SPECTROSCOPIC METHODS OF MEASUREMENT OF HIGH TEMPERATURES*

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ABSTRACT

Spectroscopic methods of measurement of high temperatures are reviewed briefly. They refer mostly to line intensities, line widths and line profiles.

Introduction

In recent years there has been much progress in the production and measurement of high temperatures in laboratory experiments. Temperatures in the range of tens of thousands of degrees Kelvin have been attained with arcs, sparks, exploding wires and shock waves.[1] Much higher temperatures, of the order of 10^6 degrees, have been reported in experiments with high power pulsed discharges.[2] Besides the utility of very high temperatures above tens of millions of degrees for the production of thermonuclear fusion reactions and power, even the attainment of lower temperatures is important for an understanding and evaluation of such physical quantities as transition probabilities, collision cross sections, interionic fields and plasma properties. Naturally much significance is attached to the measurement of the high temperatures reached in the laboratory.

No known material probe can withstand temperatures beyond a few thousand degrees. However, since all hot substances emit and absorb radiation, spectroscopy may be employed, as in experimental astrophysics, for the investigation of the physical properties of the radiating system, if necessary, from a safe stand-off distance. Time-resolved spectra permit the study of transient high temperature phenomena. Stigmatic spectroscopic analysis allows for the fixing of temperatures for a spatial temperature gradient. An obvious advantage of spectroscopy as a diagnostic tool in high temperature research is that it provides a probe which does not perturb the thermal state of the system under observation.

From the intensities of relatively sharp spectral lines, from the widths and profiles of broadened lines, from the apparent shift in the position of the series limit, and from the intensity distribution in the continuum, it is possible to derive meaningful temperatures. Actually temperature is defined only for a system in thermal equilibrium. If a system of weakly interacting particles is assigned a temperature T, it means that the velocity distribution of the atoms,

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[1] An excellent review of the work up to 1957 is given by W. Lochte-Holtgreven in *Reports on Progress in Physics*, 21, 312 (1958).

[2] See, for instance, *Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy*, Geneva (1958), Vol. 31 and 32.

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ions and electrons, and the distribution of population in the possible states of excitation and ionization correspond exactly to this temperature. In effect, the distribution of energy within such a system would be subject to Maxwell-Boltzmann laws.[3] If there is thermal equilibrium between matter and radiation, the emission from the system is subject to Planck's black body law. An isolated hot system in an ideal state of thermal equilibrium is a theoretical concept and not a practical possibility, for such a system should not lose energy to the surroundings.[4] What is realized in practice is some kind of a stationary state maintained by a constant supply of energy to compensate for a number of inevitable energy losses. The faster the internal energy sharing processes relative to those tending to change the distribution by energy losses, the nearer will the system tend to thermal equilibrium. Normally, equilibrium distribution is established by collisions. The smaller the collision frequency, the greater, therefore, is the deviation from thermal equilibrium. For instance, in a plasma, the electrons may be subject to accelerating fields and will thus have an energy of diffusion superimposed on the energy of thermal motion. Because of the relatively slow degradation of the surplus energy of the electrons in elastic collisions with atoms, the electron temperature, characteristic of the mean kinetic energy of the electrons, would be greater than the gas kinetic temperature. At atmospheric and higher pressures the mean free paths are small and a near-equilibrium situation may be realized.* At low pressures where collisions are few the difference in the electron and gas temperatures would be appreciable. The more would be the difference, the greater the accelerating field strength. One may, however, assign different temperatures to the electrons and gas particles separately, although they coexist in the same space, provided an equilibrium type distribution of energy obtains within each class of particles. Also, in the absence of thermal equilibrium, if only certain degrees of freedom of the gas particles have a Boltzmann distribution of energy, a temperature may be measured and interpreted as rotational, vibrational or electronic excitation temperature or as a translation temperature, depending on the particular spectroscopic phenomenonal employed for its determination. It should not then be surprising even if there is no correspondence between any two such measured temperatures. If the system is in a state of thermal equilibrium the same value for the temperature should be obtained whatever the spectroscopic technique employed for its determination.

In the following, some of the spectroscopic methods of measurement of high temperatures are briefly reviewed.

Excitation temperatures

Excitation temperatures determine the population of the different excited states and are determined from line intensity measurements.

The intensity $I_{m'm''}$ of a spectral line in emission is defined as the energy emitted by the source per second. For a low density, optically thin layer of gas wherein self-absorption is negligible, the observed intensity is proportional to

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[3] For a definition of temperature see, for example, K. F. Herzfeld, *Temperature*, Vol. 2 (Editor: Hugh C. Wolfe, Reinhold Publishing Corporation, New York, 1955), p. 233; see, also, in the same volume, Hugh C. Wolfe, p.3.

[4] For a critical discussion of the topic see, for example, R. C. Tolman, *The Principles of Statistical Mechanics* (Oxford University Press, London, 1938).

*At higher temperatures, increasing ionization also favours higher collision frequency.

the number $(N_{m'})$ of atoms (or molecules) in the initial state m' of energy $E_{m'}$ and the Einstein transition probability for spontaneous emission* $(A_{m'm''})$ to the final state m''.

$$I_{m'm''} \propto N_{m'} A_{m'm''} hc\nu_{m'm''} \quad .. \quad .. \quad .. \quad .. \quad (1)$$

where, $\nu_{m'm''}$ is the wave number of the emitted light quantum. For a Boltzman distribution of energy among the different excited states at an 'excitation temperature' T, we have

$$N_{m'} = N_o \frac{g_{m'}}{Q(T)} exp\left(- E_{m'}/kT \right), \quad .. \quad .. \quad (2)$$

where N_o is the total number of atoms in the source, $g_{m'}$ is the statistical weight of the state m' and $Q(T)$ is the partition function at temperature T. Combining equations (1) and (2) we have the relationship between intensity and temperature

$$I_{m'm''} = CN_o \frac{a_{m'm''} \, g_{m'}}{Q(T)} \nu^4_{m'm''} \, exp\left(- E_{m'}/kT \right), \quad (3)$$

where C is a constant depending on the units of energy, the geometry of the optical system and the efficiency of the spectrograph and recorder.

Using equation (3) temperature can be derived, in principle, from absolute intensity measurements. The constant C, however, is usually indeterminate and N_o unknown. It would be easier to evaluate the temperature from the ratio of the intensities of two lines. For lines chosen in the same wavelength region, the instrumental response characteristics being the same, the factor C is eliminated in the ratio. And, for lines emitted by the same element and in the same state of ionization, the factors N_o and $Q(T)$ are eliminated in the ratio. We may then write, for the ratio of intensities,

$$\frac{I_{m'm''}}{I_{n'n''}} = \frac{a_{m'm''} \, g_{m'}}{a_{n'n''} \, g_{n'}} \left(\frac{\nu_{m'm''}}{\nu_{n'n''}} \right)^4 exp\left[(E_{n'} - E_{m'})/kT \right] \quad (4)$$

If, therefore, the relative transition probabilities are known either from theory or from experiment, the excitation temperature T can be calculated using equation (4).†

It is relevant to assess the accuracy of this method and consider the criteria for the choice of a line pair for an accurate evaluation of temperature. According to equation (4), the relative uncertainty $\left(\frac{\Delta T}{T}\right)$ in temperature due to a

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$$* \; A_{m'm''} = a_{m'm''} \nu^3_{m'm''} = \frac{64}{3} . \frac{\pi^4}{h} \left| R_{m'm''} \right|^2 \nu^3_{m'm''}$$

where $R_{m'm''}$ is the matrix element for the transition.

†In practice it is convenient to measure the peak intensities of spectral lines rather than their integrated intensities. However, for Doppler-broadened lines the total intensity I_o is related to the peak intensity I_{max} by

$$I_{max} = \frac{I_0}{\sqrt{\pi}} \; \frac{1}{\alpha\nu}$$

where α is the most probable speed of the atoms at temperature T. If peak intensities of Doppler broadened lines are compared one has to replace ν^4 by ν^3 in equation (4). See, also, S.S. Penner, *J. Chem. Phys.*, 20, 507 (1952).

relative uncertainty $\left(\frac{\Delta R}{R}\right)$ in the observed intensity ratio $R = \left(\frac{I_{m'm''}}{I_{n'n''}}\right)$ is given by

$$\frac{\Delta R}{R} = B\ \frac{\Delta T}{T}\ ;\ B = \frac{E_{m'} - E_{n'}}{kT} = \frac{\Delta E}{kT} \quad .. \quad (5)$$

For $B \gg 1$, the accuracy of temperature measurement would be comparable to or better than the accuracy of measurement of the intensity ratio. For lines in the visible region ΔE can be as large as 10ev ($\approx 10^5$deg K) so that temperatures up to 10^5 deg. K can be evaluated with the above method to the same accuracy as that obtained in the intensity measurements. The error in R is determined by the probable errors in the measurement of individual line intensities and would be minimum if lines of near-equal intensity in the same wavelength region are chosen. Although a large ΔE is favourable for higher accuracy in temperature evaluation, the line from the higher initial level would be too weak for observation unless a high transition probability compensates for the small Boltzmann factor.

The above set of equations also holds good in the case of molecules for the rotational, vibrational and electronic transitions. At temperatures beyond, say, 10,000 deg. K molecules are dissociated and band spectra, if observed, must have arisen from molecules in the relatively cooler parts of the light source. Spectrographs of high resolving power and large dispersion are required for the measurement of rotational and vibrational temperatures[5].

It has been assumed that in an optically thin source the intensity of the spectral line is proportional to the number of emitting atoms in the line of sight. If I_o were the intensity of a line in an optically thin source of thickness x, in a slightly thicker source of thickness f times x the intensity of the same line should be fI_o. But with increasing thickness, even in a homogeneous layer of uniform temperature, self-absorption sets in and the observed line intensity I would be given, to a first approximation, by the exponential relationship

$$I = f\,I_o\, exp\,(-K\nu fx) \quad .. \quad .. \quad .. \quad .. \quad (6)$$

where $K\nu fx$ is the optical thickness, a product of the line absorption coefficient $K\nu$ and the geometrical thickness fx. If we take $K\nu$ proportional to the transition probability we may rewrite equation (6) as

$$log\ \frac{I}{I_o} = log\,f - C_1\, A_{m'm''}{}^{x} \quad .. \quad .. \quad .. \quad (7)$$

where C_1 is a constant which includes f. It is obvious from equation (7) that stronger lines with greater transition probabilities would be weakened more than the weaker lines, in an optically thick source. If one wishes to measure temperatures from line intensities it is then necessary to make a correction for self-absorption to obtain fI_o from the observed I. For moderate optical thicknesses the following procedure, applicable to lines with a multiplet structure, has been suggested.[6]

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[5] For a discussion of rotational and vibrational temperatures see, for instance, H. P Broida, *Temperature*, Vol. 2 (Editor :Hugh C. Wolfe, Reinhold Publishing Corporation, New York, 1955), p. 265; see, also, R. C. Johnson, *An Introduction to Molecular Spectra* (Methuen & Co. Ltd., London, 1949).

[6] G. H. Dieke, *Temperature*, Vol. 2 (Editor: Hugh C. Wolfe, Reinhold Publishing Corporation, New York, 1955), p. 19. See, also, A. Unsöld, *Physik der Sternatmospharen* (Springer-Verlag, Berlin, 1955), pp. 288, 306.

The relative intensities of the components of a multiplet, since their initial levels have nearly the same energy, would be proportional to their transition probabilities and, at any temperature T, be independent of the exponential factor in equation (3). For any one component we may write

$$I_o = C_2 A_{m'm''} x \quad \cdots \quad (8)$$

Combining equations (7) and (8), we have

$$\log \frac{I}{I_\circ} = \log f - CI_\circ$$

$$\text{or } \log \frac{I}{I_\circ} = \log f - C \exp [\, \mathit{loq}\, I_o \,] \quad \cdots \quad (9)$$

When the exponential factor in equation (9) is negligible, the observed intensity I is equal to the actual intensity FI_o . Thus components of the multiplet, for which self-absorption is negligible, would correspond to points on the horizontal part of a plot of $\log \frac{I}{I_o}$ *vs.* $\log I_o$ for the different components. For the stronger components, f and c can be solved for from any two measurements and the actual intensities evaluated. The components of the same multiplet are obviously not suitable for temperature evaluation from line intensity ratios. It is necessary to compare the intensities of a pair of lines belonging to two different multiplets, after corrections for self-absorption are made.

Optically thick sources

It would be interesting to study the variation in intensity of a spectral line with either increasing density or increasing geometrical depth of the emitting layer at a uniform steady temperature. According to equation (3) which is valid only for optically thin sources, the intensity increases in proportion to thickness (or density or N_o). However, as self-absorption becomes more and more appreciable with increasing thickness, the intensity increases at a slower rate, and when the layer is sufficiently optically thick reaches an asymptotic value. At this stage we will be approaching the conditions of black body radiation for the emitted spectral line.[7] (Actually, every isothermal gas should emit a continuous spectrum due to free-free and free-bound transitions since there is always some ionization, however small, in a thermally excited gas. It is only for very large thicknesses of the emitting layer that this continuum attains the Planck distribution for black body radiation.) For gas layers which are not optically very thick, only the discrete spectral lines show a near Planckian distribution in the central parts of their intensity profiles; for other spectral regions the layers may be considered as optically thin. From the measurements of absolute intensity in such profiles it is possible to derive, using Planck's law, the temperature of the source.[8]

It may be noted that, the higher the pressure and temperature and the lower the ionization potential, the smaller would be the thickness at which the emission approaches black body radiation. When the radiating mass is very

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[7] For an answer to 'How is a discrete line spectrum converted into a continuous black body spectrum?', see W. Finkelnburg, *J. Opt. Soc. Am.*, **39**, 185 (1949).

[8] In this connection it may be interesting to refer to the measurement of temperatures in flames and hot gases using the line reversal method based on Kirchhoff's and Planck's laws. See, for instance, H. P. Broida (ref. 5).

dense the continuous emission corresponds to black radiation. Using Planck's and associated laws, one can then measure the 'effective', 'brightness' and 'color' temperatures, familiar in astrophysics.[5],[6]

If there is a temperature gradient in the line of observation there would be absorption in the centre of emitted lines. Detailed analysis would be required to evaluate temperatures and assign them to the proper spatial elements of the gas.[9,10] Often, however, this is not possible. In case of absorption in the continuum, when a relatively thin cool layer envelopes the hot interior emitting black body radiation, 'curves of growth' may be constructed from the absorption profiles of different lines, preferably multiplets, and used to determine the temperature of the cooler layer.[11] The temperature of the hot interior may be obtained from intensity measurements in the nearby continuum. For a very high temperature system such as the fireball in an atomic explosion the measured 'temperatures' have to be carefully interpreted in view of the non-homogeneity of the system.[12]

Let us now consider the variation in intensity of a spectral line with increasing temperature. According to equations (1) and(2) this means that we have to consider, in effect, the variation with temperature in the population of the initial level involved in the transition giving rise to the spectral line. Equation (2) indicates that two opposing influences govern the intensity with increase of temperature, *viz*, the increase in the value of the exponential function and a simultaneous decrease, due to ionization, in N_o . The intensity, therefore, rises at first in a steep manner, then more slowly and finally falls off rather gradually. The maximum intensity occurs when the two opposing influences balance each other and the temperature at which this happens can be calculated. For lines of different elements and in different states of ionization the temperatures at which intensity maxima occur are quite apart. For example, the maximum intensities for the lines H_β ,$O^+ \lambda = 4651$ A *and* $O^{++} \lambda = 3447$A occur, respectively, at temperatures of about 14,600, 32,000 and 51,000 deg. K.[13] It is clear that for the evaluation of high temperatures from intensity measurements suitable lines belonging to different elements in proper states of ionization have to be chosen, depending on the region of temperatures involved. The intensity *vs*. temperature curve is, however, nearly flat around the maximum, sometimes over as large an interval as 20 per cent of the temperature of maximum intensity. Beyond the maximum, as is already hinted, the intensity is not as sensitive to temperature variation as it is before the maximum is reached. Hence, only those lines that have a rising intensity slope in the region of temperature to be measured are the most suitable for use as 'thermometer' lines.

It may be recalled that the classification of stars into spectral sequences in astrophysics is based on this phenomenon of variation of spectral line intensities with temperature.

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[9] H. Bartels, *Z. Phys.*, 125, 598 (1949); *ibid*, 127, 243 (1950); *ibid*, 128, 546 (1950).

[10] W. Going, *Z. Phys.*, 131, 603 (1951).

[11] See, for instance, L. H. Aller, *Astrophysics* (Editor: J. A. Hynek, McGraw-Hill Book Co. Inc., 1951), p. 29.

[12] For a critical discussion of temperatures in atomic explosions, see F. G. Brickwedde, *Temperature*, Vol. 2 (Editor: Hugh C. Wolfe, Reinhold Publishing Corp., New York, 1955), p. 395

[13] F. Burhorn, H. Maecker and Th. Peters, *Z. Phys.*, 131, 28 (1951). This paper also discusses the shift in the temperature of intensity maximum for Stark-broadened lines.

This phenomenon can also be utilized in determining high temperature in a nonhomogeneous source of cylindrical geometry wherein, due to a radia, temperature gradient, the temperature is maximum along the axis of symmetry If such a source is viewed end on with a stigmatic spectrograph, each point along the length of a spectral line would be the result of light received from a definite point along a diameter of the source and there is a point to point correspondence between the intensity *along the length* of the spectral line and the temperature across the source. If a photometric record reveals intensity maxima occurring towards either end of the spectral line—the intensity distribution is symmetric about the centre of the line—their positions on the line permit a direct assignment of the temperature (of maximum intensity) to a corresponding cylindrical 'zone' in the source. Correlating details of the photometric analysis with known data relating intensity and temperature, the temperature distribution within the source may be mapped in detail [14,15].

Similarly, variation of temperature with time in high temperature transient discharges can be studied. If high time-resolution techniques are employed, lines of different elements are seen to attain maximum intensities at different times indicating the attainment of corresponding temperatures (of maximum intensity) in the source.[1]

Gas kinetic temperatures

Gas kinetic temperatures are indicative of the mean kinetic energy of the gas particles and can be determined from Doppler broadening of spectral lines.

Before discussing Doppler effect, it is pertinent to mention here briefly the important intrinsic causes of line broadening. Broadly speaking, they are: Natural broadening (or radiation damping), a consequence of the finite width of the energy levels; Doppler broadening, arising from the random motions of the atoms; Pressure broadening (including collision damping), due to impacts between the radiating atoms and neighbouring neutral atoms; and Stark broadening, a result of the perturbation of the radiating atoms by the fluctuating fields of nearby charged particles.

The velocity distribution of the gas particles, the ion and electron densities and the pressure of a gas are functions of temperature and, therefore, the nature and extent of intensity distribution in broadened spectral lines, expressible in terms of intensity profiles and half-intensity widths, provide valuable clues to the temperature of the emitting source.

Apart from line broadening due to the above causes, there may be line shifts due to gross mass motion of the radiating gas, and Stark and Zeeman splittings due to externally applied electric and magnetic fields. Their study is useful in estimating the drift velocity and the external perturbing fields.

The different causes of line broadening may not act singly and the disentangling of the effects due to various causes in an observed broadened line poses

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[14] See, for instance, H. Maecker, *Z. Phys.*, 136, 119 (1953).

[15] Since light from a smaller volume is received from the edges of the source rather than from its centre one must correct the observed intensity distribution from the centre of the line to the edge for the geometry of the source. Details needed for making this correction are discussed by W. J. Pearse, *Conference on Extremely High Temperatures* (John Wiley & Sons, Inc., New York 1958). See, also, Meek and Craggs, *Electrical Breakdown of Gases* (Oxford) University Press, London, 1953), p. 400.

difficult problems. However, experimental conditions may be such, or so chosen, that the effects of all other causes of line broadening except the one under consideration are either negligible or easily calculable.

Quantitatively, the Doppler shift ($\Delta\lambda$) of the emitted radiation due to the motion of an emitting atom relative to the observer with a velocity v is given by

$$\Delta\lambda = \frac{v}{c}\lambda_o \quad .. \quad .. \quad .. \quad .. \quad .. \qquad (10)$$

where λ_o is the wavelength emitted when the atom is stationary and c is the velocity of light. Since the observed spectral line is a composite of radiation received from many atoms, it would appear broadened for a random distribution of velocities of the emitting atoms. For a Maxwellian distribution of velocities in the source at absolute temperature T, the observed line intensity profile is given by the Gaussian expression

$$I_\lambda = I_{max} \, exp\left[-\frac{mc^2}{2kT}\left(\frac{\Delta\lambda}{\lambda_o}\right)^2\right] \quad .. \quad .. \qquad (11)$$

where m is the atomic weight of the radiating atom.

It is seen that pure Doppler broadening gives a bell-shaped profile to an otherwise monochromatic (sharp) line. The half-intensity width, or the width of the line between the two points at which the intensity is half its maximum value, is given by

$$\Delta\lambda_D = 7{\cdot}2 \times 10^{-7} \lambda_o \, (T/m)^{1/2} \quad .. \quad .. \quad .. \qquad (12)$$

From measurements of the half-intensity widths for Doppler-broadened lines it is, therefore, possible to determine the temperature T.

Except at low pressures, pressure broadening, especially for resonance lines, becomes considerable. Low pressure sources with negligible self-absorption are therefore preferred for Doppler width measurements. (At very low pressures, however, the translational equilibrium may not be attained and the line intensities may be very weak). Again, pressure broadening, which results essentially from the polarization of atoms when other atoms approach them closely, is more for the higher members of a spectral series than for the lower members involving more tightly bound energy states. This fact has to be borne in mind in the proper choice of a line for Doppler width measurements.

It is obvious from equation (12) that the Doppler half-width would be greater for lighter elements and for higher temperatures. Even so, it is in general small. For example, for H_β line at 10,000 deg. K, $\Delta\lambda_D = 0{\cdot}35$A. Isntruments of high resolving power and dispersion are usually necessary to determine the contour of the Doppler-broadened line.* The separation of the instru-

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*It may be interesting to note here that, for work in very high resolution interferometric spectroscopy, a low temperature, low pressure source is needed to avoid Doppler and pressure broadenings.

mental profile from the observed profile to obtain the Doppler profile is a laborious process and limits the accuracy of measurements.[16]

Doppler broadening of spectral lines has been most useful for estimating the high temperatures reached in thermonuclear plasmas. Temperatures of the order of a few million degrees have been determined from the Doppler half-widths of lines emitted by impurity atoms present in a deuterium plasma in experiments with ZETA[17] at Harwell and SCEPTRE[18] at Aldermaston in the U.K. At the temperatures attained in these systems, deuterium atoms are completely ionized so that no light is emitted by them. But from the lines emitted by the multiply ionized impurity atoms* (N IV, O IV, O V) it was possible to estimate the temperatures with an error of about 20 per cent. Though the Doppler method is simple in principle, its success depends on various factors, not the least of which is the high competence and skill of the worker in identifying and choosing the lines, in the proper choice of equipment, in a proper appreciation of the possible conditions obtained inside the source, etc.

Ionization temperatures

Ionization temperature defines the distribution of atoms in the various stages of ionization in a thermally excited gas. Since ions have an effect on line broadening, the latter phenomenon may be employed for the determination of ion concentration and, in turn, the temperature. Interactions between the radiating atoms and the force fields of neighbouring particles lead to broadening of the emitted spectral line. Two types of broadening are often distinguished: 'impact' and 'statistical'. In impact broadening it is assumed that the energy levels of the radiating atom are perturbed by collisions with particles moving at such high speeds that a momentary phase change is introduced in the emitted wave train only during the short period of collision. A Fourier analysis shows that this is equivalent to broadening of the spectral line. Since the perturbations are assumed to be sudden, the impact theory describes lines at high temperatures and low densities and contributes to broadening near the line centre. This theory leads to a dispersion type line profile and, in favourable cases, the electron density may be computed from measurements of line widths[4]. In statistical broadening it is assumed that the radiating atom is continuously in the field of its neighbours which move so slowly that they may be considered stationary, the perturbation depending on the probability of locating the perturbers at different distances from the emitter. The radiated frequency is then represented as a probability distribution about some mean value. The statistical theory is valid for heavy, slow moving ions, *i.e.* at high densities and low tem-

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[16] See, for instance, A. G. Gaydon and H. G. Wolfhard, *Proc. Roy. Soc. A*. 199, 89 (1949); and T. P. Hughes and R. V. Williams, *Hilger Journal*, 5, 19 (1958).

The separation of the Doppler profile from the apparatus profile is carried out by an approximate method involving Voigt functions, See, for instance, Mitchell & Zemansky, *Resonance Radiation and Excited Atoms* (Cambridge University Press, London, 1934) p. 99; Van de Hulst and Reesinck, *Astrophys. J.*, 106, 121 (1947); D.W. Posener, *Australian J. Phys.*, 12, 184 (1959) and N. H. Olsen and W. S. Huxford, *Phys., Rev.*, 87, 922 (1952).

[17] G. N. Harding *et al.* (ref. 2, vol. 32), p. 365; E. P. Butt *et al.*, (*ibid.* vol 32), p. 42.

[18] T. P. Hughes and R. V. Williams (ref. same as in 16).

*For a fusion reactor working at temperatures of the order of a hundred million degrees, not only are the impurity atoms undesirable for the success of the reactor but also, at such high temperatures, they may be totally ionized; it would then be not possible for spectroscopic investigations to be made on the system.

peratures, and it accounts mostly for the broadening in the wings of the lines. The two theories, although they refer to two different models, are limiting instances of a more general theory.[19]

Line broadening due to perturbations of charged particles on a radiating atom whose energy levels snow a linear Stark effect is of particular interest in temperature measurement. Hydrogen and hydrogen-like atoms exhibit a large linear Stark effect due to interionic fields which can be as high as a hundred thousand volts per centimeter in a plasma at a temperature of the order of 10^4 deg. K. Since the ions are in incessant random motion, the electric fields are non-uniform and fluctuating. In the statistical theory of Holtsmark[19] the probability that a radiating atom experiences a field β is given by

$$W(\beta)=\begin{cases} \dfrac{4}{3\pi}\beta^2\left[1-0.4628\beta^2+0.1227\beta^4-0\cdot02325\beta^6+\ldots.\right], & 0<\beta<1\cdot7 \\ \dfrac{2\cdot350}{\pi\beta^{5/2}}\left[1+\dfrac{5.106}{\beta^{3/2}}-\dfrac{7.4375}{\beta^3}+\dfrac{0\cdot1}{\beta^{9/2}}-\ldots\ldots\ldots.\right], & 1\cdot7<\beta<\infty \end{cases} \quad \ldots \quad (13)$$

where β is taken for convenience as the ratio of the random field E and the 'average' or 'normal' field E_o which is given by

$$E_o=2\cdot61\ Z\,e\,n_i^{2/3} \quad \ldots \quad (14)$$

where n_i is the number density of perturbing ions. In a field E, the linear Stark effect for the k th component of the spectral line is given by

$$\triangle\lambda = C_k E = C_k\beta E_o$$

$$\text{or} \quad \frac{\triangle\lambda}{E_o} = \alpha = C_k\beta \quad \ldots \quad (15)$$

where C_k is the Stark coefficient of the k th component and α may be considered as the Stark shift corresponding to the field β Using this relation, a plot of $W(\beta)$ *vs.* β can be easily converted into a plot of $W(\alpha)$ *vs.* α, giving the probability that the k th component occurs at a distance $\alpha\left(=\dfrac{\triangle\lambda}{E_o}\right)$ from the line centre. In effect, the plot gives the relative intensity distribution of the line at various distances α from the line centre. To obtain the theoretical intensity profile for the Stark-broadened line, the Holtsmark profiles of all the component lines have to be added up after weighting them for their relative intensities. The observed profile, on the other hand, is a plot of intensity *vs.* $\triangle\lambda$ from the line centre. By fitting the theoretical contour with the observed contour, E_o is evaluated[20] and, in turn, using equation (14) n_i is determined.

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[19] For a comprehensive discussion of these two theories, their limitations and improvements, see H. Margenau and M. Lewis, *Revs. Modern Phys.* 31, 569 (1959).

[20] An ingenious procedure for the curve-fitting, which is not such an obvious matter, is adopted by P. J. Dickerman, *Conference on Extremely High Temperatures* (John Wiley & Sons, New York, 1958), p. 77. In his paper, Dickerman reports on the experimental determination of the equilibrium temperature of a plasma from the Stark broadening of H_β and H_γ lines. See also, N. H. Olsen and W. S. Huxford, *Phys. Rev.* 87, 922 (1952).

This method of evaluating n_i is fairly accurate but is limited to the study of the lower Balmer and He$^+$ lines which show linear Stark effect. For Hβ the breadth varies from 0·0006A to 130A for n_i varying from 10^{10} to 10^{18} per cm^3. An advantage of this method is that hydrogen is present in almost every flame or electrical discharge or a small amount of it may be introduced into the system. The Holtsmark theory, however, neglects perturbations other than those due to ions. The effect of electrons, at densities greater than about 10^{16} per cm^3, becomes considerable in the wings of the lines and discrepancies between the simple Holtsmark profile and the observed line contour become appreciable.* In such a case, for an asymptotic fit, the number of perturbing particles is taken to be $2\, n_i$ $(=n_i + n^{\cdot})$ instead of n_i.

Another aspect of Stark broadening, leading to the determination of the number density of perturbing particles, relates to the apparent shift of the Balmer series limit to longer wavelengths. Due to interionic Stark effect the higher members of the Balmer series, and in general lines emitted from highly excited states of atoms or ions within a plasma, are broadened and at the convergence limit of the series may no longer be distinguishable as discrete lines due to merging of the broadened states.[21] This amounts to extension of the series limit continuum to longer wavelengths and lowering of the ionization potential. For the highest energy level that is discernible the most probable Stark shift for its extreme component will be just less than half the interval between it and its neighbouring energy level. This condition leads to the Inglis-Teller relation

$$\log_{10} N = 23\cdot16 - 7\cdot5 \log_{10} n_{max} \qquad .. \qquad .. \qquad (16)$$

between N, the number density of perturbers, and n_{max}, the quantum number of the initial level of the last resolvable line at the continuum limit. At high temperatures the electrons move too rapidly to contribute to line broadening near the centre of the line so that N may be taken as equal to n_i. But the contribution of the electrons would be appreciable if the 'statistical frequency limit'[22] for electron broadening occurs closer to the line centre, within half the frequency interval between neighbouring lines at the series limit. This leads to a critical temperature[19] ($T = 5 \times 10^5/n_{max}$) below which the effects of ions and electrons are treated as additive, *i.e.* $N=n_i + n = 2n_e$. So far as equation (16) is concerned, the uncertainty in the value of N by a factor 2 hardly matters, since the number on the right side of the equation, 23·16, is hardly certain to within the amount $\log_{10} 2$ $(=0\cdot3)$. A slightly modified Inglis-Teller formula

$$\log_{10} N = 23\cdot46 - 7\cdot5 \log_{10} n_{max} \qquad .. \qquad .. \qquad (17)$$

seems to give better agreement with experimental results.[1]

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*For a discussion of theoretical and experimental limitations of Holtsmark theory see references (1) and (19). See, also, H. Griem, *Conference on Extremely High Temperatures* (John Wiley & Sons, Inc., New York, 1958), p. 93.

[21] See, for instance, W. Finkelnburg and Th. Peters, *Handbuch der Physik* (Springer-Verlag, Berlin, 1957), Vol. XXVIII, p. 79.

[22] A. Unsöld (see ref. 6). See, also, references (1) and (19).

Since the higher terms of any element are hydrogen-like, similar effects near the series limits of He + and Mg + have been observed.[23,1] The electron densities, calculated from the Inglis-Teller formula, are expected to be correct within a factor of 2.

When n_i has been determined it is a relatively simple matter to find T from the Saha ionization equation

$$\frac{n_i \; n_e}{n_o} = \frac{2Q_i \; (T)}{Q_o \; (T)} \cdot \frac{(2\pi m_e \; kT)^{3/2}}{h^3} exp \left[- \frac{I - \Delta I}{kT} \right] \qquad (18)$$

where n_i and n_e are the number densities of ions and electrons respectively, n_o is the number density of neutral atoms, Q_i and Q_o refer, respectively, to the partition functions for ions and neutral atoms, and I is the ionization potential of the neutral atom while ΔI, the correction for the lowering of the ionization potential in the presence of ions, is given by[24]

$$\Delta I = 7 \cdot 0 \times 10^{-7} n_e^{1/3} \text{ volt} \quad .. \quad .. \qquad (19)$$

In this equation n_i, n_e and n_o have first to be evaluated. The charge equilibrium condition gives the relation $n_i = n_e$. For a gas at known pressure (or total number of particles N per cm^3), Dalton's law of partial pressures gives $N = n_i + n_e + n_o$. Since n_i is known from experimental determination, the above relations* permit the computation of T.

Electron temperatures

Electron temperature is a measure of the average kinetic energy of the electrons in a hot plasma and may be determined, in principle, from electron recombination spectra, provided a reliable theory of continuous spectra is available.†

The series limit continua in emission arise from recombination of free electrons with positive ions to form neutral atoms or ions of smaller positive charge. When an electron is captured by an atom, the kinetic energy of the electron plus the binding energy (Eg) of the electron in the excited final state in which the electron finds itself on capture is emitted as a quantum of radiation. The capture of a large number of electrons with different velocities (in thermal equilibrium, Maxwellian distribution of velocities) results in a continuous spectrum with frequencies greater than $\nu_g = E_g/h$. The relative intensity distribution in the continuum depends on the velocity distribution of the electrons. Since recombinations leading to different excited states are possible there arise as many individual series limit continua as there are atomic states. The total continuum is a superposition of all these individual series limit continua and of free-free radiation.

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23. H. Wulff, *Z. Phys.*, **150**, 614 (1958); W. Bötlicher, *Z. Phys.* **149**, 62 (1957).

24. A Unsöld, *Z. Astrophys.* **24**, 355 (1948).

*For complex plasmas, composed of more than one element, it is necessary to know the relative abundances of the elements. See reference (1).

†For a review of theoretical and experimental work on continuous spectra, see W. Finkelnburg and Th. Peters (ref. 21).

The coefficient of free-free emission is given by

$$\varepsilon_{\nu} = C\, Z^2 \frac{n_i\; n_e}{(k\,T)^{1/2}} \;\; exp\,(-h^{\nu}/kT) \quad .. \quad .. \quad .. \qquad (20)$$

where

$$C = \frac{32\,\pi^2\, e^6}{3\sqrt{3}\,(2\pi m)^{3/2}} = 6\cdot 36 \times 10^{-47} \quad .. \quad .. \quad .. \qquad (21)$$

It is seen that free-free emission decreases towards higher frequencies. (For low electron velocities, *i.e.* at low temperatures, the free-free emission occurs mainly in the infra-red; but at temperatures of the order of ten million degrees or more essentially all the radiation occurs in the x-ray region.)

Mention has been made earlier of the broadening of the higher energy levels near the term series limit, in hydrogen-like atoms, due to perturbations by the microfields in a plasma. The higher members of a line series are therefore smeared up and with greater perturbations they merge into a continuum which ultimately gets connected up with the series limit continuum. On the other hand, if, above (and including) a certain excited state of energy $E_l = h\nu_l$ there is a relatively dense series of terms until the ionization limit, they form what may be called a 'term-continuum'. The individual series limit continua, involving terms in the 'term-continuum' follow each other so closely that they appear as a single continuum with intensity increasing towards higher frequencies. Superposition of free-free radiation on this continuum results in uniform intensity, independent of frequency, up to the limit ν_l.[25] The frequency—independent emission coefficient is given by

$$\varepsilon_{\nu} = C\,(Z+s)^2 \,\frac{n_e\; n_i}{(k\,T)^{1/2}} \quad .. \quad .. \qquad (22)$$

where s is a small correction in Z to account for the penetration of electrons into the electron shell of ions.[21] Thus in the frequency region in which equation (22) is valid, absolute intensity measurements would express $(n_i\; n_e)$ as a function of T. Using Saha's equation and other equilibrium conditions, the electron temperature T can be evaluated, as in the case of ionization temperatures.[26]

When the terms are no longer close to each other, the emission coefficient for the series limit continuum of the *nth* quantum state is given by

$$\varepsilon_{\nu,n} = C\,\frac{4\,\pi^2\, e^4\, m}{h^2\;\; n^3}\;(Z+s)^4\;\frac{n_i\;\, n_e}{(k\,T)^{3/2}}\;\; exp\left[h\left(\nu_n - \nu\right)\Big/ k\,T\right] \qquad (23)$$

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[25] Based on a study of their radiation properties Maecker and Peters have tried to classify the elements of the Periodic Table into 3 broad types. In type I the atoms have their energy term well separated so that frequency-independent emission is to be expected only in the infrared. H He and elements of Groups I and II and a part of Group III belong to this type. In type II the atoms have close lying terms separated by a broad termless energy gap from the ground state. In this case frequency—independent emission extends from the far infrared to the ultraviolet. The rare gases (except He), halogens, Groups V, VI and a part of Group IV elements belong to this category. In type III the energy terms are densely packed until very near the ground state so that frequency—independent emission is expected through the entire spectrum almost to the limit of the main series. To this type belong elements with the highest multiplicity. H. Maecker and Th. Peters, *Z. Phys.*, **139**, 448(1954). See, also, reference 21.

[26] See, for instance, F. Burhorn, *Phys. Verh.*, **7**, 198 (1956).

The intensity is thus seen to decrease with higher n. Further, in each series limit continuum the intensity decreases on the higher frequency side of ν_n according to exp $(-h\nu/kT)$. The same relative decrease is also shown by the total continuum for $\nu > \nu_l$, but the emission coefficient is given by

$$\varepsilon_n = C\,(Z+s)^2\,\frac{n_i\,n_e}{(k\,T)^{1/2}}\,exp\left[h\left(\nu_l - \nu\right)\Big/ k\,T\right] \quad .. \qquad (24)$$

(Of course, when one progresses from ν_l towards higher frequencies the intensity suddenly rises at the place where the first 'discrete' series limit continuum is encountered.) Equation (24) may be employed for the determination of T from the ratio of relative intensities at two frequencies. If, however, ν is any frequency in the series limit continuum of the mth quantum state ($m < l$), the total intensity at ν would be obtained by adding to equation (24) the contributions, as given by equation (23), from the recombination continua extending from the series limits of all the levels $(l-1)$ to m.

It has been found that for numerous elements the drop in intensity beyond the series limit is not exponential.* It is suggested that until exact calculations are available these continua are not suitable for a quantitative correlation with temperature.

Lastly, it may be mentioned here that at high pressures continuous radiation may result from electron attachment to neutral atoms. The most important and theoretically calculated case[27] is that of the negative hydrogen ion. Since the electrical charge of the proton is not fully shielded by the valence electron, a free electron passing close to the atom would have a probability of attaching itself to the atom, forming a negative ion. Calculation of the binding energy gives a value near 0 75 ev. Lochte-Holtgreven and Nissen have found the theory in good agreement with their experiments.[28] At a temperature of 10,000 deg. K and a pressure of one atmosphere they found that the contributions of the H^- and H to the continuum were about equal. Negative hydrogen plays an important role in the study of stellar atmospheres.

Conclusion

It is obvious that several spectroscopic techniques can be employed for the evaluation of high temperatures. The choice of any particular technique depends among other factors on (*i*) the nature of the source: its geometry; its chemical composition; its density; its probable magnitude of temperature; its state of ionization; temperature gradients; the nature and extent of the external perturbing fields, etc., and (*ii*) the spectral data recorded: the nature (emission or absorption), the type (band, line or continuum) and the region of the spectrum; the intensities and profiles of the line; the distribution of intensity in the continuum, etc. It should be mentioned, however, that considerable information of a fundamental character concerning transition probabilities

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*For a discussion and references to experimental work in this connection, see Lochte-Holtgreven (ref. 1.).

[27] S. Chandrasekhar, *Astrophys. J.*, 102, 409 (1945).

[28] W. Lochte-Holtgreven and W. Nissen, *Z. Phys.*, 133, 124 (1952).

line profiles, intensity distribution in the continua, etc., is still needed for a full utilization of the various spectroscopic methods.* Finally, in case of uncertainty about the existence of thermal equilibrium in the system, the measured 'temperature' must be understood only in terms of the particular spectroscopic phenomenon employed for its determination.

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* The scope and limitations of this paper have not permitted the inclusion of microwave methods of measurement of ion densities and electron temperatures in high temperature plasmas. Reference may be made, for instance, to G.N. Harding *et al.* (see ref 17); E. P. Butt *et al.* (see ref 17); R. F. Post, *Rev Mod. Phys.*, 28, 338 (1956); J. E. Drummond, *Conference on Extremely High Temperatures* (John Wiley and Sons, Inc., New York, 1958), p 97; M. P. Bachyuski *et al. Plasma and the Electromagnetic Field* (Canadian Armament Research and Development Establishment Technical Memorandum AB—26); and J. Schneider and F. W. Hofmann, *Phys. Rev.*, 116, 244 (1959).