Kirk-Othmer Encyclopedia of Chemical Technology.

PLASMA TECHNOLOGY

Plasma can be broadly defined as a state of matter in which a significant number of the atoms and/or molecules are electrically charged or ionized. The generally accepted definition is limited to situations wherein the numbers of negative and positive charges are equal, and thus the overall charge of the plasma is neutral. This limitation on charge leaves a fairly extensive subject area. The vast majority of matter in the universe exists in the plasma state. Interstellar space, interplanetary space, and even the stars themselves are plasmas.

Plasma technology, the use of natural or artificially produced plasmas, has grown dramatically in variety and magnitude since the late 1950s. Many different types of plasmas exist or can be naturally or artificially created by various energy sources. Whereas gas plasmas are the most common and the most commonly used, plasmas also exist and find application within solids as well as liquids. Plasmas expected to be of consequence into the twenty-first century include those associated with integrated circuit processing (see Integrated circuits), polymer production (see Polymers), surface modifications and coatings (qv), fusion energy (qv), specialized weapons, and propulsion technology (see Explosives and propellants), as well as associated interplanetary space travel (see Space processing).

1. Background

1.1. History

The term plasma was first used by Langmuir in 1928 to describe the main body of a gas discharge (1). Use of the term reflects the Greek origin of the word, to mold. Artificially induced glowing gas discharges mold themselves to the shape of their container and to items being processed within.

Work on plasmas has roots extending back to the Greeks who found that amber rubbed with various materials tended to attract certain objects. The concept of plasma as the fourth state of matter can be traced to Sir William Crookes (2) in 1879. “So distinct are these phenomena from anything which occurs in air or gas at the ordinary tension, that we are led to assume that we are here brought face to face with Matter in a Fourth state or condition, a condition so far removed from the State of gas as a gas is from a liquid.” This description has been shown to be accurate over many years of experimentation and application of plasmas.

Many have worked on plasma technology. Table 1 lists a few of the contributors (3–5) and the corresponding dates associated with their concepts.

1.2. Origins

The theory concerning the origin of the universe, called the Big Bang, indicates that all matter and energy were contained in one unimaginably hot and dense plasma about 15×10^9 years ago (6). Following the Big Bang explosion came expansion, cooling, and condensing of matter. In some areas, gravitational accumulation of matter progressed into clusters large and dense enough to reform gaseous plasmas by nuclear reaction reheating. Other natural plasmas exist, even some terrestrial types, such as lightning and the aurora borealis.

Table 1. Important Concepts in Gaseous Electronics

Date	Concept	Originator
1600	electricity	Gilbert
1742	sparks	Desaguliers
1785	charge losses	Coulomb
1803	arc (discharge)	Petroff
1808	diffusion	Dalton
1817	mobility	Faraday
1821	arc (name)	Davy
1834	cathode and anode	Faraday
1834	ions	Faraday
1848	striations	Abria
1858	cathode rays	Plücker
1860	mean free path	Maxwell
1869	deflection of cathode rays	Hittorf
1879	fourth state of matter	Crookes
1880	Paschen curve	la Rue and Müller
1886	positive ion rays	Goldstein
1887	effect of light on spark gaps	Hertz
1888	emission (photoelectrons)	Hallwachs
1889	Maxwell-Boltzmann distribution	Nernst
1891	electron (charge)	Stoney
1895	x-rays	Röntgen
1897	(cyclotron) frequency	Lodge
1898	ionization	Crookes
1899	transport equations	Townsend
1899	energy gain equations	Lorentz
1901	Townsend coefficients	Townsend
1905	diffusion of charged particles	Einstein
1906	electron (particle)	Lorentz
1906	(plasma) frequency	Rayleigh
1914	ambipolar diffusion	Seeliger
1921	Ramsauer effect	Ramsauer
1925	Debye length	Debye and Hückel
1928	plasma	Langmuir
1935	velocity distribution functions	Allis

In fact, synthetically formed plasmas are essentially surrounded and outnumbered by naturally occurring types.

1.3. Definitions

When positive charges are fixed in a solid, but the electrons are free to move about, the system is called a solid-state plasma. In a liquid-state plasma, both the positive and negative charges are fully mobile. These solid-state and liquid system are examples of condensed matter plasmas as opposed to gaseous plasmas.

Gaseous plasmas sustained by electric fields at reduced pressure, either under direct or alternating current, are sometimes referred to as glow discharges, because they emit light. There is, in fact, a slight difference between the terms plasma and discharge. There are some regions within discharges which may not strictly adhere to the neutral concept of plasmas (7). However, in general, the two terms are used interchangeably throughout the plasma technology literature.

Central to the categorization of plasmas are electron temperature and electron density. Electrons have a distribution of energies, so it is useful to assume a Maxwellian distribution, in terms of electron energy, *E,* such that

$$f(E) = \frac{2E^{1/2}}{\left((\pi)^{1/2}(kT_e)^{3/2}\right)\exp(-E/kT_e)}$$

where $f(E)$ is proportional to the number of electrons having an energy between E and $E + \Delta E$, k is the Boltzmann constant, and T_e is the electron temperature. The electron energy is given by the following:

$$E = (1/2)mV^2$$

where m is the electron mass and V is the magnitude of the electron velocity. This leads to the relation for the average energy:

$$\int E(f(E))\,dE = (3/2)kT_e$$

and thus for a Maxwellian distribution, T_e is a measure of the average electron energy (7). Some weakly ionized plasmas do not necessarily have Maxwellian distributions of electron energies but it is still common to use the electron temperature, T_e, when describing them. Electron temperatures can be expressed in eV or in degrees K, using $1\text{ eV} = 11,600\text{ K}$ from $E = kT_e$. Densities of electrons and ions are measured per unit volume, usually as the number of particles per cubic centimeter.

An important characteristic of plasma is that the free charges move in response to an electric field or charge, so as to neutralize or decrease its effect. Reduced to its smallest components, the plasma electrons shield positive ionic charges from the rest of the plasma. The Debye length, λ_D, given by the following:

$$\lambda_D = \left(\frac{kT}{4\pi ne^2}\right)^{1/2}$$

where n is the electron density and e is the electron charge, is a measure of the extent to which plasma electrons collect in the vicinity of a charge and create a shielded potential. Ordinary, nonplasma gases have an average interparticle spacing of $d = n^{-1/3}$ and a mean free path between collisions of $\lambda = (\pi nD^2)^{-1}$ where D is the atomic or molecular particle size. The number of electrons within a Debye sphere, N_D, around an ion is then $N_D = 4\pi\lambda_D^3 n/3$. The volume of a plasma must be significantly larger than N_D or else the shielding would not be complete, a charge imbalance would exist, and the definition of a plasma having overall charge neutrality would be violated.

The primary characteristic frequency of an ordinary gas is the rate of collision $f = \overline{V}/\lambda = \pi\overline{V}nD^2$, where $\overline{V}$ is the mean particle velocity, and $\overline{V} = (8kT/\pi m)^{1/2}$ for particles of mass m. Among the special frequencies associated with plasmas, the most notable is the plasma frequency:

$$\omega_P = \left(4\pi ne^2/m\right)^{1/2}$$

This frequency is a measure of the vibration rate of the electrons relative to the ions which are considered stationary. For true plasma behavior, plasma frequency, ω_P, must exceed the particle-collision rate, *f.* This plays a central role in the interactions of electromagnetic waves with plasmas. The frequencies of electron plasma waves depend on the plasma frequency and the thermal electron velocity. They propagate in plasmas because the presence of the plasma oscillation at any one point is communicated to nearby regions by the thermal motion. The frequencies of ion plasma waves, also called ion acoustic or plasma sound waves, depend on the electron and ion temperatures as well as on the ion mass. Both electron and ion waves, ie, electrostatic waves, are longitudinal in nature; that is, they consist of compressions and rarefactions (areas of lower density, eg, the area between two compression waves) along the direction of motion.

1.4. Plasma Types

Figure 1 (7–9) indicates the various types of plasmas according to their electron density and electron temperature. The colder or low electron energy regions contain cold plasmas such as interstellar and interplanetary space; the earth's ionosphere, of which the aurora borealis would be a visible type; alkali-vapor plasmas; some flames; and condensed-state plasmas, including semiconductors (qv).

Gaseous plasmas are sometimes classified as equilibrium or nonequilibrium referring to the electron temperature as compared to the gas temperature. Low pressure glow discharges are generally classified as nonequilibrium plasmas because the electron temperature is significantly greater than the gas temperature. Commonly, glow discharges have electron temperatures in the 10^4–10^5 K (1–10 eV) range, whereas the gas temperature in those discharges is generally less than 5×10^2 K or near ambient. Low and high pressure arc discharges, also known as plasma jets, have no such large difference and the electron and gas temperatures are both in the $5 \times 10^3 - 10^4$ K range, thus being called equilibrium plasmas. The areas of most interest to plasma chemistry are the glow discharges and arcs.

Controlled thermonuclear fusion experiments and certain types of confined arcs known as pinches have temperatures in the $5 \times 10^5 - 10^7$ K range. However, to be successful, controlled thermonuclear fusion needs to take place from $6 \times 10^7 - 10^9$ K. In fact, the goal of all fusion devices is to produce high ion temperatures in excess of the electron temperature (10).

Also shown in Figure 1 are the Debye screening length and Debye sphere size. For gaseous plasmas, $N_D \gg 1$ (11). Solid-state plasmas or condensed-state plasmas generally exist where $N_D \leq 1$.

1.4.1. Field Effects

Velocities, lengths, and frequencies are intrinsic to gases and plasmas, independent of incident radiation or existing fields. However, some of the more interesting plasma phenomena only appear in the presence of static or dynamic fields. External static electric fields tend to separate and accelerate plasma charges. Such fields and the resultant electron motions can both produce plasmas and heat them. Magnetic field effects in plasmas are so important that at one time plasma physics and magnetohydrodynamics (qv) (MHD) were practically synonymous. However, some plasmas are not magnetized, and some MHD processes do not involve plasmas, eg, the fluid motions in the earth's core which produce the terrestrial magnetic field.

Transverse electromagnetic waves propagate in plasmas if their frequency is greater than the plasma frequency. For a given angular frequency, ω, there is a critical density, n_c, above which waves do not penetrate a plasma. The propagation of electromagnetic waves in plasmas has many uses, especially as a probe of plasma conditions.

$$n_c = m\omega^2/4\pi e^2$$

The presence of a static magnetic field within a plasma affects microscopic particle motions and microscopic wave motions. The charged particles execute cyclotron motion and their trajectories are altered into helices along the field lines. The radius of the helix, or the Larmor radius, is given by the following:

$$mcV_\perp/qB$$

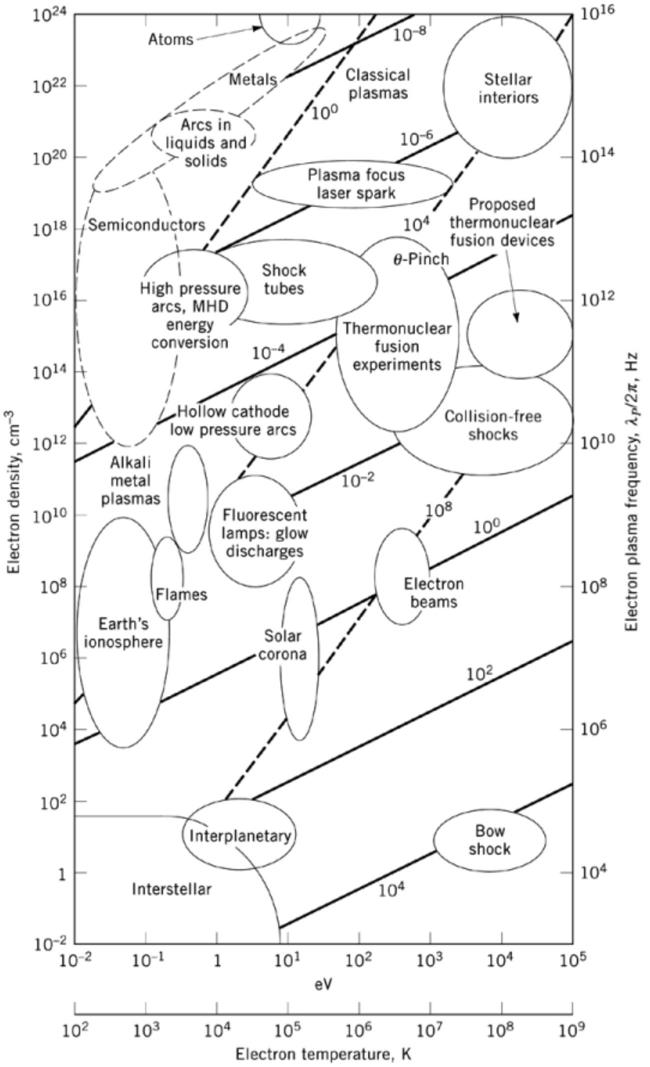


Fig. 1. Electron temperature and density regions for plasmas (7–9) where the numbers and the diagonal lines represent (—) the Debye screening length, λ_D, in centimeters, and (— — —) Debye sphere volume, N_D, in cubic centimeters. The plasma frequency is given on the right-hand axis. Condensed-state plasmas, indicated in dashed line areas, have relatively low temperatures, small Debye spheres, and high densities. Plasmas in metals and semimetals fall along the line separating degenerate quantum plasmas from nondegenerate classical plasmas. Gaseous plasmas, shown in solid line areas, have characteristics that vary widely. MHD=magnetohydrodynamic.

for a particle of mass m and charge q, and velocity $V_\perp$ normal to the magnetic field of strength B, where c is the velocity of light. The cyclotron frequency, ω_c, which is introduced by the presence of the field, is

$$\omega_c = qB/mc$$

The particle–field interaction is the means by which magnetic fields can exert pressures on plasmas and vice versa.

The presence of static magnetic fields does not alter the propagation of longitudinal electrostatic electron or ion waves if the propagation direction is parallel to the field. However, propagation that is orthogonal to the field involves new frequencies that depend on the field strength. In contrast, the propagation of transverse electromagnetic waves in plasmas is altered by a magnetic field regardless of the relative geometry of the direction of motion and the field vector.

Magnetic fields introduce hydromagnetic waves, which are transverse modes of ion motion and wave propagation that do not exist in the absence of an applied B field. The first of these are Alfven, A, waves and their frequency depends on B and ρ, the mass density. Such waves move parallel to the applied field having the following velocity:

$$V_{\mathrm{A}} = B/(4\pi\rho)^{1/2}$$

and are similar to the waves that travel along a string. Magnetosonic waves are a second type of hydromagnetic wave, and these propagate perpendicular to the magnetic field. Their frequency depends on the Alfven and the acoustic velocities. Hydromagnetic waves are electromagnetic waves. Even though the applied B field is static or nonoscillatory, the waves are transverse and are characterized by oscillatory electric, E, and magnetic, B, components.

A good discussion of plasma waves and a tabulation of their characteristics is available (12). Useful plots of the dispersion relations for various frequencies, field conditions, geometries, and detailed mathematical relationships are given in Reference 13.

1.5. Gaseous Plasmas

Gaseous plasmas are often far from equilibrium and therefore can exhibit microscopic or particle instabilities, and macroscopic or hydromagnetic instabilities (14, 15). Microscopic instabilities are caused by departures from the equilibrium Maxwellian distributions for the electrons or ions. Examples of such situations include a plasma expanding while cooling, anisotropies in the velocity distribution caused by applied magnetic fields, or the motion or streaming of a particle beam through a plasma. Macroscopic instabilities produce the motion of the plasma as a whole. Causes include pressure or density gradients or magnetic field curvature. All instabilities represent the tendency of plasmas to reach equilibrium more quickly than is possible by ordinary collisions alone. Instabilities can reduce plasma confinement times by many orders of magnitude, a significant problem in fusion research. The conduction and diffusion of energy through plasmas, and the way in which these processes are influenced by magnetic fields, are described (12, 13).

The high energy densities of many gaseous plasmas raise safety concerns. The sources of energy used to produce and heat plasmas, eg, steady-state, high voltage, and high current generators, and capacitors for pulsed electron-discharge heating and laser beams, can be hazardous (16, 17). Work with plasmas usually requires careful attention to proper electrical safety precautions and to eye hazards. Even in the absence of lasers (qv), plasmas can pose a threat to vision because the plasmas often are very bright and can emit dangerous levels of uv radiation. X-radiation from plasmas usually is not a safety concern. Most energy from 10^6 K plasmas is soft and does not escape from the experimental chamber or traverse significant distances in air. The hard x-rays emitted by most plasma sources usually are of very low intensity. However, some low energy, low pressure plasmas, such as electron cyclotron resonance sources, high ($>10^4$ V) voltage, plasma-generating machines and some fusion-energy research devices can emit unsafe x-ray emissions. Shielding, eg, lead or concrete, and distance from the source reduce exposures to acceptable levels.

2. Production

Sources of matter and energy are necessary for the production of gaseous plasmas, and such plasmas serve as sources of matter and energy in their applications; ie, gaseous laboratory plasmas can be viewed as transducers of matter and energy. The initial and final forms of the material that enters a plasma and the requisite energy vary widely, depending on the particular plasma source and its utilization.

The molecules that are dissociated and the atoms that are ionized during plasma production can be in any state at the start. Steady-state plasmas are formed most often from gases, although liquids, such as volatile organics, and solids are also used. Gases and solids routinely serve as sources of material in pulsed plasma work.

The energy for plasma formation may be supplied in a variety of ways. The source may be internal, eg, the release of chemical energy in flames. Another energy source involves electrical excitation (18). The externally applied d-c or a-c field excites the plasma, which becomes part of the electric circuit. Electromagnetic fields, eg, in the radio frequency (rf) or microwave range (19), can be used to form plasmas that interact with or feed back into the source. It should be noted that electron motion in an a-c field, especially a r-f one, yields a stable plasma without the secondary electron emission required for d-c plasmas. A fourth kind of energy source includes externally produced beams of photons, eg, laser beams or other energetic particles, that create a plasma by impact and absorption independent of the source. Plasmas may be produced in a fifth manner by strong shock waves. Chemical, discharge, and high frequency sources often produce steady-state plasmas, whereas beam and shock heating usually produces pulsed plasmas.

In the production of plasmas by steady-state electric discharge heating, the current across two electrodes in the gas can vary widely, as indicated in Figure 2 (4, 11, 20–22). At low current values, externally induced ionization is needed to maintain current flow. Milliampere currents in gases having pressures at about 100 Pa (10^{-3} atm) produce a glow discharge that is sustained by electrons produced by positive-ion bombardment of the cathode. If the current is increased to around 10 A, a self-sustaining arc forms and exists even at pressures above 101 kPa (1 atm).

2.1. Modification and Dissipation

Changes in the composition or energy of a plasma after it is formed are often desired. For example, materials can be introduced into a plasma and excited, thereby producing information for spectrochemical analysis. Plasma heating is a more common modification. Plasma heating, ie, raising the energies of all the particles comprising the plasma, is of primary importance or interest in fusion science and technology. Many energy sources and coupling mechanisms can be employed to heat plasmas (12). Plasma formation and heating often are driven by the same energy source. However, an entirely separate second source can be used for heating. For example, laser beam and particle beam sources often are used to heat plasmas produced by electric discharges. Some commercial equipment uses simple infrared heat sources to boost the energy of their plasmas. Energetic neutral, ie, atomic beams are employed to heat plasmas that are formed initially by discharges.

Restraining a gaseous plasma from expanding and compressing is also a form of plasma modification. Two reasons for plasma confinement are maintenance of the plasma and exclusion of contaminants. Plasmas may be confined by surrounding material, eg, the technique of wall confinement (23). A second approach to confinement involves the use of magnetic fields. The third class of confinement schemes depends on the inertial tendency of ions and associated electrons to restrain a plasma explosion for a brief but useful length of time, ie, forces active over finite times are required to produce outward particle velocities. This inertial confinement is usually, but not necessarily, preceded by inward plasma motion and compression.

Low density plasmas are confined magnetically by a variety of field configurations that are designed to prevent particle losses and overall fluid instabilities (Fig. 3). Fusion-research plasmas, low temperature plasmas used for sputtering and high temperature, can be contained by magnetic confinement which can take

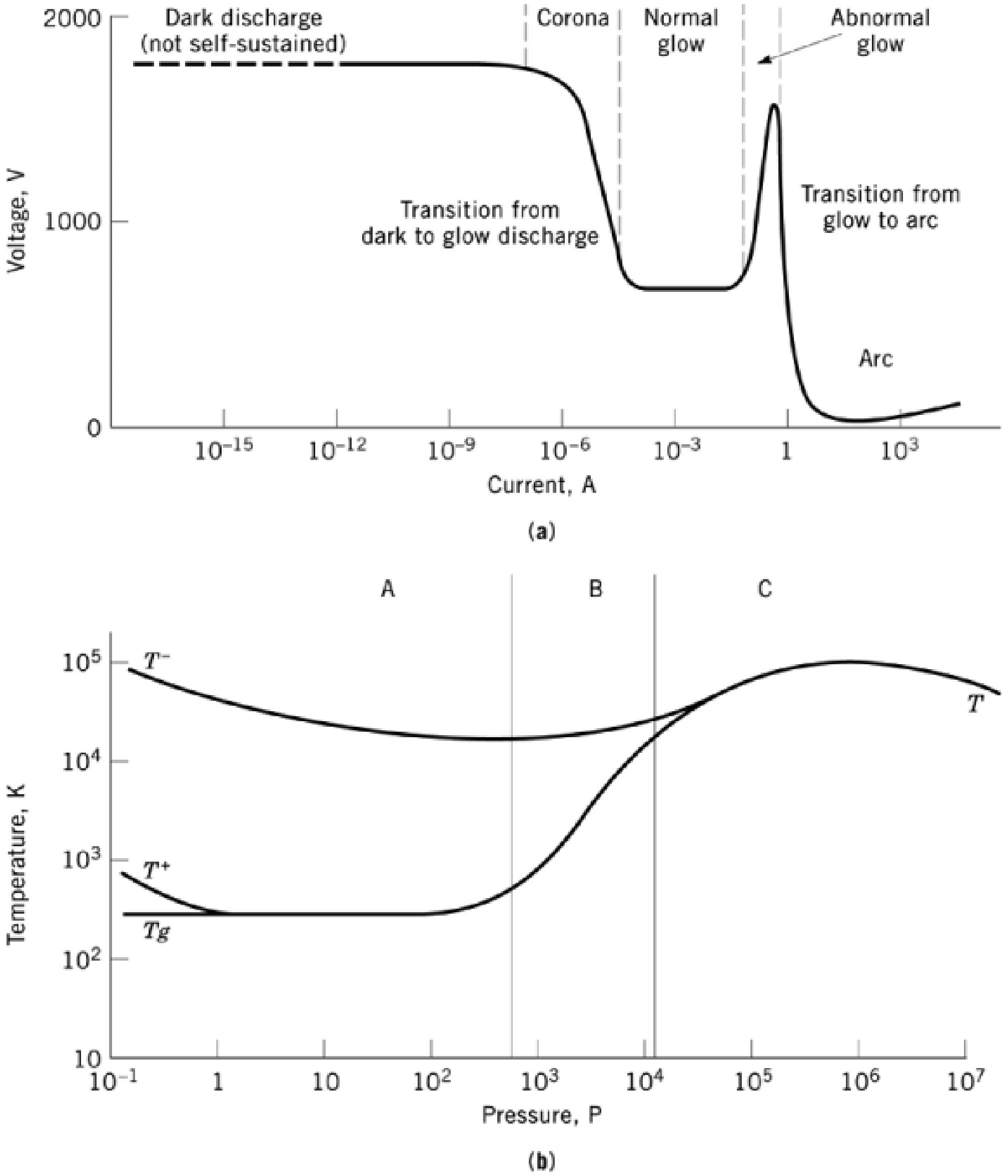


Fig. 2. (**a**) Voltage–current relationship for an electrical discharge (4, 11, 21, 22); (**b**) plasma temperature vs pressure. Temperatures, *T*, are indicated for the plasma electrons, T^-, and ions, T^+, and the neutral gas, *Tg*. Region A is the low pressure nonequilibrium cold-arc regime where $T^+ \approx Tg$, B is the transition area, and C is the high pressure equilibrium hot-arc regime where $T^- \approx T^+ \approx Tg$ (20). To convert Pa to atm, multiply by 9.87×10^{-6}.

several different forms (24). Magnetron sputtering sources include a variety of magnetic field configurations designed to restrain plasma particles near the cathode from which atoms are sputtered by impact of ions (24). The two basic magnet configurations for fusion-research plasmas are open and closed (25). Increasing strength along magnetic field lines produces magnetic mirrors which exert a retarding force on particles that tend to escape the plasma. However, the plasma in a simple mirror is not stable against overall fluid motion. For

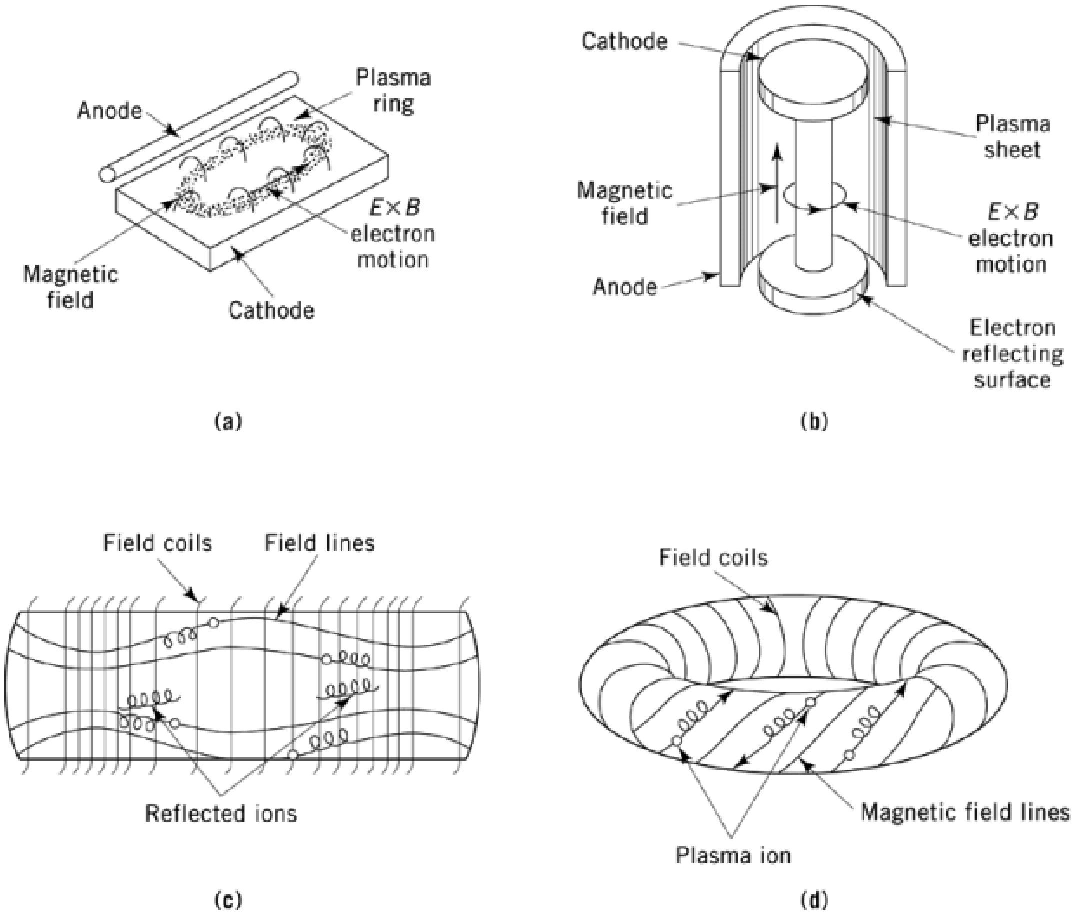


Fig. 3. Schematics of magnetic confinement geometries: (**a**) planar and (**b**) cylindrical geometries for magnetron sputtering sources (24); (**c**) open-ended mirror and (**d**) closed toroidal geometries for containing fusion-research plasmas (25).

stability, the B field must increase in all directions from the plasma outward, ie, the plasma must be in a minimum B location to be magnetohydrodynamically stable against gross translational motion. Curvature of the magnet geometry for mirror systems produces such stability. Nevertheless, sufficiently energetic particles can penetrate the mirror, producing end losses. Closure of the field lines to form loops counteracts such losses, but the field strength decreases radially from the center and particles tend to drift out of the plasma normal to planar closed field lines. Addition of out-of-plane fields, which yields helical fields in a toroidal configuration, produces both particle confinement and MHD stability. The history and physics of magnetic confinement of fusion plasmas are available (26).

High density plasmas can be confined and compressed magnetically by fields produced by strong electric currents flowing in and heating the plasmas, as well as by externally applied fields (27). The radial force produced by the magnetic field, which affects the flowing plasma electrons ($v \times B$ force), produces inward plasma motion and compression. Such confinement is short-lived and not stable, but it produces plasmas with high energy densities. High density plasmas are studied primarily as x-ray and neutron sources.

Inertial confinement depends on plasma heating outpacing plasma expansion. When a target is struck by a short ($<\mu$s) pulse of laser photons, electrons, or ions, it is heated on a time scale comparable to or shorter than that on which the resulting plasma expands and cools. This is true for targets of any geometry. If a cylindrical or spherical target is simultaneously irradiated from two or more sides, the outer surface separates violently, producing a reaction in the opposite direction that accelerates the remainder of the target inward, thereby compressing and heating the central materials (28).

Hot, elevated pressure, fusion-type plasmas lose matter and energy through particle escape and radiation of photons. When matter or energy are no longer supplied to a hot plasma, it expands and cools before interacting with the surroundings and totally dissipating. In low pressure cold plasmas, electron loss to chamber walls and atomic and molecular recombination affects are of more importance. Such processes must be offset during the lifetime of a plasma because the material and energy from a plasma can produce undesirable effects. Energetic particles impinging on solids near plasmas can profoundly alter the material properties. Plasma effects on materials are especially important in proposed thermonuclear fusion reactors. Materials in the high pressure plasma reactors must withstand high temperatures and stresses for an economically useful period (29). Low pressure plasmas generally deliver no such debilitating exposures. It is not uncommon for commercially available plasma units to operate for 20–30 years in production environments with little or no effect on the materials of construction.

3. Diagnostics

Plasma diagnostics, the determination of conditions within plasmas, also refers to the broad collection of experimental techniques and associated calibration and analytical methods used to assess the characteristics of plasmas. Noteworthy properties include the identities, concentrations, and energy distributions of the various particle species such as neutrals, electrons, and ions, and their velocity distributions as functions of space and time. Quantities such as plasma flow velocities, turbulence, instabilities, and flow of energy into and out of plasmas by various means also are desired. Most diagnostic methods have limited resolution spatially, temporally, and spectrally. Therefore, plasma characteristics that are derived from measurements generally are averaged. Measured quantities in plasma diagnostics usually are integrated along a line of sight through the plasma to the instrumentation, yielding spatially integrated results. It is possible, however, to measure point temperatures within low temperature plasmas using fluoroptic thermometers (30). No one method for assaying plasmas is universally applicable. A variety of diagnostic tools is needed to characterize a plasma empirically and to compare its empirical and theoretical characteristics.

Diagnostic methods can be categorized most broadly according to those that involve external probes of plasmas or those that rely only on plasma selfemission. Probes of plasmas include solid instruments inserted into gaseous plasmas and beams of photons or charged particles, which are shot through plasmas. Electric voltage and current measurements for discharge-heated plasmas provide useful information, thus the energy source also is a plasma probe. Self-emission can include radiated fields, photons, electrons, ions, and neutrons, ie, essentially any plasma effect or constituent. Gaseous plasma diagnostic methods or techniques and useful compilations of gaseous plasma characteristics measured by them are available (31–43). Plasma diagnostics is, by necessity, a key field of plasma technology.

Electrodes or Langmuir probes may be inserted into plasmas that are large enough (>1 cm) and relatively cool ($<10^4$ K). The net current to the probe is measured as a function of the applied voltage. Electron temperatures, electron and ion densities, and space and wall potentials may be derived from the probe signals. Interaction of plasmas with solid probes tends to perturb plasma conditions.

Monochromatic light from short-pulse lasers may be focused into plasmas that are large enough (≥ 1 cm) regardless of their temperatures. These beams cause little alteration of plasma conditions. Elastic Thomson scattering of the light at right angles to the incident direction is measured. Spectral or Doppler broadening of the light, which results from motion of the scattering electrons, yields the electron temperature. The overall scattered intensity is a measure of the electron density. Thomson scattering is a primary diagnostic method for magnetic fusion research plasmas.

Diagnostic techniques that involve natural emissions are applicable to plasmas of all sizes and temperatures and clearly do not perturb the plasma conditions. These are especially useful for the small, high temperature plasmas employed in inertial fusion energy research, but are also finding increased use in understanding the glow discharges so widely used commercially.

The small ($\leq$1 cm) sizes and brief ($<$1 μs) lifetimes of the fusion research plasmas preclude the use of most probe techniques. Laser pulse imaging of such plasmas does yield valuable spatial information, however. Diagnostic methods involving plasma emissions can be used to resolve spatial and temporal nonuniformities in plasma emission (44). For high temperature plasmas, diagnostic methods based on x-ray emission are especially useful, because the x-rays are preferentially emitted from the hottest and densest parts of plasmas. Emission spectrometry is useful in determining relative concentrations of species, reactants, or products in glow discharges. This information can be used to determine process efficiencies and proper end-of-process times to prevent damage to items being plasma treated. Figure 4**a** is an example of emission spectrometry data for the removal of chlorine contamination from small electronic components using an r-f plasma (45). Figure 4**b** shows the monitoring of the etching and eventual removal of a polymer layer from a metal substrate (45).

4. Types of Plasmas

4.1. Natural Gaseous Plasmas

Lightning is the most common atmospheric, plasma related phenomenon (46, 47). The separation of charges in clouds, and between clouds and the ground, produces potentials as high as 100 MV. The currents of the discharges are as high as 100 kA. Spectroscopic data have yielded considerable information on plasma conditions within a lightning discharge (48, 49).

Meteors produce atmospheric plasmas as their kinetic energy is converted to thermal energy (50). Most particles from space are consumed before they reach an altitude of 50 km. Meteors are of little practical use, although radio waves can be bounced off the plasmas left in their wakes (see Extraterrestrial materials).

Auroras are observed primarily at polar latitudes near the geomagnetic poles and result from impact on the atmosphere of energetic particles that are guided by the earth's electromagnetic field (51, 52). The emissions are produced at altitudes of one to several hundred kilometers by electrons having energies up to 10 keV, or by protons having energies as high as 200 keV. Ionization densities that produce auroras reach plasma levels generally following intense solar flare activity.

Absorption of solar uv radiation high in the atmosphere produces a tenuous but important plasma, the ionosphere (53). Many physical processes occur in the ionosphere during the creation and loss of free electrons (54). As shown in Figure 5, the electron density can exceed 10^6 cm^{-3} and the electron temperature generally is less than 1000 K (0.1 eV) (55). Atmospheric motions below and solar activity above the ionosphere influence its characteristics, which vary markedly with the time of day and the solar cycle and emission. Understanding of the ionosphere has led to the increasingly effective use of it in long-range communication.

The ionosphere is part of the larger magnetosphere, a cavity in the stream of particles from the sun. The cavity is produced by the earth's magnetic field (56, 57). The ionosphere and the Van Allen radiation belt lie within the plasmasphere, which extends to a maximum distance of about 15,000 km above the earth's surface.

Magnetospheric plasmas are produced and heavily influenced by solar emissions and activity and by magnetic fields of the planets. Interplanetary plasmas result from solar emission processes alone. Protons in the solar wind have low densities (10–100/cm^3) and temperatures below 10^4 to more than 10^6 K (1–10 eV). Their average outward kinetic energy from the sun is approximately 400 eV (58, 59). The various zones and phenomena from the sun's visible surface to the upper atmosphere of the earth have been discussed (60–62).

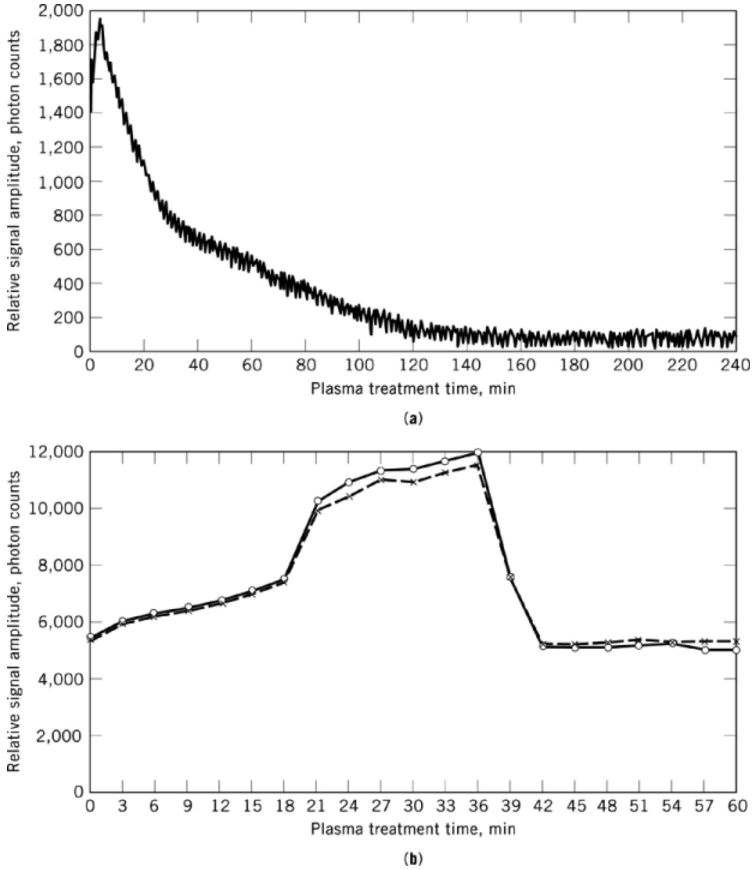


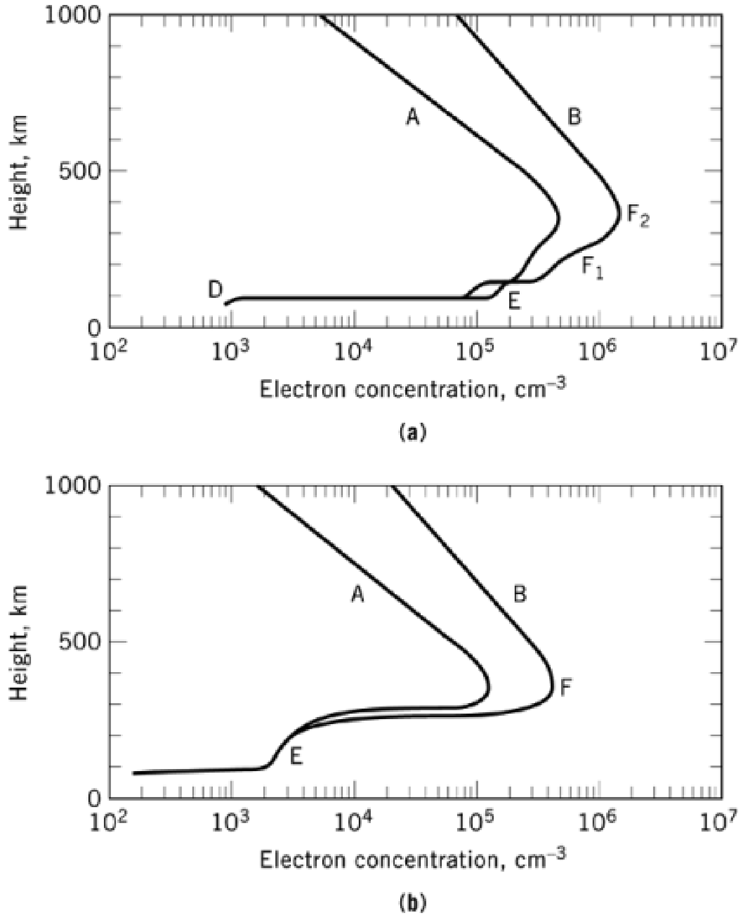
Fig. 4. Examples of emission spectrometry as a diagnostic monitoring tool for plasma processing. (**a**) The removal of chlorine contamination from copper diode leads using a hydrogen–nitrogen plasma. Emissions are added together from several wavelengths. (**b**) The etching and eventual removal of a 50-μm thick polyimide layer from an aluminum substrate, where (×) and (∘) correspond to wavelengths (519.82 and 561.02 nm, respectively) for molecular CO_2 (45).

Classical astronomy is largely concerned with the classification of stars without regard to the details of their constituent plasmas (63). Only more recently have satellite-borne observations begun to yield detailed data from the high temperature regions of other stellar plasmas. Cosmic plasmas of diverse size scales have been discussed (64).

4.2. Plasmas in Condensed Matter

In contrast to gaseous plasmas, which can be described by kinetic and fluid theories, plasmas in condensed matter are intimately related to the theory of solids (65–67). The formation of a diatomic molecule is a good example of the freedom and high velocities that electrons experience in the condensed state. Electrons that initially are confined to either atom, once the atoms bond, are free to range over the larger molecular volume. In the buildup of larger aggregates of condensed matter, addition of more atoms similarly expands the accessible volume. Bonding electrons increase their velocities when atoms form into molecules and condensed matter.

The energy levels of bonding electrons in a conductor are shown in Figure 6 (68). Because electrons are Fermions, no two can occupy the same spatial and energy states simultaneously, according to the Pauli exclusion



(a)

(b)

Fig. 5. Ionospheric electron density vs height above the earth at the extremes (A=minimum , B=maximum) of the 11-yr sunspot cycle during (**a**) day and (**b**) night (54). D, E, F, F_1, and F_2 are conventional labels for the indicated regions of the ionosphere.

principle. Energy bands develop as more atoms agglomerate, forming a solid. These may be continuous, as for metals, or have an energy gap. Such gaps are narrow for semiconductors and wide for insulators. The Fermi distribution or the distribution of electrons in metals is uniform with energy. The bands and the distribution are filled to an energy called the Fermi level, E_{F}, at absolute zero. Above this temperature there are vacancies below E_{F} and electrons in levels above E_{F}. Electrons at E_{F} move with velocities near 10^8 cm/s, which is equivalent to temperatures near 1 eV, even though the lattice is cold ($\sim$300 K). Densities of mobile electrons in metals are approximately 10^{22} particles/cm^3. The presence of plasmas in metals is readily shown by the excitation of electron plasma waves or plasmons. The characteristic energies of plasmas introduce additional peaks into electron and x-ray spectra from metals (67).

In perfect semiconductors, there are no mobile charges at low temperatures. Temperatures or photon energies high enough to excite electrons across the band gap, leaving mobile holes in the Fermi distribution, produce plasmas in semiconductors. Thermal or photoexcitation produces equal numbers of electrons and holes, similar to the neutral charge situation in gaseous plasmas where the charges of electrons and ions usually balance. Photoexcited plasmas, which are characterized by particle densities of around 10^{17}–10^{18}/cm^3, are stable in silicon at temperatures below 20 K and in germanium below 8 K (69, 70).

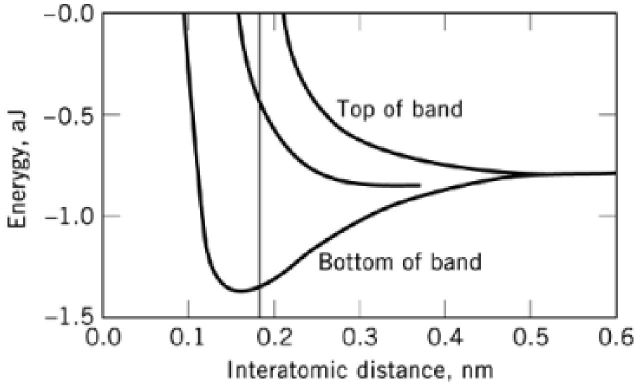


Fig. 6. Schematic energy levels of a solid as a function of interatomic distance where the vertical line represents the equilibrium spacing (68). A band of states obeying Fermi distribution is required by the Pauli principle. High electron velocities and equivalent temperatures exist in conductors even when the lattice is at ordinary temperatures. To convert J to cal, divide by 4.184.

Impurity-produced plasmas in semiconductors do not have to be compensated by charges of the opposite sign. These plasmas can be produced by introduction of either electron donors or electron scavengers, ie, hole producers, into semiconductor lattices. Their densities range from a lower limit set by the ability to produce pure crystals ($\sim 10^{12}$ particles/cm^3) to values in excess of 10^{20} particles/cm^3. Plasmas in semiconductors generally are dilute, so that the Pauli principle cannot be used to determine their energy distribution. These plasmas are Maxwellian and have the same temperature as the lattice in equilibrium. The uncompensated nature of plasmas in semiconductors, and especially their unique and very wide ranges of density and temperature, make them particularly interesting and useful. Numerous plasma effects, including waves and instabilities, are studied in semiconductor plasmas (71, 72). Effects peculiar to solids such as photon scattering of plasma particles and anisotopic effective masses, also are unique to semiconductor plasmas.

Plasmas in gaseous and condensed states are related by more than the principles that govern them. For gaseous matter, there is a continuum of behavior from a low density Maxwellian plasma to a high density Fermion plasma. The boundary region in the density–temperature plane is given by the equality of the thermal energy, kT_{F}, and the Fermi energy, E_{F}, where h is Planck's constant (73).

$$kT_F = E_F = \overline{h}^2/2m_e \left(3\pi^2 n_F\right)^{2/3}$$

Densities less than n_{F} indicate classical, nondegenerate behavior, whereas those above n_{F} imply quantum, degenerate conditions, such as can be found in condensed-state plasmas (see Fig. 1).

Gaseous and condensed plasmas have been summarized (65, 74). Fundamental differences between gaseous and condensed plasmas include their states of excitation and characteristic lengths. Gaseous plasmas are produced by classical collisional effects. Some gaseous plasmas, although clearly not all, are not in equilibrium thermodynamically and are accompanied by photons. In contrast, solid-state metallic plasmas are produced by quantum effects, can be in or near the ground state, and can exist in the absence of photons. Instabilities are common in gaseous plasmas but can be avoided or excited as desired in condensed-state plasmas. Long, mean free paths, compared to the plasma size, are common in gaseous plasmas. However, in solids, scattering usually produces short mean free paths in comparison to the millimeter sizes of ordinary samples. Scattering often interferes with plasma behavior in semiconductor plasma experiments.

5. Uses

5.1. Radiation Sources

Ordinarily, electron beams are produced from solids *in vacuo* by thermal or field-assisted processes. Plasmas also serve as electron sources, but are more uniquely used as ion sources. Whereas ions can be produced by sputtering and field assisted processes in the absence of plasmas, most ion sources involve plasmas (75).

Pulsed plasmas containing hydrogen isotopes can produce bursts of alpha particles and neutrons as a consequence of nuclear reactions. The neutrons are useful for radiation-effects testing and for other materials research. A dense plasma focus filled with deuterium at low pressure has produced 10^{11} neutrons in a single pulse (76) (see Deuterium and tritium). Intense neutron fluxes also are expected from thermonuclear fusion research devices employing either magnetic or inertial confinement.

Plasmas frequently are used as sources of incoherent and coherent electromagnetic radiation. Infrared radiation is emitted by plasmas, but these usually are not employed expressly as ir sources. Visible light sources involving steady-state plasmas, in which the electrons are hot compared to the ions, are common. Fluorescent lights and carbon-arc searchlights are examples. Inert gas plasma displays that are flat and are replacing bulky cathode-ray tubes, also depend on emission of visible light. Direct-current plasmas emit visible and uv radiation for chemical analysis. Pulsed sources of visible and uv light for high speed photography (qv) usually involve plasmas. Plasma uv sources are used commercially for production of microelectronics circuits by lithography. Multimillon-degree ($\times 10^6$ K) plasmas provide uniquely short pulses of incoherent uv and soft x-radiation for spectroscopy, materials analysis, and other applications.

Lasers act as sources and sometimes as amplifiers of coherent ir–uv radiation. Excitation in lasers is provided by external particle or photon pump sources. The high energy densities required to create inverted populations often involve plasma formation. Certain plasmas, eg, cadmium, are produced by small electric discharges, which act as laser sources and amplifiers (77). Efforts that were directed to the improvement of the energy conversion efficiencies at longer wavelengths and the demonstration of an x-ray laser in plasma media were successful (78).

5.2. Chemistry

The material and energy available in plasmas can be used to excite materials and drive chemical reactions. The unique characteristics of plasmas, especially their abundance of energetic species, have been exploited in plasma chemical applications (79–84).

The analysis of existing materials and the production of new chemicals and materials involve a gamut of gaseous plasma sources. Nonequilibrium or cold plasmas, in which the ion or gas temperature is much less than the electron temperature, are widely used. In these, the electrons provide energy that induces excitations and reactions without excessive heating of the desired products or the surroundings by the heavier particles in the plasmas. Equilibrium or hot plasmas, in which the electrons and ions are characterized by approximately the same temperature, also are used in plasma chemistry, especially for spectrochemical analysis and the processing of refractory materials (see Refractories) (85) (see Figs. 1 and 2). Plasma-electron temperatures below 50,000 K ($\leq$5 eV) are most useful for plasma chemistry.

5.3. Chemical Analysis

Plasma oxidation and other reactions often are used to prepare samples for analysis by either wet or dry methods. Plasma excitation is commonly used with atomic emission or absorption spectroscopy for qualitative and quantitative spectrochemical analysis (86–88).

Samples to be analyzed may be collected on filter papers, either directly from the air, water, or other carriers, or after wet chemical separation or concentration. The filters, composed of organic materials, interfere with subsequent analysis steps. Thus, if the sample is to be heated or excited in steps following filtration, the filter must be removed or destroyed. Ashing to rid the samples of organic materials can be accomplished in oxidizing or nonoxidizing plasmas (89). Excitation is provided by r-f energy coupled either inductively or capacitively to the plasma, although capacitive coupling is the most common commercially available method. Ashing also is used in the preparation of samples for microscopic examination (90).

Many sources of energy are used to excite samples to emit characteristic wavelengths for chemical identification and assay (91, 92). Very high temperature sources can be employed but are not necessary. All materials can be vaporized and excited with temperatures of only a few electron volts. The introduction of samples to be analyzed into high temperature or high density plasmas and their uniform excitation often are problematic.

Use of glow-discharge and the related, but geometrically distinct, hollow-cathode sources involves plasma-induced sputtering and excitation (93). Such sources are commonly employed as sources of resonance-line emission in atomic absorption spectroscopy. The analyte is vaporized in a flame at 2000–3400 K. Absorption of the plasma source light in the flame indicates the presence and amount of specific elements (86).

Pulsed spark sources, in which the material to be analyzed is part of one electrode, are used for semiquantitative analyses. The numerous and complex processes involved in spark discharges have been studied in detail by time- and space-resolved spectroscopy (94). The temperature of d-c arcs, into which the analyte is introduced as an aerosol in a flowing carrier gas, eg, argon, is approximately 10,000 K. Numerous experimental and theoretical studies of stabilized plasma arcs are available (79, 95).

Plasmas can be produced by radio frequencies that are inductively coupled to aerosol samples in argon streams. Inductively coupled high temperature plasma chemical analysis devices are operated at close to 30 MHz (96). Temperatures of 10,000–15,000 K are produced having electron densities of about $10^{15}/\text{cm}^3$ (91). These conditions tend to ensure vaporization, dissociation, and excitation. Microwaves near 2 GHz also can be used to excite plasmas for analysis (see Microwave technology). The analyte is carried in an argon gas flow which passes through a cavity excited by a magnetron or other source of microwaves. Temperatures of 6000 K and electron densities of 10^{12}–$10^{15}/\text{cm}^3$ are normal in microwave-excited analytical plasmas (97). Low temperature analysis is also possible in some situations. A device using low temperature plasma to analyze a surface for organic contamination has been developed. The surface is flushed with low temperature gas plasma species which react with organic molecules and emit light in characteristic wavelengths (98).

High power pulsed lasers are used to produce plasmas and thus to sample and excite the surfaces of solids. Improvements in minimum detectable limits and decreases in background radiation and in interelement interference effects result from the use of two lasers (99) (see Surface and interface analysis).

In plasma chromatography, molecular ions of the heavy organic material to be analyzed are produced in an ionizer and pass by means of a shutter electrode into a drift region. The velocity of drift through an inert gas at approximately 101 kPa (1 atm) under the influence of an applied electric field depends on the molecular weight of the sample. The various sonic species are separated and collected every few milliseconds on an electrode. The technique has been employed for studying upper atmosphere ion molecule reactions and for chemical analysis (100).

5.4. Plasma Processing

Plasma processing is an extremely broad and growing field. Radio-frequency gas plasma processing, made commercially available in the late 1960s, is an environmentally conscious surface modification and material production technology. The literature covering plasma processing is quite extensive and grows by thousands of references each year. Space permits the listing of only a small number herein (79, 101–118).

Plasmas can accelerate reactions that are otherwise slow to the point of impracticality. Moreover, plasmas are often used to accomplish processes not possible by other means, eg, providing atomically clean surfaces of materials that would be damaged by high temperature or wet chemical cleaning. In the plasma processing generally used in industry, no hazardous wastes are generated and, in fact, plasma usage has proven effective at decomposing hazardous waste materials (119). Most plasma processes take a few minutes and after the plasma treatment process is completed, parts or assemblies are immediately ready to be bonded, potted, welded, painted, soldered, or assembled in whatever manner necessary. It is, however, possible to overprocess or damage items being treated. Even low pressure plasmas can result in damage to materials owing to ion, electron, or photon bombardment. Analysis of materials exposed to plasmas is often useful and usually required in both experimental and commercial operations (120).

Plasma processing also offers several operational and cost advantages, eg, replacement of batch with flow processes. Plasma equipment often is smaller than other process hardware, resulting in associated savings in capital expenditure and floor space. Plasma units generate much smaller amounts of waste heat than most types of processing equipment and provide rapid start-up and shutdown. Plasma processing based on hydroelectrical power can be less expensive than processes that derive energy from fossil fuels. Plasma sources that are used to drive chemical reactions range from relatively low pressure and temperature, nonequilibrium glow-discharges, to dense, hotter arcs.

5.5. Surface Modification

Plasma surface modification can include surface cleaning, surface activation, heat treatments, and plasma polymerization. Surface cleaning and surface activation are usually performed for enhanced joining of materials (see Metal surface treatments). Plasma heat treatments are not, however, limited to high temperature equilibrium plasmas on metals. Heat treatments of organic materials are also possible. Plasma polymerization crosses the boundaries between surface modification and materials production by producing materials often not available by any other method. In many cases these new materials can be applied directly to a substrate, thus modifying the substrate in a novel way.

Treating a surface with activated gas plasma is a dry process requiring no solvents or rinses of any kind. Using the correct choice of gases and process parameters, plasma cleaning can render a surface atomically clean of organic contaminants and/or activate a surface for enhanced bonding without damage to that surface (121). Figure 7 shows a continuous plasma fiber/wire treatment system that can provide surface treatments in a spool-to-spool or air-to-air mode. The plasma removal of some inorganic contaminants is possible using certain reducing, rather than oxidizing, atmospheres (see Fig. 4**a**). Plasma surface cleaning is done in a fully contained and controlled vacuum environment. The only effluents are the volatile reaction products of the plasma gas and the surface contaminants (see Fig. 4**b**). Surface drying by plasma treatment has taken on increased importance in the climate of aqueous-based wet chemical cleaning for environmentally conscious manufacturing.

Gas plasma activation of low surface energy polymers for enhanced adhesive bonding has been recognized as a viable process for many years (111, 118, 122–124). Plasma treatments are able to increase the surface energy of most polymers, making their surfaces more polar and wettable, thus enhancing adhesive bondability. Polar or active sites on the polymer surfaces are formed when activated species present in the plasma collide with the surface and transfer energy to it. This energy can break bonds on the surface of the material causing unsaturation, remove atoms or molecules of material, substitute atoms or molecules onto a surface, or leave partial charges where bonds have reformed in less stable ways. In some instances, oxidation of the substrate is undesirable. In these cases, activation of a surface can be accomplished using plasma gases such as argon, helium, nitrogen, or mixtures of nonoxidizing gases such as a nitrogen and hydrogen mix. Because of their inert nature, these gases do not provide the organic contaminant removal capabilities that oxygen-containing gases do (125). However, if the surface is sufficiently clean, these gases can activate the surface and provide enhanced bonding.

Direct-current arcs into which no material is introduced have many applications as heat sources. Industrial processing of metals using plasma torches has been carried out in the former USSR (126). Thermal plasmas also are used in surface and heat treatment of materials (127, 128). Metals can be hardened by

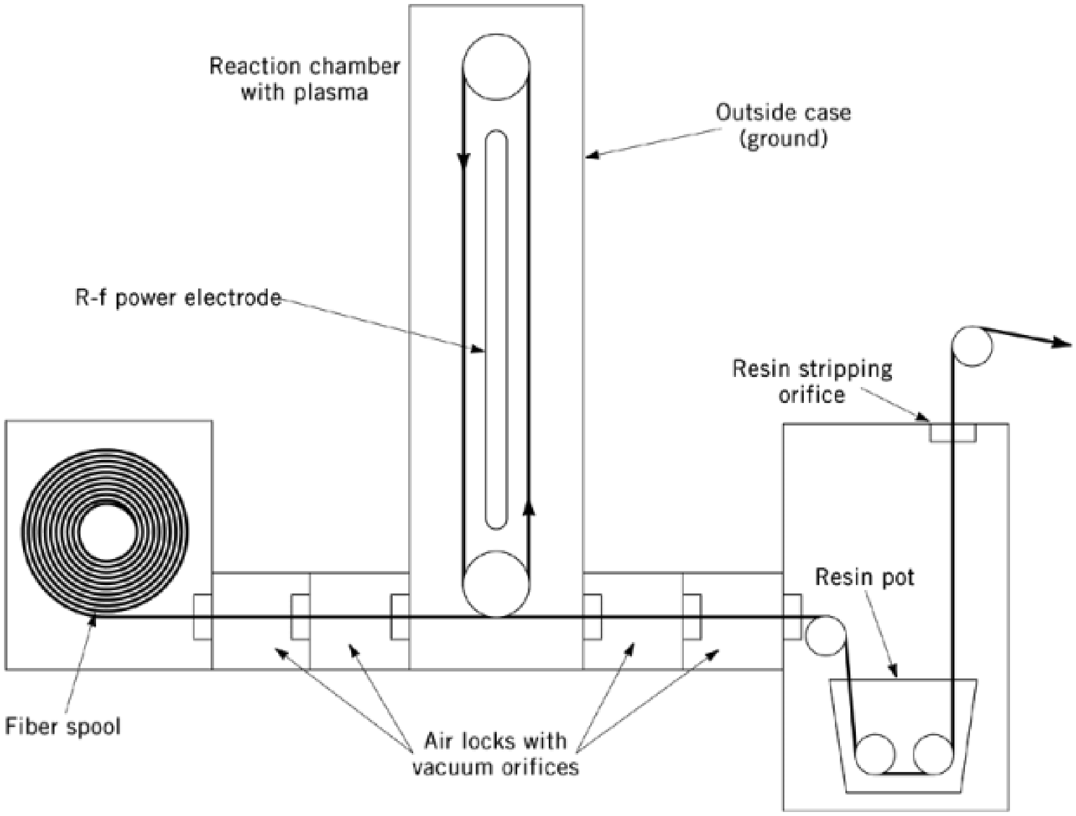


Fig. 7. Schematic of a self-contained plasma processing unit designed to continuously plasma-treat and impregnate with resin, reinforcing fibers for enhanced composite strength. The unit can also be used to plasma-treat wires to be coated or treated for improved adhesion. Throughput speeds of over 100 m/s are attainable for commercial use.

exposure to heat from thermal or equilibrium plasmas. Natural fibrous materials such as wool (qv) can be made shrink resistant by careful exposure to equilibrium atmospheric pressure plasmas at 150°C or less (129). Alteration of surface properties such as wettability using plasmas has been reviewed (130). The forming of materials using plasmas is widespread (131); plasma torches are employed to cut thick metal plates (22); and the use of d-c arcs for joining metals by welding (qv) is common.

5.6. Plasma Polymerization

Plasma polymerization is becoming a commercially viable method for modifying low cost organic substrates. Organic and other complex molecules that are exposed to low temperature nonequilibrium plasmas can be affected in terms of polymerization, rearrangements (isomerizations), surface activation, elimination of constituent parts, and total destruction of the original molecules accompanied by the generation of atoms and ions (132). The production of polymers and other heavier molecules from gaseous monomers is an attractive application of plasmas in organic chemistry (21, 133, 134). A wide variety of chemically inert, adherent films such as plasma-polymerized fluorocarbon films can be produced using simple, commercially available apparatus (21, 133, 135, 136). Radio-frequency discharge polymerization of organic chemical monomers is employed to produce organosilicon films, which are useful as light guides for integrated optics (137). Semipermeable membranes for hyperfiltration also are prepared by the use of plasmas, eg, poly(vinylene carbonate) deposited on a Millipore filter. Such composite filters are dense, pinhole-free, easy to prepare, and provide high salt rejection (138). The attachment of fluorine (qv) directly onto the surface of polymers can provide fluorocarbon-like surfaces on low cost polymer substrates (139).

5.7. Materials Production

Substances not producible by conventional means can be made using plasmas. Plasma materials production and modification embraces processes such as production of thin coatings (qv), heat treatment, and the joining of materials. Simple organic and inorganic molecules are produced in reactions driven by plasma arcs, eg, the fixation of nitrogen to hydrogen, carbon, or oxygen (140). Numerous fluorine compounds that have been produced by plasma chemistry are tabulated in Reference 105. Reactions involving many other elements also are accomplished by plasma stimulation (79).

Inorganic small molecules also are produced in glow discharges and rf-induced plasmas by chemical vapor deposition (CVD), generally termed plasma-assisted CVD (PACVD) or plasma-enhanced CVD (PECVD). The molecules are introduced in the gaseous state and the products usually deposit on a chosen substrate. Collisional processes relevant to PECVD have been analyzed and tabulated (141–149). Amorphous silicon containing controlled concentrations of hydrogen can be produced by decomposition of SiH_4 in a glow discharge (150) as can layers of amorphous selenium using a hydride precursor gas, eg, H_2S_e (151).

Plasma sources utilized for the production of materials and their modification are similar to those used to effect chemical reactions. Low temperature, glow-discharge, and r-f devices are employed to coat and heat the surfaces of solids and to alter them by ion bombardment sputtering. Higher temperature plasmas are used in materials processing. Plasma torches are produced by confining the heating by r-f fields or arcs to a chamber through which gas flows at high velocity. Temperatures in excess of 10,000 K are attained in the plasma, which cools as it is swept along to form a jet.

The reduction of high melting and other inorganic compounds to produce elemental solids also is achieved with plasmas. Extractive metallurgy requires breaking up ores and similar compounds (see Metallurgy, extractive metallurgy). The decomposition of MoS_2 to the metal and sulfur has been demonstrated using an induction plasma torch (152). Plasma arc powered furnaces have been used for gaseous reduction of metal-containing materials (126).

Thin surface films also can be produced by plasma-sputtering deposition, without chemical reaction (see Thin films). Both single- and multiple-layer materials are produced. Especially important is the use of sputtering to produce multilayered microstructures consisting of dozens of layers of two elements or compounds (153). The microstructures are used as x-ray reflectors (154). Bulk as well as thin materials can be produced, albeit at low rates, by vapor deposition. For example, PECVD can be used as a source for growth of refractory crystals such as TiN (102). Plasma deposition and etching techniques are being used to modify materials to produce fine patterns such as diffraction gratings and Fresnel lenses for use with uv and soft x-radiation, and in the >$85 billion per year semiconductor industry (155–157).

The manufacture of semiconductor chips, wafers, and devices makes extensive use of plasma processing. In the 1970s and 1980s a revolution occurred in the way that multiple layers of silicon compounds and other semiconductor materials were deposited, etched, modified, and removed, when dry plasma processing replaced the wet chemistries used previously. Significant equipment innovations in the early 1970s essentially split the fledgling plasma equipment industry into two different areas of focus: semiconductor processing and industrial applications for surface modification and cleaning. The need for higher throughput and better consistency, wafer-to-wafer and within the same wafer, required a different set of processing geometries and the equipment to handle them. The units used to process semiconductors as of the 1990s bear little resemblance to the barrel-type reactors used in industrial processes. This has led to dramatic increases in the production of devices, better quality, consistency and reliability, higher device compactness, lower costs per device, and significantly lowered environmental, health, and safety concerns regarding processing materials (158–164). Semiconductor manufacturing is a large and far reaching industry, and possesses its own distinct literature. The world market for semiconductor manufacturing equipment is in excess of $11.9 billion per year. Approximately half of that amount is plasma-related (165).

Plasmas are used extensively to melt materials for a variety of purposes. In many cases, the materials are introduced as a powder into the gas stream in a plasma torch. The molten droplets can be used to grow crystals of refractory materials such as niobium (166).

Another common and important use of plasma is spray coating of materials with plasma-melted substances (167, 168). Plasma torches heated by d-c arcs can be hand-held for spray coating (22). Plasma spraying is employed to apply oxidation-resistant coatings to metals; for example, ceramic coatings of aircraft engine components and a proprietary cobalt–chromium–aluminum–yttrium coating for gas-turbine blades (169, 170) (see Refractory coatings). High temperature, self-lubricating coatings have also been applied to materials using plasma techniques (171).

In addition to coating existing structures by plasma spraying, it also is possible to build composite materials by spraying fibers or whiskers with a binding substance (see Composite materials) (167). The molten droplets produced in a plasma torch can be cooled without impacting a surface in order to obtain fine particles. Refractory metals and oxides can be made into powders of spherical particles using plasma torches. The resulting materials are used, for example, to produce filters and electrodes (126).

5.8. Energy Production

The fusion or joining of two light nuclei, generally isotopes of hydrogen, leads to the formation of a heavier nucleus, eg, helium, with conversion of mass to energy. High energy is needed to overcome the mutual electrical repulsion experienced by two positive particles when they are near each other. The high velocities required for nuclear contact and reaction can be produced in plasmas if the ion temperature is greater than a few thousand electron volts. Because of the far greater number of nuclei in plasmas compared to beams of light nuclei, net energy production by nuclear fusion may occur in a plasma. Many exothermic fusion reactions are known. The easiest reaction to initiate is the deuterium–tritium reaction (see Deuterium and tritium).

$$^{2}\mathrm{D} + {}^{3}\mathrm{T} \xrightarrow{4} \mathrm{He} + n^{1} + 17.6\ \mathrm{MeV}$$

Deuterium is abundant in and easily separated from water. There is enough deuterium on earth to provide power for geological time scales. In contrast, tritium is not available in nature, but can be produced from $n+$ lithium reactions (see Lithium and lithium compounds). Natural lithium is exhaustible, but sufficient tritium can be provided from it until fusion energy production is efficient enough to involve only D–D reactions:

$$^{2}\mathrm{D} +^{2}\mathrm{D} \longrightarrow^{3}\mathrm{T} + p^{1} + 4.0\ \mathrm{MeV} \quad \text{or} \quad ^{2}\mathrm{D} +^{2}\mathrm{D} \xrightarrow{3} \mathrm{He} + n^{1} + 3.3\ \mathrm{MeV}$$

Deuterium–deuterium reactions are harder to ignite and yield less energy than D–T reactions, but eventually should be the basis of fusion energy production (172). Research into the production of fusion power has been ongoing since the 1950s (173–177) (see Fusion energy).

High temperature is an important requirement for the attainment of fusion reactions in a plasma. The conditions necessary for extracting as much energy from the plasma as went into it is the Lawson criterion, which states that the product of the ion density and the confinement or reaction time must exceed 10^{14} s/cm^3 in the most favorable cases (173). If the collisions are sufficiently violent, the Lawson criterion specifies how many of them must occur to break even. Conventional magnetic confinement involves fields of as much as 10 T (10^5 G) with large (1 m^3) plasmas of low densities ($<10^{14}$ particles/cm^3) and volumes and reaction times of about 1 s. If the magnetic flux can be compressed to values above 100 T (10^6 G), then a few cm^3 of plasma can be confined at densities of approximately 10^{19} particles/cm^3 for correspondingly shorter times ($\sim 10\ \mu s$). Inertial confinement requires compression of minute plasma ($< 10^{-3}\ cm^3$) to densities in excess of those of solids ($\sim 10^{25}$ particles/cm^3) for very short reaction times (~ 10 ps). The goal of all fusion devices is to produce high ion temperatures, which usually are in excess of the electron temperature, in contrast to low energy plasmas in which the electrons are often much hotter than the ions (see Fig. 2).

5.9. Guns and Missiles

The rapid burning of powder in a gun barrel produces relatively cold plasmas which eject the projectile on a ballistic trajectory. Missiles carry a propellant which burns during flight, generating motion by high velocity ejection of mass. Modern missiles contain liquid or solid propellants having high energy densities. The chemical reactions that occur during their burning produces plasmas in the reaction chamber and exhaust nozzles.

High velocities can be reached by a variety of means (178). The highest muzzle velocities of conventional guns are about 10^6 cm/s. Rockets can attain higher speeds and are limited by the weight of the nonfuel parts of the rocket. Laser plasma ablation can propel small masses at over 10^7 cm/s but the technique is not likely to be useful for weaponry. A more promising plasma-based launcher is the rail gun (179), in which a plasma created by an electric discharge provides pressure to accelerate the projectile. Rail guns have the potential of speeds in excess of 10^7 cm/s, although the motion of bullets at such speeds in the atmosphere may be problematic (see Explosives and propellants).

5.10. Impacts and Explosives

The collision of high velocity bullets or other projectiles with solids causes rapid conversion of kinetic to thermal energy. Plasmas result incidentally, whereas the primary effects of impact are shock and mechanical effects in the target. Impact-produced plasmas are hot enough to cause thermonuclear burn (180).

Most modern projectiles and virtually all missiles contain explosives. The plasmas that result from explosives are intrinsic to operation of warheads, bombs, mines, and related devices. Nuclear weapons and plasmas are intimately related. Plasmas are an inevitable result of the detonation of fission and fusion devices and are fundamental to the operation of fusion devices. Compressed pellets, in which a thermonuclear reaction occurs, would be useful militarily for simulation of the effects of nuclear weapons on materials and devices.

5.11. Directed-Energy Weapons

Modern weapons mostly involve the propulsion of masses to inflict damage. Energetic quanta from lasers and accelerators have potential as directed-energy weapons (181). These would be based on much of the same pulsed-power technology employed to produce high temperature plasmas, and their impact on targets could produce surface plasmas. Potential laser weapons are likely to be produced within a few decades and could be useful in the atmosphere, weather permitting, and in space.

5.12. Communications and Space Travel

Electromagnetic waves in and near the r-f region permit communications between points on or near earth or in space (182). The F layer of the ionosphere has the greatest electron density (see Fig. 5) and reflects radio waves of the greatest frequency. The plasma frequency, which is determined by the electron density and the angle of incidence, determines the frequency cutoff, below which reflection occurs and above which r-f waves penetrate and are partially absorbed by the ionosphere. Low frequencies (long wavelengths) which bounce off the F layer are partially absorbed in the lower D and E regions of the ionosphere.

The ionosphere is subject to sudden changes resulting from solar activity, particularly from solar eruptions or flares that are accompanied by intense x-ray emission. The absorption of the x-rays increases the electron density in the D and E layers, so that absorption of radio waves intended for F-layer reflection increases. In this manner, solar flares disrupt long-range, ionospheric bounce communications.

Earth to space (satellite) to earth communication links are relatively insensitive to ionospheric disturbances. Communications between earth and manned space vehicles are barely affected by plasmas when the spaceships are well away from the atmosphere, eg, in orbit or in a translunar trajectory. However, during reentry of a spaceship, a low temperature plasma forms around the vehicle and interrupts the communication links to it (183). Plasmas are incidental to the performance of modern rockets used to explore the solar system.

Spaceships capable of reaching stars other than the sun are expected to be more directly involved with plasmas than are contemporary spacecraft, in terms of their motion through the interstellar plasmas and their propulsion. Very high velocities are expected to be required for travel to other stars, eg, Proxima Centauri, which is 4.3 light years distant and would require 43 years at one-tenth the speed of light.

Most schemes that have been proposed to propel starships involve plasmas. Schemes differ both in the selection of matter for propulsion and the way it is energized for ejection. Some proposals involve onboard storage of mass to be ejected, as in modern rockets, and others consider acquisition of matter from space or the picking up of pellets, and their momentum, which are accelerated from within the solar system (184, 185). Energy acquisition from earth-based lasers also has been considered, but most interstellar propulsion ideas involve nuclear fusion energy; both magnetic, ie, mirror and toroidal, and inertial, ie, laser and ion-beam, fusion schemes have been considered (186–190).

5.12.1. Nomenclature

Symbol	Definition	Units
B	magnetic field strength	
c	velocity of light	3×10^8 m/s
D	particle size; region of ionosphere	
d	average interparticle spacing	
E	electric field strength; region of ionosphere	
E	oscillatory electric field	
e	charge on electron	
E_F	Fermi energy	
F	region of ionosphere	
f	particle collision rate	
h	Planck's constant	6.626×10^{-34} J·s
$\hbar$	$h/2\pi$	
k	Boltzmann's constant	1.38×10^{-23} J/K
m	mass	
m_e	mass of electron	
n	density	particles/cm^3
n_c	critical density	
q	charge	
T	temperature	K or eV $(1\ \mathrm{eV} \sim 11,600\ \mathrm{K})$
T_F	Fermi temperature	
V	velocity	m/s
$\overline{V}$	average velocity	
V_A	Alfven velocity	

Symbol	Definition	Units
$V_\perp$	velocity normal to magnetic field	
λ	mean free path between collisions	
λ_D	Debye length	
ρ	mass density	g/cm^3
ω_P	plasma frequency	
ω_c	cyclotron frequency	

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