels available to them, their velocities have a Maxwellian distribution. Then the number of electrons of mass \( m \) and velocities between \( v \) and \( v + dv \) is given by [17],

\[
dn_v = 4\pi n_e \left( \frac{m}{2\pi kT_e} \right)^{\frac{3}{2}} \exp \left\{ -\frac{(mv^2)}{2kT_e} \right\} \frac{v^2}{2} dv \tag{2.20}
\]

where \( n_e \) is the total density of free electrons and \( T_e \) is the electron temperature.

For bound levels, the distributions of population densities are given by the Boltzmann and Saha equation viz,

\[
\frac{n(p)}{n(q)} = \left( \frac{\omega(p)}{\omega(q)} \right) \exp \left\{ \frac{\chi(p,q)}{kT_e} \right\} \tag{2.21}
\]

\[
\frac{n(z+1,g)}{n(z,g)} = \left( \frac{\omega(z+1,g)}{\omega(z,g)} \right) \left[ 4\pi n_e kT_e \right] \frac{m_e kT_e}{\hbar^2} \exp \left\{ \frac{\chi(z,g)}{kT_e} \right\} \tag{2.22}
\]

where \( n(p), n(q), n(z+1,g) \) and \( n(z,g) \) are the population densities of various levels designated by their quantum numbers \( p, q \) and \( g \) (ground level) and ionic charge \( \cdot z+1 \) and \( \cdot z \), \( \omega(z,g) \) is the statistical weight of designated level, \( \chi(p,q) \) is the energy difference between level \( \cdot p \) and \( \cdot q \), \( \chi(z,g) \) is ionization potential of the ion of charge \( \cdot z \) in its ground level \( \cdot g \). The above three equations described the state of the electrons in an LTE model plasma.

If the plasma is optically thin, then the intensity, \( I(p,q) \) of a spectral line arising from a transition between bound levels \( \cdot p \) and \( \cdot q \) is given by,

\[
I(p,q) = \frac{1}{4\pi} \int n(p)A(p,q)h\nu(p,q)ds \tag{2.23}
\]
where \( A(p,q) \) is atomic transition probability and \( h\nu(p,q) \) is photon energy. The intensity of radiation \( I(p,q) \) is measured in units of power per unit area per unit solid angle.

Continuum radiations from LTE model plasma arise from Bremsstrahlung (either free-free or free-bound). The total intensity at any particular frequency \( I(\nu) \) is the sum of all the contribution from all such processes having component at the specified frequency. Thus,

\[
I(\nu) d\nu = \frac{1}{4\pi} \int n_e \sum_i n(i) \{ \gamma(i,T_e,\nu) + \sum_p \alpha(i,p,T_e,\nu) \} h\nu ds dv \quad \text{.........2.24}
\]

where \( \gamma(i,T_e,\nu) \) is atomic probability of a photon of frequency \( \nu \) being produced in the field of an atom or ion (specified by \( i \)) by an electron of mean kinetic temperature \( T_e \) making a free-free transition and \( \alpha(i,p,T_e,\nu) \) being the corresponding probability where the electron makes a free bound transition in a level \( 'p' \). The co-efficient \( A, \gamma \) and \( \alpha \) may be evaluated with reference to atomic physics literature [18]. The above equation gives the spectral intensity of plasma in LTE.

### 2.3.5 Condition for fulfillment of LTE

At a sufficiently low density, the probability of a radiative transition (spontaneous decay) becomes comparable with or even exceeds the probability of the corresponding collisional transition. Since in optically thin plasma the emission of a photon is a process that is not balanced by its inverse, the population distribution among the levels departs from that depicted by the Boltzmann equation. Only one transition in one atom or ion need be unbalanced in this way to invalidate the assumption of LTE. So LTE model is not applicable to plasma at low density.
Since the electrons, because of their great velocity, are the most efficient particles in causing collisional transitions, it is their collision rates that need to be compared with the radiative decay rates. Consider atoms or ions in some level ‘p’ suffering transition to a lower level ‘q’ because they are struck by electrons. The rate at which these transitions take place may be expressed as,

Collisional transition rate = \( n_e n_p \chi(t_{e,p,q}) \) transitions/unit volume/unit time \( \ldots2.25 \)

where \( \chi(t_{e,p,q}) \) is de-excitation co-efficient

For radiative decay rates to cause less than 10% departure from LTE, the collisional rate must be at least about 10 times the radiative rates.

That is, for all levels ‘p’ and ‘q’

\[ n_e n_p \chi(t_{e,p,q}) \geq 10 n_p A(p,q) \] \( \ldots2.26 \)

Substituting the values and after some algebra, we get the final expressing as

\[ n_e \geq 1.6 \times 10^{12} T_e^{1/2} \chi(p,q) \times 3^{-3} \] \( \ldots2.27 \)

where \( T_e \) is electron temperature in °K, and \( \chi(p,q) \) is the excitation potential of level \( p \) from level \( q \) and is in eV. The above inequality is a necessary condition for plasma to be in LTE.

This is possible in high pressure plasma (high density) where the number of collision between the electrons and heavy particles is sufficiently high to keep the two systems in same thermodynamic equilibrium. In electric arcs or in plasma jets operating in pressure of about 1 atmosphere, the temperature of electron is
approximately equal to that of gas. This type of plasma is called thermal plasma. So in thermal plasma, LTE model is suitably applicable.

2.3.6 Atomic Boltzmann plot method

The Boltzmann plot is a simple and widely used spectroscopic measurement method for plasma electron temperature by using the relative intensity of two or more line spectra having a relatively large energy difference. But this method is applicable to plasma where the excitation level is reached under LTE condition [19]. The basic principle of the Boltzmann plot method is given below [20].

Consider two energy levels, $E_i$ and $E_j$ ($E_i$ for lower level and $E_j$ for upper level), of two different line intensities with respective atomic densities of $n_i$ and $n_j$. Under the thermal equilibrium condition, the Boltzmann distribution gives,

$$\frac{n_j}{n_i} = \frac{g_j}{g_i} \exp \left\{ \frac{-(E_j-E_i)}{kT} \right\} \tag{2.28}$$

where $g_j$ and $g_i$ are statistical weights of the respective states, $k$ is Boltzmann constant, and $T$ is temperature in °K.

If the total population density is $n$, then,

$$\frac{n_j}{n} = \frac{g_j}{Z(T)} \exp \left\{ \frac{-(E_j-E_i)}{kT} \right\} \tag{2.29}$$

where $Z(T)$ is the sum of the weighted Boltzmann function of all the discrete energy levels, called partition function and is given by,
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\[ Z(T) = \sum_m g_m \exp \left\{ \frac{-E_m}{kT} \right\} \] ........................................2.30

Now, when plasma atom is de-excited from the upper energy level, \( E_i \), to the lower energy level, \( E_f \), the emission co-efficient can be expressed as,

\[ \varepsilon_{ji} = \frac{\hbar c}{4\pi \lambda_{ji}} A_{ji} N_j \] .................................................2.31

where \( \lambda_{ji} \) is the wavelength of the emitted light, \( \hbar \) is Planck's constant, \( c \) is velocity of light in vacuum, and \( A_{ji} \) is the transition probability.

Putting Eq. (2.31) in Eq. (2.29) and rearranging, we get,

\[ \frac{\varepsilon_{ji} \lambda_{ji}}{A_{ji} \beta_j} = \frac{\hbar c n_c}{4\pi Z(T)} \exp \left\{ \frac{-E_j}{kT} \right\} \] .................................................2.32

Taking logarithm on both sides of Eq. (2.32)

\[ \ln \left( \frac{\varepsilon_{ji} \lambda_{ji}}{A_{ji} \beta_j} \right) = \frac{-E_j}{kT} + C \] .................................................2.33

where \( C \) is a constant.

Now, plotting the above equation with \( E_j \) in the horizontal axis and \( \ln(\varepsilon_{ji} \lambda_{ji}/A_{ji} \beta_j) \) in the vertical axis will result in a straight line, and the electron density can be determined from the slope of the straight line.

In practice, \( \varepsilon_{ji} \lambda_{ji}/A_{ji} \beta_j \) is substituted by intensity and the values of \( A_{ji} \) and \( E_j \) can be obtained online from [18].
2.3.7 Plasma density measurement using stark width

The emission of a discrete radiation quantum should produce a monochromatic spectral line. But the line profiles emitted by atoms or ions, which are embedded in dense plasma, will be predominantly determined by interactions of the emitters with the surrounding particles leading to the broadening of spectral line. This type of broadening is called pressure broadening or collision broadening. From the physical point of view, it may be further subdivided (a) resonance, (b) Van der Waals, and (c) Stark broadening, depending on whether the broadening is caused by interaction with (a) atoms of same kind, (b) atoms or molecules of different kinds, or (c) charged particles, i.e. ions and electrons. In plasma, with ions and electrons present in sufficiently high concentrations (greater than 1%), the long range Coulomb forces are dominant, and one is only concerned with Stark broadening [21].

Analysis of the spectral line using the Stark broadening effect is one of the most common methods of plasma diagnostics. Measurement of the broadening resulting from the Stark effect allows determining the electron density in the plasma. This measurement technique is mostly used with hydrogen because the spectral lines of hydrogen are easily broadened by the presence of charged particles. The electron density can be determined from the Stark broadening by the following relation [22],

\[
N_e = C(N_e, T) \Delta \lambda_s^{3/2} \tag{2.34}
\]

where \( N_e \) is electron density, \( \Delta \lambda_s \) is Full Width at Half Maxima (FWHM) of the Stark broadened spectral line and the co-efficient \( C(N_e, T) \) can be obtained from literature [23].
Usually, Hβ spectral line is used for measurement of the broadening. Hβ line gives an accuracy of about 5% for the determination of electron density while Hα line gives 20% [22]. Moreover, there is no self absorption in the case of Hβ line and the broadening effect is stronger than for Hα. For Hβ line, equation 2.34 can be written as [16],

\[ \Delta \lambda_{1/2} = 0.54 \alpha_{1/2} n_{20}^{2/3} \text{nm} \] \hspace{1cm} 2.35

where \( n_{20} \) is the ion density in units of \( 10^{20} \text{m}^{-1} \) (\( n_{20} = N_e/10^{20} \)) and the parameter \( \alpha_{1/2} \) for Hβ is 0.08.

On simplification, we get,

\[ N_e = 111 \times 10^{20} \times \Delta \lambda_{1/2}^{3/2} \] \hspace{1cm} 2.36

Putting \( \Delta \lambda_{1/2} \) in nanometer, we get the electron density per meter\(^3\).

### 2.4. References

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18. National Institute of Standards and Technology (NIST): Atomic spectra database (Online) Available at “www.nist.org”.

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