

10.3.1.1 Excitation and radiation of spectra

10.3.1.1.1 Plasmas

A *plasma* of the type occurring in spectrochemical radiation sources may be described as a gas which is at least partly ionized and contains particles of various type, viz. electrons, atoms, ions and molecules. The plasma as a whole is electrically neutral.

A plasma which is in *thermodynamic equilibrium* can be characterized by a single temperature, called the *thermodynamic temperature*. This temperature describes the energy distribution of all particles, the state of ionization, the abundance of the chemical species and the spectral energy distribution through *Maxwell-Boltzmann's law*, *Saha-Eggert's law*, the *law of Mass Action* and *Planck's law* respectively. In practice, serious departures from thermodynamic equilibrium may exist, and different temperature values will be found according to the types of measurement. Several types of "temperature" may then be used for describing the state of plasma:

Radiance temperature is the temperature of a black-body radiator that has the same spectral radiance, according to Planck's law, as the radiator considered.

Electron temperature is the temperature that describes, through Maxwell's law, the kinetic energy distribution of the free electrons.

Gas temperature describes in a similar way the kinetic energy distribution of the gas atoms.

Excitation temperature is the temperature that describes, through Boltzmann's law, the relative population distribution of atoms or molecules over their energy levels. We distinguish between *electronic excitation temperature*, *vibrational temperature*, and *rotational temperature*.

Ionization temperature is related to the ionization equilibrium described by the Saha-Eggert equation.

With a plasma in thermodynamic equilibrium, all these temperatures should be equal. When only the radiance temperature deviates from the others, we speak of *thermal equilibrium*. In this case, all degrees of freedom of all particles are in equilibrium with each other, but not with the radiation field. The particles then emit *thermal radiation*, but not black-body radiation. When the temperature that describes such a state of thermal equilibrium varies with position inside the source, we speak of *local thermal equilibrium* (LTE), characterized by a *local (gas) temperature*.

Norm temperature is the temperature of a plasma at LTE for which a spectral line has maximum spectral radiance. This is the result of the competing effects of ionization and excitation processes.

TABLE 10.5 General classification of radiation sources

Type	Sort	Gas Pressure Range	Types of Spectra Radiated*
Arcs	dc	atmospheric (~100 kPa)	a,m,c
	ac	atmospheric	a,m,c
	current-carrying plasmas	atmospheric	a,m,c
	non-current carrying plasmas	atmospheric	a,m,c
	high pressure	100-600 kPa	c, broad a
	low pressure	10-100 kPa	a,m,c
Lasers	continuous	-	a,m (primary) a,m,c (secondary)
	pulsed	-	a (primary)
		-	
Low pressure electrical discharge	arc lamps	1-100 kPa	a,m,c (secondary)
	Geissler	1-10 kPa	a,c
	glow discharge; hollow cathode	0.1-10 kPa	a,m,c
	plane cathode	0.1-10 kPa	a,m,c
Microwave plasmas	loaded line	atmospheric	a,m,c
	induced (electrodeless)	low or atmospheric	a,m,c
Radiofrequency plasmas	inductively-coupled	atmospheric	a,m,c
	capacitively-coupled	atmospheric	a,m,c
Sparks	high voltage	atmospheric	a,m,c
	medium voltage	atmospheric	a,m,c
	low voltage	atmospheric	a,m,c
	vacuum sparks	<10 Pa	a,m,c

*a - atomic (neutral or ionized)
m - molecular (neutral or ionized)
c - continuous

TABLE 10.6 Terms, symbols and units for measurable quantities for radiation sources

Term	Symbol	Practical Unit*
analytical calibration function	$x=g(c)$	same as x
	or $x=g(q)$	same as x
analytical evaluation function	$c=f(x)$	same as c
	$q=f(x)$	same as q
atomic number	Z	1
atomic mass unit	m	1
atomic mass (of nuclide B_X)	$m_a(B_X)$	g
atomic number of species X	$Z(X), Z_X$	1
Avogadro constant	N_A	mol^{-1}
Boltzmann constant	k	J K^{-1}
capacitance	C	F
charge density	ρ	C m^{-3}
conductance (electrical)	G	$\text{S} \cong \Omega^{-1}$
current density	j	A m^{-2}
electric current	I	A
electric field strength	E	V m^{-1}
electron current density	J	A m^{-2}
electron mass	m_e	g
electron temperature	T_e	K
elementary charge	e	C
energy	E	J
excitation energy	E_{exc}	J, ev
excitation energy of state q of species X	$(E_q)_X$	J, ev
excitation potential	V_{exc}	V
excitation temperature	T_{exc}	K
flow rate	ρ	$\text{Pa m}^3 \text{s}^{-1}$
frequency (electrical)	f	Hz
frequency (in optical spectroscopy)	ν	Hz
frequency of spectral line emitted due to transition $u \rightarrow l$	ν_{ul}	Hz
gas constant	R	$\text{J K}^{-1} \text{mol}^{-1}$
gas temperature	T_g	K

Term	Symbol	Practical Unit*
inductance	L	H
ionization energy	E_{ion}, E_i	J, eV
ionization potential	$V_{\text{ion},i}$	V
ionization temperature	T_{ion}	K
irradiance	E	W cm^{-2}
kinetic energy of particle	E_{kin}	J, eV
magnetic flux	ϕ	Wb
magnetic flux density	B	T
mass	m	kg
metastable excitation potential	V_{meta}	V
number of particles	N	l
number of particles of species X	$N(X), N_X$	l
number density: (number of particles per unit volume)	n	cm^{-3}
number density of particles in state q	n_q	cm^{-3}
number density of element as free atom	n_{at}	cm^{-3}
number density of element as free ion	n_{ion}	cm^{-3}
number density of electrons	n_e	cm^{-3}
number density, <i>total</i> , of element in different forms (atom, ion, molecule) in the gaseous state	n_t	cm^{-3}
number density of ground state species	X_0	cm^{-3}
number density: n_{at} for atoms of X	$X, n_{\text{at}}(X)$	cm^{-3}
number density: n_{ion} for ions of X^+	$X^+, n_{\text{ion}}(X)$	cm^{-3}
number density: n_t for element X	$X_t, n_t(X)$	cm^{-3}
number density of excited species X^*	X^*	cm^{-3}
number of oscillations	P	l
oscillator strength for absorptions by transitions from states $l \rightarrow U$ (lower \rightarrow upper)	f_{lU}	l
partial pressure	P	Pa
partial pressure of species X	$p(X), p_X$	Pa
partition function	Z	l
partition function of species X	$Z(X), Z_X$	l
period	τ	s

Term	Symbol	Practical Unit*
Planck constant	h	J s
potential difference	U	V
power	P	W
quantity of electricity	Q	C
radiant energy density	u	J cm ⁻³
radiant intensity	I_e	W sr ⁻¹
radiant power	ϕ	W
reactance	X	Ω
re-ignition potential	U_z	V
relative intensity of spectral line emitted by transitions from state u→l	I_{ul}	l
spark duration	θ	s
spark gap potential	U_g	V
spectral radiance	L_λ	W cm ⁻² nm ⁻¹ sr ⁻¹
sputtering rate	q_{sp}	g s ⁻¹
sputtering yield (number of atoms sputtered per incident ion)	S_{sp}	l
statistical weight of state q	g_q	l
statistical weight of ground state	g_o	l
statistical weight of state q of species X	$g_q(X), (g_q)_X$	l
thermodynamic (absolute) temperature	T	K
time	t	s
total gas pressure	p, p_t	Pa
transition probability for absorption (by transition from l to u state)	B_{lu}	s ⁻¹ J ⁻¹ cm ³ nm
transition probability for spontaneous photon emission (by transition from u to l state)	A_{ul}	s ⁻¹
wavelength	λ	nm
wavenumber	$\tilde{\nu}, \delta^{**}$	cm ⁻¹
work function	ϕ	V

* Practical units are decimal multiples or fractions of SI units

** $\tilde{\nu}$ is only used for $\nu/c = 1/\lambda$ in vacuum

10.3.1.1.2 Pressure effects

The pressure within a plasma influences the characteristics of the radiation, in that it affects the *mean free path* of the particles and their *collisional cross-sections* and the number of collisions per unit of time.

Sources may broadly be classified into 4 different groups, depending on the average gas pressure at which they operate, viz.

- Low pressure (<10 kPa)
- Medium pressure (10-100 kPa)
- Atmospheric pressure (~100 kPa)
- High pressure (>100 kPa)

10.3.1.1.3 Collisional processes

A particle (atom or molecule) characterized by its collisional cross-section can undergo a change in its state of excitation as a result of collisional processes with other particles. In an *elastic collision*, an exchange only of kinetic energy takes place between the colliding species; in an *inelastic collision* there is an interchange between the kinetic energy and internal energy of the particle.

In *quenching*, a particle in an excited state may lose its energy by *collisional de-excitation*.

Energy transfer from a particle in a higher state to one in a lower state may occur. A *metastable state* (level) is any excited state which, in principle, by virtue of the selection rules, cannot radiatively combine with any lower state. These metastable states usually have considerably longer lifetimes than ordinary excited states.

10.3.1.1.4 Radiative processes

The change in the internal energy of a particle may also be due to *radiative processes*, i.e., the emission or absorption of a photon. A particle in an excited state may undergo a transition to a lower energy level by emission of a photon. This is known as *radiative de-excitation*. If such a transition occurs spontaneously, its probability per second for a given excited particle is termed the *transition probability for spontaneous emission*.

A particle in the *ground state* or an excited state may undergo a transition to a higher energy level by *absorption* of a photon. This is known as *radiative excitation*. For a given particle in the lower state, the probability per second of such a transition in a field with a continuous spectrum is proportional to the *spectral radiant energy density* of the field at the wavelength of the absorption line. The proportionality constant is termed the *transition probability for absorption*.

The *transition probability for stimulated emission* is defined in a similar way for the reverse radiative de-excitation process that is induced by the same radiation field.

The *oscillator strength* for absorption is often used instead of the transition probability for the (reverse) spontaneous emission process to which it is proportional. (Note: oscillator strength is the historical term relating to the Rutherford atomic model.)

Atomic fluorescence is a combined process of photon absorption by an atom followed by spontaneous photon emission.