High-Pressure Thermal Plasmas and Sources (Plasma Sources II)

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“Low Temperature Plasma Physics: Basics and Applications”
What is a Thermal Plasma?

At or close to atmospheric pressure (at least 0.1 atm)
Temperature ~ 1 to 2 eV (10 000 to 20 000 K) for electrons and heavy species
Highly ionised (typically 100%, at least 5%)
High electron densities (~ $10^{23}$ m$^{-3}$)
Formed by dc or ac electric arcs, radio-frequency or microwave electromagnetic fields
Dominated by collisions

Very widely used in manufacturing and other industries
• High power fluxes
• High fluxes of reactive species
• Strong radiative emission
Thermal Plasma Applications: Arc Welding
Thermal Plasma Applications: Plasma Cutting
Thermal Plasma Applications: Plasma Spraying
Thermal Plasma Applications: Waste Treatment
Thermal Plasma Applications: Arc Lighting

Carbon arc lamp

Xenon arc lamp
Thermal Plasma Applications: Mineral Processing

- Plasma remelting
- Electric arc furnaces
- Aluminium dross recovery
Thermal Plasma Applications: Circuit Breakers
Thermal Plasma Applications: ICP-OES, ICP-MS

Inductively-coupled plasma – optical emission spectroscopy

Inductively-coupled plasma – mass spectroscopy
Thermal Plasma Applications: Nanoparticle Synthesis and Particle Spheroidization
Thermal Plasmas in Nature: Lightning
The First Thermal Plasma Application?

The Miller-Urey experiment
Outline

1. Thermal plasma properties
   • Local thermodynamic equilibrium (LTE)
   • Composition
   • Thermodynamic and transport properties
   • Radiative emission

2. Generation of thermal plasmas
   • Transferred arcs
   • Non-transferred arcs
   • RF inductively-coupled plasmas
   • Microwave plasmas
   • Types of plasma flow

3. Modelling of thermal plasmas
   • Equations
   • Turbulence, electrode sheaths, gas mixtures

4. Thermal plasma diagnostics
   • Enthalpy probes
   • Emission spectroscopy
   • Laser scattering

5. Thermal plasma applications
   • Plasma waste destruction
Collisions between Electrons and Ions

\[ a = \frac{F}{m} = \frac{qE}{m} \]

Cathode

\( e \)

\( \text{Ar}^+ \)

Anode
Collisions between Electrons and Heavy Species Transferring Little Energy

\[ \Delta E_{\text{kin}} \approx 2m_e/m_h \]
Lots of Collisions between Electrons and Ions
Transfer A Lot of Energy

For 15 000 K, 1 atm:
\[ \tau_e = \frac{l_e}{v_e} \]
\[ \sim \frac{3 \times 10^{-6} \text{ m}}{7 \times 10^5 \text{ m/s}} \]
\[ \sim 5 \text{ ps} \]
Increasing pressure increases the number density, and therefore the collision rate and the transfer of energy from electrons to heavy species.
Local Thermodynamic Equilibrium (LTE)

LTE exists if all species satisfy

- Maxwellian distribution for translational temperatures
- Boltzmann distribution for excitation temperatures
- Chemical equilibrium equations for reactions, e.g., ionisation

and all these temperatures are the same

LTE exists if the collision rate is much greater than the rates of diffusion and convection

It is generally valid in the bulk of the plasma (away from the edges and electrodes)
If LTE exists, then if we know (at a given point in the plasma)

- the pressure

- the temperature (or instead the density of any species)

- if there is a mixture of gases, the proportions of each gases

then we can fully describe the composition of the plasma at that point

This greatly simplifies modelling and diagnostics
Why Calculate Plasma Properties?

1. They are needed for computational modelling

\[ \frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0 \]

\[ \frac{\partial (\rho \mathbf{v})}{\partial t} + \nabla \cdot (\rho \mathbf{v} \mathbf{v}) = -\nabla P - \nabla \cdot \mathbf{\tau} + \mathbf{j} \times \mathbf{B} + \rho \mathbf{g} \]

where \( \tau_{rr} = -2\eta \frac{\partial \mathbf{v}_r}{\partial r} \), etc

\[ \frac{\partial (\rho h)}{\partial t} + \nabla \cdot (\rho \mathbf{v} h) = \frac{j^2}{\sigma} - \mathbf{U} - \nabla \cdot \left( \frac{\kappa}{c_p} \nabla h \right) + \frac{5k_B}{2ec_p} j \cdot \nabla h \]

where \( h \) is a function of \( T \)

\[ \nabla \cdot (\sigma \nabla \phi) = 0 \]
Why Calculate Plasma Properties?

2. Measurements are inaccurate and inadequate

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**Nitrogen, 1 atm**

- **Thermal conductivity (W m\(^{-2}\)K\(^{-1}\))**
  - Calculated (Murphy)
  - Measured (Hermann & Schade)
  - Measured (Plantikow)

- **Viscosity (kg m\(^{-1}\)s\(^{-1}\))**
  - Calculated (Murphy)
  - Measured (Guevara et al.)
Classification of Properties

Thermodynamic properties
• Mass density (kg/m³)
• Specific heat at constant pressure $c_p$ (J/kg/K)
• Specific enthalpy (J/kg)

Transport properties (transport coefficients)
• Viscosity (kg/m/s)
• Thermal conductivity (W/m/K)
• Electrical conductivity (S/m)
• Ordinary diffusion coefficient (m²/s)
• Thermal diffusion coefficient (kg/m/s)

Radiation properties
• Net emission coefficient (W/m³/sr)
Relation between Basic Data and Material Properties

- Basic data
  - Species thermo-dynamic data
  - Binary collision integrals
- Composition
- Thermodynamic properties
- Transport properties
- Fluid dynamic equations
Plasma Composition

Use either:

• Saha equations for ionisation reactions & Guldberg-Waage equations for dissociation reactions
  – Solve simultaneously (one equation for each reaction)

• Minimisation of Gibbs free energy \( G = H - TS \) (\( H = \) enthalpy, \( S = \) entropy)
  – Restrictions: chemical elements conserved, charge neutrality
  – Input data (specific heat of each species / partition functions for each species) can be calculated from spectral data, or taken from tables
Examples

Argon, 1 atm

50% Argon, 50% Nitrogen, 1 atm
Thermodynamic Properties

These are easily calculated once the plasma composition is known

\[ \rho = \sum_{i=1}^{N} n_i m_i \]

\[ h = \frac{1}{\rho} \sum_{i=1}^{N} n_i m_i h_i \quad (+ \text{minor correction term}) \]

\[ C_p = \left. \frac{\partial h}{\partial T} \right|_p \]
Enthalpy for Various Plasmas

Temperature (K)

Enthalpy (MJ kg\(^{-1}\))

- Argon
- Nitrogen
- Oxygen
- Helium
- Hydrogen

0 5000 10000 15000 20000 25000 30000

0 200 400 600 800 1000 1200 1400 1600 1800 2000
Transport Properties

- Viscosity: transport of momentum perpendicular to flow
- Thermal conductivity: transport of heat
- Electrical conductivity: transport of charge
- Diffusion coefficients: transport of mass

Determined by collision cross-sections (mean free paths) of all species

For plasmas, have many species present – need information about collision cross-sections between all pairs of species:

- neutral-neutral
- neutral-ion
- neutral-electron
- charged-charged (Coulomb)
Viscosity

To first order: \( \eta = \frac{1}{2} k_B T \sum_j n_j b_{j0} \)

where

\[
\sum_{j=1}^{q} Q_{ij}^{00} b_{j0} = 5n_i
\]

\[
Q_{ij}^{00} = \frac{16}{3} \frac{n_i m_i}{m_j} \sum_{k=1}^{q} \frac{n_k m_k}{(m_i + m_k)^2}
\]

\[
\times \left[ 5m_j \left( \delta_{ij} - \delta_{jk} \right) \Omega^{(1,1)}_{ik} + \frac{3}{2} m_k \left( \delta_{ij} + \delta_{jk} \right) \Omega^{(2,2)}_{ik} \right]
\]
Collision Integrals are Calculated from the Intermolecular Potentials (using 3 integrations)

\[
\Omega_{ij}^{(l,s)}(T) = \sqrt{\frac{kT}{2\pi\mu_{ij}}} \int_{0}^{\infty} \exp\left(-\gamma_{ij}^2\right)\gamma_{ij}^{2s+3} Q_{ij}^{(l)}(g) \, d\gamma_{ij} \quad \text{where} \quad \gamma_{ij} = \sqrt{\frac{\mu_{ij}}{2kT}} g_{ij}
\]

are averages over a Maxwellian distribution of the gas kinetic cross-section

\[
Q_{ij}^{l}(g) = 2\pi \int_{0}^{\infty} \left(1 - \cos^l \chi\right) b \, db
\]

where the angle of deflection is

\[
\chi(b, g) = \pi - 2b \int_{r_m}^{\infty} \frac{dr/r^2}{\sqrt{1 - \varphi(r)/\frac{1}{2} \mu g^2 - b^2/r^2}}
\]

intermolecular potential \(\varphi(r)\)

reduced mass \(\mu\)

initial relative speed \(g\)

impact parameter \(b\)
Viscosity $\eta$ describes relationship between shear stress and velocity gradient $F = -\eta \frac{dv_x}{dy}$

$\eta \sim \sqrt{\frac{m_i T}{\Omega}}$, $\Omega$ is collision cross section
Thermal conductivity $k$ describes relationship between heat flux density and temperature gradient $q = -k \frac{dT}{dx}$

$k \sim \frac{C_p}{\Omega} \sqrt[3]{\frac{T_i}{m_i}}$, $\Omega$ is collision cross-section
Components of Thermal Conductivity for Nitrogen

Thermal Conductivity (W m$^{-1}$K$^{-1}$) vs Temperature (K)

- Total
- Heavy species
- Reaction
- Electron
- Internal
Electrical conductivity $\sigma$ describes relationship between current density and voltage gradient $j = \sigma \frac{dV}{dx}$

$\sigma \sim \frac{n_e}{\sqrt{Tn\Omega}}$, $n_e$ is electron density, $n$ is density of other species, $\Omega$ is collision cross section
Radiative Emission

Important in thermal plasmas
A full treatment is difficult:
• Determine emission and absorption at every volume element
• A large number of wavelength intervals required to cover line and continuum radiation

Net emission coefficients are a very successful approximation
• For a given temperature, integrate emission over all wavelengths
• Take into account absorption in a sphere of a given radius

For applications in which radiation flux at boundary is important, need more complex treatments

Net Emission Coefficients for Argon at 1 atm

L is the radius of the absorbing sphere

2. Generation of Thermal Plasmas

a) Electric Arcs: Transferred Arcs

- Arc between one electrode (usually cathode) and metal or conducting workpiece
- High energy transfer efficiency to workpiece
- Low gas flow
- Relatively inexpensive
- High peak temperature, narrow distribution (high gradients)
- Used in welding, plasma cutting, electric arc furnaces, arc lamps, waste destruction, etc.
b) Electric Arcs: Non-transferred Arcs

- Arc is confined within plasma torch
- High efficiency heating of bulk gas (“arc heater”)
- High gas flow
- Broader heat flux distribution, lower peak temperature
- Used in plasma spraying, waste destruction, etc.
c) RF Inductively-Coupled Plasmas

- No electrodes, so low contamination
- Generates a larger, more uniform, plasma volume
- More expensive; lower efficiency
- More sensitive to process variations
- Used for powder processing (densification, spheroidisation), nanoparticle production, etc.
d) Microwave Plasmas

- No electrodes
- Several different designs
- Relatively small and expensive
- Strongly non-equilibrium (gas temp. < 5000 K, electron temp. > 10 000 K)
- Applications include MP-AES (microwave plasma - atomic emission spectroscopy), gas treatment
Types of Plasma Flow

Gravity-driven flow
- Low current (< 20 A) arcs
- Flow driven by buoyancy
- Arc lamps

Flow driven by $j \times B$ forces
- Higher current (> 30 A) arcs
- Pressure gradient = $j \times B$ (the magnetic pinch effect)
- Maximum velocities from 100 to 1000 m/s
- Arcs for welding, plasma cutting, etc
Magnetic Pinch (Lorentz or $j \times B$) Force
Types of Plasma Flow

Flows driven by thermal expansion
- In plasma torches, the arc occurs in a confined region, causing the pressure to rise
- Supersonic velocities (over 2000 m/s) typically achieved
- Arc stabilised by high gas flow and often swirl of gas
- Typical in plasma spraying

Shock diamonds indicating supersonic flow
3. Modelling of Thermal Plasmas

- Use computational fluid dynamic equations for viscous incompressible flow
- A conservation of energy equation is required because the temperature is not constant
- Maxwell’s equations are used to describe current continuity (charge conservation) and magnetic fields
- Additional terms describing ‘plasma’ effects are included (ohmic heating, radiative emission, magnetic pinch effect, electron diffusion)
- The equation of state is implicit in the dependence of thermophysical properties on temperature
- Modifications required for electrode regions, turbulent flows, departures from LTE, high Mach number flow, etc.
Conservation Equations: Single Gas

\[ \frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0 \]

\[ \frac{\partial (\rho \mathbf{v})}{\partial t} + \nabla \cdot (\rho \mathbf{v} \mathbf{v}) = -\nabla \cdot \tau - \nabla P + \mathbf{j} \times \mathbf{B} + \rho \mathbf{g} \]

\[ \frac{\partial (\rho h)}{\partial t} + \nabla \cdot (\rho \mathbf{v} h) = -\nabla \cdot \left( \frac{\kappa}{c_p} \nabla h \right) + \frac{j^2}{\sigma} - \mathbf{U} + \frac{5k_B}{2e} \mathbf{j} \cdot \nabla T \]

\[ \nabla \cdot (\sigma \nabla \phi) = 0 \quad \nabla^2 A = -\mu_0 \mathbf{j} \]
Conservation of Mass (Mass Continuity)

\[ \frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0 \]

- $\rho$ mass density
- $t$ time
- $\mathbf{v}$ velocity

Note: if there is a source of mass (e.g., evaporation of a surface) then a source term is required
Conservation of Momentum

\[ \frac{\partial (\rho \mathbf{v})}{\partial t} + \nabla \cdot (\rho \mathbf{v} \mathbf{v}) = -\nabla \cdot \boldsymbol{\tau} - \nabla P + j \times \mathbf{B} + \rho \mathbf{g} \]

where \( \tau_{ii} = \eta \left( 2 \frac{\partial v_i}{\partial x_i} - \frac{2}{3} \nabla \cdot \mathbf{v} \right) \), \( \tau_{ij} = \eta \left( \frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} \right) \), \( i \neq j \)

\( \rho \) mass density, \( t \) time, \( \mathbf{v} \) velocity

\( \boldsymbol{\tau} \) viscous stress tensor, \( \eta \) viscosity

\( P \) pressure

\( j \) current density, \( \mathbf{B} \) magnetic field strength

\( \mathbf{g} \) acceleration due to gravity
Conservation of Energy

\[
\frac{\partial (\rho h)}{\partial t} + \nabla \cdot (\rho \mathbf{v} h) = -\nabla \cdot \left( \frac{\kappa}{c_p} \nabla h \right) + \frac{j^2}{\sigma} U + \frac{5k_B}{2e} j \cdot \nabla T
\]

\( \rho \) mass density, \( t \) time, \( \mathbf{v} \) velocity, \( T \) temperature

\( h \) enthalpy, \( \kappa \) thermal conductivity, \( c_p \) specific heat

\( j \) current density, \( \sigma \) electrical conductivity

\( U \) radiative emission coefficient

\( k_B \) Boltzmann constant, \( e \) elementary charge

For compressible flow (Mach number \( > 0.5 \)), need to add

\[-(\tau : \nabla \mathbf{v}) + \frac{Dp}{Dt}, \text{ where } \frac{Dp}{Dt} \equiv \frac{\partial p}{\partial t} + \mathbf{v} \cdot \nabla p, \text{ to right-hand side}\]
Charge Continuity, Magnetic Potential, Maxwell’s Equations

\[ \nabla \cdot (\sigma \nabla \phi) = 0 \]
\[ \nabla^2 A = -\mu_0 j \]
\[ j = -\sigma \nabla \phi \]
\[ \nabla \times B = \mu_0 j \]

\[ \sigma \] electrical conductivity, \( \phi \) electric potential
\[ A \] magnetic potential, \( j \) current density
\[ \mu_0 \] permeability of free space
Complications: Turbulence

Many thermal plasma flows are turbulent
• Plasma jets (e.g., for plasma spraying)
• Plasma cutting arcs

Different approaches
• Direct numerical simulation (DNS)
  – *Solves* all the scales of flow
  – Very expensive, and unfeasible for industrial problems
• Large eddy simulation (LES)
  – *Solves* for large scales and *approximately models* small scales of the flow
  – Turbulence model needed to approximate the small scales
• Reynolds-averaged Navier-Stokes (RANS)
  – *Approximately models* all scales of the flow
  – The most common approach for industrial problems
  – Include:
    – 0 equations: Prandtl mixing length
    – 1 equation: Spalart-Allmaras
    – 2 equations: K-\(\varepsilon\), K-\(\varepsilon\) RNG, K-\(\omega\)
The K-ε Model

Turbulence is modelled as an additional diffusion mechanism

Solve additional transport equations for \( K \) (turbulence kinetic energy) and \( \varepsilon \) (turbulence energy dissipation), which then give viscosity and thermal conductivity

\[
\frac{\partial (\rho K)}{\partial t} + \nabla \cdot (\rho \nu K) = \nabla \cdot \left[ \left( \eta + \frac{\eta_t}{S_K} \right) \nabla K \right] + 2G - \rho \varepsilon
\]

\[
\frac{\partial (\rho \varepsilon)}{\partial t} + \nabla \cdot (\rho \nu \varepsilon) = \nabla \cdot \left[ \left( \eta + \frac{\eta_t}{S_\varepsilon} \right) \nabla \varepsilon \right] + 2C_1 \frac{\varepsilon}{K} G - C_2 \rho \frac{\varepsilon^2}{K}
\]

\[ G = 2\eta_t \left| \nabla \nu + \nabla \nu^T \right|^2 \]

\[ \eta_t = C_\eta \rho \frac{K^2}{\varepsilon} \] is turbulent viscosity, \( \kappa_t = \frac{\eta_t C_p}{\Pr_t} \) is turbulent thermal conductivity

\( S_K, S_\varepsilon, C_1, C_2, \Pr_t \) are constants
Effect of Turbulence

Mass fraction of air for argon plasma jet discharging into air

Effect of Turbulence

Temperature (1000 K) of argon plasma jet discharging into air

**Ar plasma jet into Air**

(2D-axisym)

\[ \omega (s^{-1}): -50,000 \rightarrow 50,000 \]

\[ T(K): 300 \rightarrow 12,000 \]

Direct numerical simulation captures small~large eddies.

Eddy-breakup

Courtesy Dr Masaya Shigeta, Osaka University
Complications: Electrode Sheath Regions

$10^{-1}$ mm

$T_e > T_h$

$10^{-5}$ mm

$n_e \neq n_i$
Anode Treatments

**Problem:** the temperature adjacent to the anode is low, so if assume LTE, then $n_e \approx 0 \Rightarrow \sigma \approx 0$

**Approach 1:** Add electron diffusion term (Sansonnens et al.)

$$j = -\sigma \nabla \phi + e D_e \nabla n_e$$

$$\nabla \cdot (D_a \nabla n_e) + \alpha \left( n_e n_0 n_e^* / n_0^* - n_e^3 \right) = 0$$

$D_e$ and $D_a$ are electron and ambipolar diffusion coefficients

$\alpha$ is three-body recombination coefficient, * indicates LTE value

**Approach 2:** "LTE-diffusion approximation" (Lowke and Tanaka)

Set mesh size near anode to width of region in which electron diffusion dominates ($\Lambda = k_B T / eE \approx 0.1$ mm).

Then use LTE everywhere.

Comparison of Approaches 1 and 2

(Lowke & Tanaka)

(Sansonnens et al)
Thermionic Cathode Treatment

- Applies to high melting point materials e.g., W, C, Mo, Zr
- Electrons emitted from cathode
- Cathode heated through ion bombardment
- Current densities around 100 A/mm$^2$

Richardson equation

$$j = AT^2 \exp\left(-\frac{e\phi_w}{k_B T}\right)$$

$A \approx 6 \times 10^5$ A mm$^{-2}$ K$^{-2}$ for most metals

$\phi_w$ (work function) $\approx 4.5$ V for W

$\approx 2.5$ V for W(Th)
Decreasing work function by 2 V reduces the cathode temperature by 1700 K (for 100 A mm\(^{-2}\))

Metals that don’t have high melting points (Cu, Al, Fe etc) cannot be thermionic emitters
Complications: Plasmas in Gas Mixtures

If more than one gas present, these gases can mix or demix

Even in LTE, need to know their relative fractions

For each species $i$

$$\frac{\partial (\rho Y_i)}{\partial t} + \nabla \cdot (\rho v Y_i) = -\nabla \cdot J_i + r_i$$

$Y_i$: mass fraction  $r_i$: reaction source term  $J_i$: diffusion mass flux

$$J_i = \frac{n^2 m_i}{\rho} \sum_{j=1}^{q} m_j D_{ij} \nabla x_j - D_i^T \nabla \ln T$$

$D_{ij}$: ordinary diffusion coefficient  $D_i^T$: thermal diffusion coefficient  $x_i$: mole fraction

Combined Diffusion Coefficients

Group species into gases

E.g., for Ar-He arc

- argon gas = Ar, Ar\(^+\), Ar\(^{2+}\), Ar\(^{3+}\), e\(^-\)
- helium gas = He, He\(^+\), He\(^{2+}\), e\(^-\)

Model diffusion of helium gas through argon gas

Typically 50 ordinary and thermal diffusion coefficients replaced by two combined diffusion coefficients

Exact for homonuclear gases that do not react for plasmas in LTE
Gas Conservation Equation

Species conservation equations for each species (Ar, Ar\(^+\), Ar\(^{2+}\), Ar\(^{3+}\), He, He\(^+\), He\(^{2+}\), e\(^-\))

\[ \nabla \cdot (\rho \nu Y_i) = -\nabla \cdot J_i + r_i \]

replaced by a single gas conservation equation

\[ \frac{\partial (\rho \overline{Y_{Ar}})}{\partial t} + \nabla \cdot (\rho \nu \overline{Y_{Ar}}) = -\nabla \cdot \overline{J_{Ar}} \]

\[ \overline{J_{Ar}} = \left( \frac{n^2}{\rho} \right) \overline{m_{Ar}} \overline{m_{He}} D_{Ar,He}^x \nabla x_{He} - D_{Ar}^T \nabla \ln T \]

The overbarred quantities are averaged over all species

Example: Demixing in an Argon-Helium Arc

Example 2: Metal Vapour in Welding Arc

Argon arc with steel wire

All emission  Atomic iron line  Atomic argon line

Goecke S F, Metzke E, Spille-Kohoff A and Langula M 2005
ChopArc. MSG-Lichtbogenschweißen für den Ultraleichtbau (Stuttgart: Fraunhofer IRB)
Measurements Show a Relatively Cool Arc, and a Local Temperature Minimum on Axis

Current = 326 A
Steel wire
6 mm above workpiece
4.5 mm above workpiece
3 mm above workpiece
Modelling Indicates Cooling Can Occur due to Increased Radiative Emission from Metal Vapour

Schnick M, Füssel U, Hertel M, Spille-Kohoff A and Murphy A B

4. Thermal Plasma Diagnostics

Probes
• Langmuir probes
• Enthalpy probes

Spectroscopy
• Emission spectroscopy
• Absorption spectroscopy

Laser scattering
• Elastic scattering
  – Rayleigh scattering
  – Thomson scattering
  – Raman scattering
• Inelastic
  – LIF (laser-induced fluorescence)
  – Two-photon LIF
  – CARS (coherent anti-Stokes Raman scattering)
Enthalpy

\[ h = \frac{n_{w}}{n_{g}} C_{p \text{ water}} \left( \Delta T_{\text{gas flow}} - \Delta T_{\text{no gas flow}} \right) \]

- \( n_{w} \) is cooling water mass flow rate
- \( n_{g} \) is gas sampling mass flow rate

Flow velocity

\[ v = \sqrt{2 \left( P_{\text{stagnation}} - P_{\text{atm}} \right) / \rho(T)} \]

Can also measure composition using gas analyser
Enthalpy Probe Results

Entrained air %, temperature (K) and velocity (m/s) for enthalpy probe (●) and laser scattering (Δ)

Plasma torch, 900 A, argon, 2 mm downstream from orifice

Optical Emission Spectroscopy

Diagram:
- Spectrometer
- CCD camera
- Lens f = 45 cm
- ND filters (optional)
- Rotational prism
- Iris diaphragm D = 18 mm
- Lens f = 35 cm
- Arc
Emission Spectroscopy: Determining the Temperature

Intensity \[ S(T) = \frac{n(T)}{Z(T)} A_{mn} g_m \hbar \nu_{mn} \exp \left( -\frac{E_m}{k_B T} \right) \]

- \( E_m \) is energy of upper level
- \( A_{mn} \) is transition probability
- \( g_m \) is statistical weight of upper level
- \( \nu_{mn} \) is transition frequency
- \( n \) is number density of species (e.g. atoms)
- \( Z \) is partition function of species

The measurement system has to be calibrated

Three standard methods:
1. Use a calibrated radiation source
2. Use ratio of intensity of two or more lines
3. Fowler-Milne method – use maximum in \( S(T) \)
Laser Scattering

Light is scattered from electrons – both bound (to atoms or ions) and free. The intersection of the laser beam and the observation axis defines a point.

Elastic scattering: $\lambda_{\text{laser}} \neq \lambda_{\text{transition}}$

$\lambda_{\text{scattered}} = \lambda_{\text{laser}}$

Thomson scattering: elastic scattering from free electrons
Rayleigh scattering: elastic scattering from bound electrons

Inelastic scattering: $\lambda_{\text{laser}} = \lambda_{\text{transition}}$

$\lambda_{\text{scattered}} = \lambda_{\text{laser}}$

Resonance scattering: inelastic scattering from bound electrons

Laser-induced fluorescence: inelastic scattering from bound electrons
Thomson Scattering

Spectrum of scattered light depends on $T_e$ and $n_e$

Approach 1. Wavelength-resolved scattering:
Measure scattered light as a function of wavelength – need to be careful of heating the plasma!

Approach 2. Integrated scattering:
No wavelength resolution
Accept all light in a given range of wavelengths around laser wavelength
Laser Scattering: Wavelength-Resolved Scattering

M. Kuhn-Kauffeldt, J.-L. Marques, J. Schein,
Laser Scattering: Integrated Scattering

Rayleigh scattering (elastic scattering from atoms/ions)
Thomson scattering (elastic scattering from free electrons)
Resonance scattering (inelastic scattering from atoms/ions)

Ar ion laser – 514.5 nm

100 A argon arc: T vs r

5. Thermal Plasma Applications

Arc welding
Plasma spraying
Plasma cutting
Mineral processing
  • Arc furnaces
  • Plasma remelting
Plasma spheroidisation
Arc lighting
Circuit interruption
Chemical synthesis
Production of nanostructured materials
  • Nanoparticles
  • Bulk nanostructured materials
  • Carbon nanomaterials (nanotubes, graphene, etc.)
Plasma waste treatment
Plasma Waste Treatment

Compared to high-temperature incineration, plasma gives:

Higher temperature and energy densities
  • Shorter residence times
  • More compact systems

Heat source is independent of waste
  • Exhaust gas flow decreased
  • Rapid shut-off possible

No lower limit on size
  • Easy integration into processes
  • On-site destruction possible

BUT:

High cost
Component lifetimes can be limited
High power plasma source difficult to make
Trend from Niche to Mainstream Applications

Highly-concentrated wastes or wastes requiring high temperatures:
- Asbestos-containing wastes
- Incinerator fly-ash and grate-ash
- Ozone-depleting substances
- Other concentrated chemicals

General wastes:
- Municipal solid wastes
- Medical wastes
- Auto-shredder residues
- Tyres
- Sewage sludge
Westinghouse Plasma: Waste Treatment & Fuel Production

DC plasma torch, up to 2.5 MW
Treat MSW, auto-shredder residue, industrial liquid and solid wastes
Plants capacities from 25 to 300 tonnes per day
E.g., Eco Valley Utashinai, Japan: 165 t auto-shredder waste per day, 8 MW electrical power from burning syngas (CO + H2) produced
PLASCON

Treats liquid and gaseous waste streams

150 kW non-transferred arc

10 plants in Australia, Japan, USA, Mexico

Treats

- Ozone-depleting substances
- PCB-contaminated oils
- Greenhouse gases
- Liquid organic wastes

A. B. Murphy, T. McAllister, Appl. Phys. Lett. 73 (1998) 459
Fluorocarbon Greenhouse Gases are Formed as a By-product of HCFC Production

HFC-23 = CHF$_3$ = trifluoromethane

Global warming potential of 11 700

Byproduct of CHClF$_2$ (HCFC-22) production (2.4% by mass)

$$6\text{HF} + 2\text{CHCl}_3 \rightarrow \text{CHCl}_2\text{F} + \text{CHClF}_2 + \text{CHF}_3 + 6\text{HCl}$$

185 tonne/year produced at Quimobasicos SA d CV, Monterrey, Mexico
185 tonnes per year of HFC 23

is equivalent to 2.2 million tonnes per year $\text{CO}_2$

i.e., the annual emissions from

a 300 MW coal-fired power station

a 600 MW gas-fired power station

or 500 000 cars
Trifluoromethane is Successfully Destroyed By PLASCON

$$\text{CHF}_3 + \text{H}_2\text{O} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2 + 3\text{HF}$$
PLASCON Destruction of HCF 23 is Very Profitable

Carbon accounting:

Destroying 1 t HFC 23
- Destroys equivalent of 11 700 t CO₂
- Produces direct emissions of 0.6 t
- and indirect emissions of 6 t CO₂

Economics (under Kyoto Protocol Clean Development Mechanism):

Destruction of 1 t HCF 23
- Equivalent to destruction of 11 663 t CO₂
- Carbon credits (@ $10/t CO₂) have value of $120 000
- Cost of destruction < $10 000

185 t/year gives a profit of ~$20M/year
Thank you

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