

Spectrographic Determination of Species in a High-Temperature Gas

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Nomenclature

$A_{mn}^{(i)}$	= transition probability
$c^{(i)}$	= species concentration
$E_m^{(i)}$	= energy of the m th state
$g_m^{(i)}$	= degeneracy (statistical weight)
h	= Planck's constant
$I_{mn}^{(i)}$	= intensity in emission for transition from state m to state n
k	= Boltzmann's constant
$n^{(i)}$	= number density
s_1, s_2	= scale factors
T	= temperature
$Z^{(i)}(T)$	= partition function
$\nu_{mn}^{(i)}$	= frequency of the line
τ	= volume of gas

Subscripts

m	= upper state
n	= lower state
λ	= arbitrary state

Superscripts

i	= species
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Introduction

SPECTROGRAPHIC methods of measuring temperatures¹⁻³ of high-temperature arc discharges and plasmas have been discussed at length in the literature, but relatively little⁴ has been written about determining the concentration of species spectrographically. The usual experimental method of determining species concentration is the spectrochemical analysis technique in which an internal standard is introduced⁵ as an impurity into the gas. However, this technique has serious objections at high temperatures since impurities alter the gas temperature and since it is difficult to mix the impurities uniformly in a gas stream. Likewise, the standard theoretical technique for calculating species concentration in which chemical equilibrium is assumed, is not necessarily valid in high-temperature flows, except in a stagnation chamber where the resident time is long enough for chemical equilibrium to occur. The temperature determination from the relative intensities of spectral lines has been given attention,^{1,2} but it has not been pointed out that similar methods are applicable for determining the concentration of the various gas species. Three such methods and a method for determining the density will be discussed in this note.

Derivation

It is assumed that the gas is in thermal equilibrium, that the radiation that enters the slit of the spectrograph originates from a region of constant density, and that there is no self-absorption. The latter two assumptions could be removed by introducing refinements in the calculation of the intensities, but it will not be done here.

With these assumptions, the intensity of radiation (energy/time-solid angle) emitted by the i th species in a transition from an initial energy state E_m to a final energy state E_n is²

$$I_{mn}^{(i)} = \frac{n^{(i)} \tau h \nu_{mn}^{(i)} g_{mn}^{(i)} A_{mn}^{(i)}}{4\pi Z^{(i)}(T)} \exp\left(\frac{-E_m^{(i)}}{kT}\right) \quad (1)$$

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where $Z^{(i)}(T)$ is the partition function defined by

$$Z^{(i)}(T) = \sum_{\lambda} g_{\lambda}^{(i)} \exp\left(\frac{-E_{\lambda}^{(i)}}{kT}\right) \quad (2)$$

and the range of the summation is over-all energy states of the i th species. Fishburne and Petrie⁴ obtained the ratio of the intensities I_{mn} for two species and solved for the ratio of the concentrations of the two species. Explicit expressions will now be derived for the species concentrations. The same type of data is required in each of the final expressions, but the amount of data varies from expression to expression.

Equation (1) may be rewritten as

$$\log \left[\frac{I_{mn}^{(i)}}{h \nu_{mn}^{(i)} g_m^{(i)} A_{mn}^{(i)}} \right] = - \left[\frac{E_m^{(i)}}{k} \log e \right] \frac{1}{T} + \log \left[\frac{n^{(i)} \tau}{4\pi Z^{(i)}(T)} \right] \quad (3)$$

This may be simplified to

$$\log F_{mn}^{(i)} = -(G_m^{(i)}/T) + \log H^{(i)} \quad (4)$$

where $F_{mn}^{(i)}$, $G_m^{(i)}$, and $H^{(i)}$ are defined by a term-by-term correspondence with Eq. (3).

For the present discussion, it is assumed that $A_{mn}^{(i)}$, $g_m^{(i)}$, and $E_m^{(i)}$ are known from theory or previous experiments. Then the temperature and species concentration can be determined from the measured intensities $I_{mn}^{(i)}$ of the emission lines $\nu_{mn}^{(i)}$. This holds true whether or not absolute values of $A_{mn}^{(i)}$ and $I_{mn}^{(i)}$ are available. If $A_{mn}^{(i)}$ and $I_{mn}^{(i)}$ are known only in some arbitrary units so that

$$I_{mn}^{(i)} = s_1 I_{mn}^{(i)'}, \quad A_{mn}^{(i)} = s_2 A_{mn}^{(i)'} \quad (5)$$

then

$$F_{mn}^{(i)} = (s_1/s_2) F_{mn}^{(i)'}$$

$$\log F_{mn}^{(i)'} = \log(s_2 H^{(i)}/s_1) - G_m^{(i)'}(1/T)$$

Note that $A_{mn}^{(i)'}$ and $I_{mn}^{(i)'}$ each must be given relative to the same reference for the various species.

If $F_{mn}^{(i)'}$ is plotted vs $G_m^{(i)'}$, for each species, the reciprocal of the slope equals the temperature, and the intercept with the ordinate yields

$$H^{(i)'} = (s_2/s_1) H^{(i)} = s_2 n^{(i)} \tau / 4\pi s_1 Z^{(i)}(T) \quad (6)$$

and the species concentration is then obtained from

$$c^{(i)} = n^{(i)} / \sum_i n^{(i)} = H^{(i)'} Z^{(i)}(T) / \sum_i H^{(i)'} Z^{(i)}(T) \quad (7)$$

This equation may then be used for computing the species concentration, since all the quantities on the right-hand side are known.

An alternate equation for the species concentration can be derived by using a particular line from the spectrum of each species. If Eq. (1) is summed over i and substituted into Eq. (7), one obtains

$$c^{(i)} = \frac{F_{mn}^{(i)'} Z^{(i)}(T) \exp\left(\frac{E_m^{(i)'}}{kT}\right)}{\sum_i F_{mn}^{(i)'} Z^{(i)}(T) \exp\left(\frac{E_m^{(i)'}}{kT}\right)} \quad (8)$$

This equation has the advantage that it is not necessary to construct an F - G plot for each species. One F - G plot from which to obtain the temperature is sufficient.

A third expression (which does not involve the graphically obtained temperature) may be derived by summing Eq. (1) over m and substituting it into Eq. (7). The result is

$$c^{(i)} = \frac{\sum_m \left[\frac{I_{mn}^{(i)'}}{\nu_{mn}^{(i)} A_{mn}^{(i)'}} \right]}{\sum_{im} \left[\frac{I_{mn}^{(i)'}}{\nu_{mn}^{(i)} A_{mn}^{(i)'}} \right]} \quad (9)$$

In the summation over i , the range of the summation is over all observable species.

If $I_{mn}^{(i)}$ and $A_{mn}^{(i)}$ are known in absolute units and if τ , the gas volume, can be determined with sufficient accuracy, the species number density $n^{(i)}$ can be evaluated from

$$n^{(i)} = 4\pi H^{(i)} Z^{(i)}(T)/\tau \quad (10)$$

Finally, the total density of the gas may be calculated by summing Eq. (10) over i .

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Radiant Energy Loss from a Seeded Plasma

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THE purpose of this note is to describe briefly the method and results of an investigation¹ into the radiant energy loss and its effect on the electronic energy balance of a seeded, slightly ionized plasma. Such a plasma may be in a state of nonequilibrium if the electron temperature is elevated above the gas temperature. A typical plasma, such as used for nuclear MHD generators, was considered, i.e., a noble gas, seeded with about 0.1% cesium at atmospheric pressure and 2000°K.

The computation of the radiant energy loss is divided into two parts, namely, the determination of the spectral absorption coefficient and the solution of the radiant transport equation.

The spectral absorption coefficient can, in turn, be divided into four parts, three due to continuum and one due to line radiation. Of the continuum parts, Bremsstrahlung (electron-ion radiation) is about 10^{-10} times smaller than line radiation² and electron scattering (electron-atom radiation) is about 10^{-5} times smaller than line radiation. The remaining two parts are free-bound and line radiation. A detailed treatment of the free-bound radiation shows it to be small enough that one can consider only line radiation for engineering calculations.

Doppler, pressure, and Stark broadening must all be combined to obtain the correct line profile. Since the latter two have a dispersion profile which falls off more slowly in the wings than that of the first, a dispersion profile is assumed for the entire line with a total line half-width taken as the sum of those for the three processes.^{3,4}

The transport equation is then formulated for a uniform plasma contained between plane parallel absorbing walls separated by a distance d . The electron temperature T is assumed to be elevated above the gas temperature T_g by

Table 1 Radiant flux to one wall, watts per centimeter squared

Plane separation		Temperature		
		2000°K	2500°K	3000°K
1 cm	continuum	1.0×10^{-4}	1.2×10^{-2}	2.5×10^{-1}
	line	1.7×10^{-1}	1.0	5.6
	total	1.7×10^{-1}	1.0	5.9
10 cm	continuum	1.0×10^{-3}	1.1×10^{-1}	2.4
	line	5.5×10^{-1}	3.6	21
	total	5.5×10^{-1}	3.7	23
100 cm	continuum	1.0×10^{-2}	1.0	20
	line	1.8	12	81
	total	1.8	13	101

some energy input, such as Joule heating. Kirchhoff's law is assumed to be valid locally.⁵ In the uniform plasma, the spatial integrations in the transport equation can be carried out analytically, but the frequency integration is done numerically.

This calculation has been carried out for an argon-cesium plasma at atmospheric pressure and 2000°K, with a seed concentration of $10^{16}/\text{cm}^3$. A total of 120 cesium lines were considered, using the oscillator strengths of Ref. 6. The resulting energy fluxes to one wall of the enclosure are given in Table 1. For completeness, the free-bound energy fluxes are also included. It will be noted that the continuum radiation is quite small, even at electron temperatures of 3000°K.

Of the 120 lines, it is found that the two principal resonance lines contribute approximately 80% of the radiation in all cases. Of this radiation, approximately 25% is in frequency ranges near the line center where the plasma is optically thick, with the remaining 75% coming from the wings.

Using this information, it has been possible to obtain an approximate solution to the transport equation, obviating the numerical integration. The result is that the energy flux to the wall, for fixed electron temperature, behaves as

$$F \propto (n_g n_s)^{1/2} T_g^{1/4}$$

where n_g is the gas concentration, n_s is the seed concentration, and T_g is the gas temperature.

It has recently come to attention that these results agree with Holstein,^{7,8} who considered the escape of resonance radiation from gases.

The present calculations show that for practical purposes, at electron temperatures below 3000°K, the radiant energy loss from an alkali metal seeded plasma may be approximated by the energy loss from the two principal resonance lines alone, and this can be treated simply by the method of Holstein.

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