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CHAPTER 1

Production and Measurement of High Temperatures

JOHN L. MARGRAVE
Department of Chemistry, Rice University
Houston 1, Texas

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SUMMARY

The gap between room-temperature chemistry (interactions of molecules) and the high energy phenomena of traditional interest to nuclear scientists (interactions of ions, nuclei and elementary particles) has now been extensively filled by nearly two decades of active research in high temperature chemistry, ceramics, and metallurgy with interest concentrated in the energy regime 0.1–10 electron volts. (1 electron volt = 11,500°K.) In this range one has condensed phrases, neutral and excited gaseous atoms and molecules as well as significant numbers of gaseous ions as important species.

Induction heaters, plasma arcs, microwave discharges, lasers, flash lamps, shock tubes, chemical flames, resistance heaters, exploding wires, etc., have been developed

to make high temperature research practical in both static and transient systems. It is possible to study either small amounts of material heated very quickly or to study macroscopic quantities and envision tons of products.

The various solid-state electrical devices for measuring low temperatures (thermometers, thermocouples, photosensitive devices, etc.) have been refined and extended for use up to nearly 3000°K. At higher temperatures, electromagnetic radiation provides the main basis for temperature measurement, for example, through observation of the relative populations of energy levels for atoms, molecules, or ions, of the Stark broadening of spectral lines in partially ionized gases, of Planckian radiation, of recombination radiation, or of Bremsstrahlung radiation.

1. INTRODUCTION

In the evolution of chemical and physical research there appeared about fifty years ago one group of scientists interested mainly in phenomena which occurred at temperatures up to about 1000°C (chemists, most engineers, ceramists, etc.) and another group concerned primarily with the effects caused by particles having 1–10^9 electron-volts of energy, i.e. effective temperatures in the range 10^4–10^{13}°K (physicists, electrical engineers, etc.). The former group has been largely concerned with the changes involving the interaction of electrons bound to atoms and molecules which produce new molecules, while the latter group has been more concerned with the interaction of free electrons, ions, nuclei, etc. with each other or with atoms, molecules, etc. Except for metallurgists, and a few chemists and ceramists there was little activity in the temperature range 1000–3000°K.

Thus, from 1900 to 1940 there existed a borderline area (1000–20,000°K) for which there was a serious gap in the knowledge of physico-chemical phenomena. This relatively unexplored region, which could be called either "high-temperature chemistry" or "low-energy physics," is characterized by the possible presence of atoms, molecules, radicals and/or ions as equilibrium species. Early in the 1940's there was initiated in the laboratories of Professor Leo Brewer of the University of California at Berkeley a new interest in high temperature phenomena, and this renaissance has spread widely until now several hundred researchers profess to an active interest in chemical and physical phenomena in the range 1000–20,000°K, as evidenced by attendance at symposia and meetings. It is the goal of this paper to outline some of the more important recent developments in this field, with special emphasis on the techniques for production and measurement of high temperatures in chemically useful systems.

2. PRODUCTION OF HIGH TEMPERATURES

It would be needless to attempt a complete review of all of the ways for generating high temperatures since there have already been many excellent review papers which describe the various types of electrically-powered wire-wound furnaces, of silicon carbide rod furnaces, of metal and graphite tube furnaces, of inductively-heated susceptors, and of gas-fired furnaces.[1–5] Among the recent developments in the art of producing high temperatures by resistance heating are the use of iridium,[6] of silicon–carbide tubes,[7] of slotted graphite or refractory metal tubes,[8] and of high frequency induction heaters for heating semiconducting oxides[9,10] or for levitation of samples,[11,12] of eddy current concentrators[104] and of electron bombardment apparatus for large and small scale applications.[105] These new approaches allow the attainment of higher temperatures in controlled atmospheres, including highly oxidizing, and with better control. Grosse and associates[13] have proposed to extend still further the temperature range accessible by resistance heating with liquid metals which are maintained in the form of a cylinder by rotating a long pipe inside of which the molten metal is held by an insulating refractory. For example, they report work with molten aluminum held in Al_2O_3 and suggest that one should be able to approach the boiling point of aluminum by pumping more power into the metallic conductor. Fused oxides and similar materials should be conducting and usuable for the 3000–6000°K range in oxidizing atmospheres.

The attainment of high temperatures by chemical combustion processes depends on the formation of product molecules which are extremely stable. The limiting temperatures for hydrocarbon–oxygen flames depend on the dissociations energies of OH and of H_2O and CO_2 and the acetylene–ozone flame represents the ultimate to be expected from the H—C—O system with a flame temperature only slightly above 3500°K. More stable product molecules include certain metal oxides, chlorides, fluorides, CO, N_2, etc. One finds then, that Al-powder + oxygen, Mg-powder + oxygen, Be + F_2, H_2 + F_2, etc.[14] yield flame temperatures in the range 3000–4500°K, and that the very highest flame temperatures are obtained from the combustion of C_2N_2 with O_2 or O_3 (4800–5000°K) or of C_4N_2 with O_2 or O_3 (5300–5600°K).[15]

Undoubtedly the most significant new tool for producing high temperatures of the past decade is the plasma arc or jet. For many years scientists have used the ordinary low-intensity electric arc for analytical work and there was some activity among physicists, especially in Germany, to study the nature of high-intensity and of physically-constricted arcs.[16–19] Temperatures as high as 50,000°K were claimed and the possibility of using an electric arc as the fuse for a hydrogen bomb or to maintain controlled fusion reactors promoted intensive research programs in several laboratories.

The status of plasma arc devices has been discussed in several recent symposium papers.[20, 21] The original water-pipe arc of Maecker[22] has been modified to allow more convenient operation, and gas-stabilized arcs which allow atmospheres of argon, helium, nitrogen, hydrogen, etc. are now commercially available.[23–25] Temperature contours for such arcs show regions in which electronic excitation corresponds to over 15,000°K although it is unlikely that true equilibrium temperatures this high exist over very large volumes. Attempts to produce higher temperatures in commercial devices fail because of (1) erosion and corrosion of the nozzles, and (2) the difficulty of removing heat by the cooling fluid.

Reed has developed an induction-heated plasma torch which also produces temperatures of 10,000–15,000°K easily.[26] A slow flow of a starting gas, often argon, is passed through a quartz tube over an inductively-heated carbon or metal rod until the system reaches a temperature high enough that ionization of the gas begins and the flow-gas plasma begins to couple with the induction field and extract power effectively. At this point, the starting rod can be withdrawn and the ball of hot plasma gases will continue to take energy from the induction coil. By introducing other gases, one can then study chemical reactions in the plasma, or one can drop powders through the plasma region and melt refractory materials which may then fall on seed crystals and produce single crystals in a process similar to the Verneuil technique, and in various atmospheres, even practically pure oxygen.[27]

Plasma arc devices have also found applications in producing high velocity, high temperature gases for duplicating conditions of high speed flight, and of nose-cone-re-entry.[28] The high-velocity gases may be utilized for cutting steel and other solids, for piercing, surfacing, welding, and similar shop operations.[29] Spheroidal particles of W, ZrO_2, UO_2 and similar refractories may be prepared by passing powders through a plasma torch or nucleating from metal vapors.[30]

From a chemical viewpoint, plasmas appear to be attractive for the production of endothermic molecules like C_2H_2, C_2N_2, NO, HCN, etc. although only the acetylene synthesis has really been developed to anything near an industrial process.[31, 32] Basically, the biggest question about the chemical use of plasma devices is, "Why use a plasma torch operating at 10,000°K when a flame at 3000°K gives plenty of conversion to products if one could just recover them?" One would guess that there are some chemical reactions which would be favored mechanistically by starting with a plasma rather than an assembly of molecules, but such cases have not yet been reported, or even predicted.

In any case, a temperature of 10,000–15,000°K means that one has available a mixture of atoms, molecules, ions, and electrons in approximately the proportions predictable from normal equilibrium calculations and the Saha equation, with suitable modifications for known energy levels, and for interionic attraction effects.[33] Thermodynamic functions for atoms, molecules, and the various atomic ions have been tabulated[34] but there are so many serious gaps in our knowledge of molecular parameters and electronic energy levels that calculations of functions at temperatures above 5000°K are subject to large uncertainties, and the results must be used cautiously to predict chemical behavior in plasmas. It is true, however, that the highly endothermic species present in plasmas can undergo almost any reaction to form molecules with a decrease in free energy and thus, the possibilities for chemical synthesis from high temperature plasmas are almost infinite.

Another new technique for heating which one should consider is flash heating as developed by Nelson and colleagues at the Bell Telephone Laboratories.[35] By absorbing the light generated in a high energy flash on surfaces of small particles or wires (of carbon, tungsten, etc.), it is possible to attain temperatures up to 4000°K or higher for short times, and spectra of various molecules have been excited in this way.

Finally, the versatile LASER has been utilized to burn holes in razor blades and recently to evaporate sufficient material from surfaces to allow analytical work via emission and mass spectroscopy.[36] In narrow ranges of wave-length, LASER intensities correspond to 10^6–10^9°K temperatures or higher and a variety of high temperature applications are to be anticipated.

3. MEASUREMENT OF HIGH TEMPERATURES

Modern developments in science and engineering have created a need to know higher temperatures faster, and with greater precision and reliability. For example, the interests of the high temperature technologist now cover the range from about 25°C to at last 10^8°C; gas temperature measurements to 8000°K and plasma temperature measurements to 10^8°K are becoming common as rocket technology and plasma physics develop; and temperatures up to 10^{20}°K are apparently attainable over small surface areas with lasers. To meet the needs of an expanding high temperature technology, there have been several recent symposia[37] and reviews[38] on temperature measurements.

In the discussion here it is assumed that thermodynamic temperature is a familiar concept and attention is mainly to be directed to new experimental techniques which are being used by experienced observers to record the temperature of an experiment relative to established scales.

There have been some recent modifications of the International Practical Temperature Scale of 1948 (IPTS).[39] The thermodynamic temperature scale is now defined by a single experimental point, the triple point of water (0.01°C = 273.16°K) and by 0°K, the temperature at which a Carnot engine can completely convert heat into work. The IPTS and the thermodynamic temperature scale agree fairly well up to 1000°C but new gas thermometric determinations indicate that the IPTS may be in error by as much as 1.5°C at the gold point. The utilization of a newly developed photoelectric pyrometer with a precision better than 0.1°C at high temperatures should help bring these two sides into agreement.

Lovejoy[40] and Kostkowski and Lee[41] have reviewed the state of the art in precision optical pyrometry and estimate that because of the present uncertainty in the gold point, optical pyrometer temperatures presently being recorded on the IPTS (1948) are below the thermodynamic temperature by 4° at 2000°C, 12° at 4000°C, and 40° at 8000°C.

3.1. Thermocouples

Most laboratory scientists agree that the thermocouple, properly used, is the most versatile and rugged temperature-sensing element. Its unique value lies in the fact that it indicates the true temperature of its junction. Thermocouple materials are now available which are stable at temperatures up to 2800°C in neutral atmospheres or vacuum and to 2200°C in oxidizing atmospheres. Wires are available in various diameters, to satisfy either the most delicate or the most rugged temperature measuring requirements, either bare or in metal sheaths with swaged ceramic insulation. Of particular interest to the high temperature technologist is the recent availability of the following pairs of thermocouple wires: tungsten vs rhenium, tungsten vs tungsten–rhenium 26%, and iridium vs iridium–rhodium 40%.

F. R. Caldwell[42] of the National Bureau of Standards has published a comprehensive review of all thermocouple materials and also includes e.m.f.-temperature tables for the new refractory metal couples, extensive tables of physical properties, use and performance data, a discussion of sheathed thermocouples, and an extensive bibliography.

3.2. High-temperature Resistance Thermometers

The International Practical Temperature Scale (1948) is defined from 0°C to 630.5°C by the platinum resistance thermometer with the interpolation formula $R_t = R_0 (1 + at + bt^2)$. There have been several proposals to use the platinum thermometer to define the IPTS in the range 0°C to 1000°C in order to provide a simpler, smoother temperature scale.

Evans and Burns[43] have described a strain-free construction using protection tubes of platinum or dense alumina, and platinum wires supported on sapphire discs for temperature measurements to 1063°C. Barber and Blanke[44] used recrystallized alumina tubes to support four coils of 0.3 mm diameter wire inside an alumina tube for temperature measurements up to 1063°C. A resistance thermometer with the platinum wire fused into a ceramic matrix for use up to 1600°C has been described,[45] and a tungsten resistance thermometer, enclosed in a quartz capillary, has been manufactured and recommended for temperatures to 1000°C.[46] Several companies have available a variety of non-standard and custom engineered resistance probes for aerodynamic, surface, high-pressure, etc., temperature measurement.

3.3. Optical Pyrometry

There have been many different designs (e.g. see Margrave[47]) of optical pyrometers described in the literature but present practice has almost universally accepted two types of instrument based on identical operating principles. By making a brightness match in a narrow spectral region, the steradiance of a hot body of unknown temperature is compared to the steradiance of a hot tungsten wire which has been calibrated directly or indirectly against a blackbody at the gold point.

One either varies the temperature of the tungsten filament until it matches the brightness of the experimental hot body, or attenuates the radiation from the hot body to get a match, or both. In all cases, the optical pyrometer is a blackbody steradiance meter with the scale calibrated relative to the steradiance of the gold-point blackbody. The success of the optical pyrometer is due to the fact that steradiance ratios are more easily and more accurately determined than are absolute intensities. Moreover, brightnesses can be matched with good precision by eye.

It is customary to limit the brightness temperature of the tungsten filament to a maximum of 1350°C in order to preserve its calibration. To measure higher brightness temperatures, the beam from the high temperature source is attenuated to bring it to within the brightness range of a tungsten filament operated below 1350°C. This is done by inserting neutral absorbing screens or rotating sectors into the path of the target image as needed.

Because the color of the target image shifts toward shorter wavelengths, i.e. lighter red, as the temperature increases, the effective wavelength of the pyrometer tends to decrease. Experience at the National Bureau of Standards indicates that the correction due to the change of effective wavelength with temperature may be $\sim 4^\circ$ at 2500°C and less at lower temperatures.

When an optical pyrometer is sighted upon a non-blackbody with a spectral emissivity less than unity, the net effect is a less-intense object brightness image. Molten steel, for example, generally has an emissivity of about 0.4 at 0.65 micron, and many oxides have emissivities around 0.2–0.3. The true temperatures for materials with known emissivities at 0.65 micron are conveniently determined from the extensive tabulation of corrections by Poland, Green, and Margrave.[48]

It is usually not too difficult to create a blackbody in an object whose true temperature is desired. A 10°V-groove in a solid, a V-bend in foil, a small hole in a spherical cavity, a long cylindrical tube with a small hole at the center, or a hole with a length to diameter ratio greater than about five drilled into a solid are all good blackbodies. Thus, if any of these small probes can be put into the high temperature non-blackbody, emissivity can be determined as a function of temperature, or the true temperature may be read directly by sighting into the blackbody cavity. If blackbody conditions are achieved experimentally, no details of the interior are observable since each element of the surface being sighted upon is radiating with equal intensity.

3.4. Recent Developments in Optical Pyrometry

A high-precision photoelectric pyrometer being tested at the National Bureau of Standards has been described by Lee.[49] Basically, the experimental arrangement is the same as is used in the optical pyrometers previously discussed; however, three interchangeable pyrometer lamps are included—one working standard and two reference standards. A combination of interference filters and the usual pyrometer red glass are used to isolate a 0.6530 micron band with a half-width of 0.0110 micron. The phototube alternately sees the source and the tungsten filament at 30-second intervals and the output is read-out on a recorder. Equal output of the source and the pyrometer lamp is taken as a radiance match. Precision at 1063°C is said to be better than 0.02°C. With this precision, the size of the source has been found to influence the observed temperature as much as 0.1 to 0.2°C. Similarly, pyrometer lamp instabilities corresponding to as much as 0.5°C change in 150 hours of use were detected.

An instrument of very different design but similar in performance to the National Bureau of Standards photoelectric pyrometer has been described by Middlehurst and Jones.[50] Treiman[51] built a photomultiplier pyrometer for operation at 0.4500 micron, and Elder[52] has constructed a recording pyrometer which uses a photosensitive transistor. The response time is of the order of 0.02 sec.; however, the calibration is sensitive to ambient temperature changes.

Tingwaldt[53] has described a novel method for determining the thermodynamic temperature of a heated metal under non-blackbody conditions. The metal surface is illuminated with radiation from a blackbody source and the reflection is viewed at an oblique angle with a standard disappearing filament optical pyrometer. The reflection of the blackbody image from the surface of the metal is unpolarized only when the blackbody and the metal have equal temperatures. Accordingly, if a polarizer is inserted in the beam entering the pyrometer, the metal and the blackbody are at the same temperature when the rotation of the polarizer produces no change in the brightness match.

Blum[54] constructed an optical pyrometer to record temperatures in the range 1300°C to 3000°C from a target area 3/8 in. diameter at a distance of 50 inches. The Instrument Development Laboratories[55] manufactures an automatic brightness pyrometer which has approximately one second response to an instantaneous step-change corresponding to full scale deflection. The output is suitable for electronic recording and control.

According to Planck's Law, the intensity ratio of blackbody radiation at two wavelengths is a unique function of temperature and can accordingly be used to measure blackbody temperature. Among the advantages claimed for two-color pyrometry are: (1) no thermal contact; (2) reasonable variations in intensity due to smoke or absorptance in the source optical path do not change the indicated temperatures; (3) limited variations in target area do not change the indicated temperature; and (4) radiance changes of the source tend to cancel and make the temperature indication relatively independent of surface effects or surface condition.

There are at least two commercially available two-color pyrometers[56, 57] embodying the principles outlined above. Their properties have been described by Ackerman,[58] and Shaw *et al.*[59] Russell, Lucks, and Turnbull[60]also described the use of a two-color pyrometer with the assumption of greybody conditions.

Hill[61] has described a novel two-color pyrometer which uses a 0.005 to 0.013 in. diameter quartz fiber as a light pipe instead of the usual optical system. Temperatures as low as 538°C may be determined with a PbS detector.

Hornbeck[62] has discussed the problems associated with the design of a three-color pyrometer with the assumption that emissivity varies linearly with wavelength. The work was carried only sufficiently far to prove the feasibility of the idea.

Brenden[63] has described a ratio pyrometer which uses a PbS detector and two bands in the infrared, 1.5 to 2.8 microns and 2.1 to 3.0 microns, respectively. Hecht[64] used interference filters with 5% band width to chop the source beam at 1.65 and 1.95 microns. The chopped beam was made the input to a pulse height analyzer to measure intensity ratios.

The new infrared detectors make it possible, in principle, to use Planck's Law to determine the gold point on the thermodynamic scale by using an infrared monochromatic pyrometer calibrated at the sulfur or zinc points with a gas thermometer.

An infrared radiometer suitable for temperature measurements from ambient to 3600° has been described by Astheimer and Wormser.[65] The commercial model[66] of this instrument uses a thermistor detector, sensitive to about 50 microns, in conjunction with a glass filter which shuts out light below 1.8 microns. Thus, reflected light does not affect operation. Response time is reported to be 10 milliseconds, sensitivity 0.1°C, and the absolute accuracy of the instrument calibration ±2.0°C.

A portable instrument is available commercially for the temperature range 0–850°C. Another commercial infrared pyrometer[67] uses a thermistor bolometer and has a spectral bandpass of 1–12 microns with optics for targets as small as 1 mm^2. An operating range from 15° to 5500°C above ambient, 0.25 sec. response, and 1 % accuracy are claimed.

An infrared detector which uses an InSb detector is also commercially available.[68] This instrument has the fastest response of any known detector, being less than one microsecond. While this instrument is especially good for recording, indicating, and controlling fast temperature changes near 25°C, the range can also be extended to 3500°C.

Commercially available thermopile receivers are well suited to electronic instrumentation and for this reason they are being successfully applied to temperature control problems to an increasing extent. Units are available for sighting between the turns of an induction heating coil,[69] for use with an 1/8 in. diameter sapphire rod light pipe for small openings,[70] and special receivers are available for target temperatures as low as 100°C.

3.5. Measurement of Gas Temperatures

It is much easier to measure the thermodynamic temperature of solids and liquids and their surfaces than it is to measure the thermodynamic temperature of gases above the range of the gas thermometer. Yet, paradoxically, the theoretical understanding of the properties of gases as a function of temperature is relatively more complete than for solids and liquids and there are accordingly more methods to determine gas temperatures. For this reason, it is customary to refer to several kinds of temperature for gases; e.g. total temperature, static temperature, vibrational temperature, translational temperature, rotational temperature, electron temperature, stagnation temperature, etc. Such terminology is merely a manifestation of the dependence of gas temperature on environmental factors and the temperature dependence of the degrees of freedom associated with the properties of gases. In order to specify completely the properties of a gas, it is necessary to indicate all of its various individual temperatures or else bring the gas to thermodynamic equilibrium and measure temperature in the conventional sense.

Often, as in a flame front, the temperature gradient in a gas may be of the order of 10^5 °K per mm and the interesting phenomena may occur in the order of 10^4 collisions; or the cooling or heating rate of the gas may be as high as 10^6 °K per second. Under such conditions, the thermodynamic properties of the gas may lag the heat transfer process; hence, there is a need to know the temperatures characteristic of particular energy modes in order to describe correctly the changes occurring in the gaseous system.

Gas temperature measurements are usually accomplished by radiation methods or by the insertion of a probe of some sort to determine a local property of the gas which is temperature dependent and from which the temperature may be derived either by calibration or by theory. Radiation methods use a large target area which is viewed through a layer of semi-transparent gas whose properties must also be considered when determining temperature. Probes may be used to determine the gas stream temperature point by point; but, heat exchange occurs between the probe and the gas and between the probe and the gas duct and must either be eliminated or corrected for in order to obtain accurate temperatures.

Gas temperatures may be measured with a thermocouple up to the temperature limit of the thermocouple by designing an environmental shield[71] which permits the junction to indicate the true temperature of the gas. The design of the environmental shield is determined principally by the size of the probe required for a particular measurement as well as the velocity, heat capacity, molecular weight, pressure, and temperature of the gas and the wall temperature of the confining duct.

Warshawsky[72] has reviewed the pyrometry of high velocity gases and included a summary of the types of thermocouple probes, their design parameters, and a brief bibliography, and Moffat[71] has collected most of the available design information and gives a detailed account of the application of the data to the construction of complex probes.

Many of the engineering applications of gas temperature measurements exceed the temperature limit of thermocouple materials in oxidizing and corrosive environments. In order to develop rugged sensing elements, several types of probes have been tested which show promise of making good engineering measurements up to 3000°C to 4000°C. Krause, Glawe, and Johnson[73] have given a recent report of the design and heat transfer analysis of cooled-tube, cooled gas, and stagnation point probes. Raezer and Olsen[74] have used chromel–alumel thermocouples to measure temperatures to 3200°C in a plasma torch by cycling the junction between the plasma and a water cooled sheath at the rate of 40–200 cycles per minute. Fingerson and Blackshear[75,76] have constructed a probe similar to a hot wire aneometer in which the sensing element is a thin platinum film deposited on a glass tube about 0.2 mm outside diameter and 2.5 mm long.

The rate of flow of a gas through a restriction is a function of the molecular weight, orifice area, total temperature, total pressure, and the static pressure. The maximum discharge rate of a gas through an orifice, venturi, or nozzle will increase as the pressure drop across the orifice increases until the throat velocity equals the velocity of sound. A further increase of pressure drop or decrease in discharge pressure will not change the discharge rate. The critical pressure ratio, $r_c = P_2/P_1$, for sonic flow in an orifice is given by $r_c = (2/\gamma + 1)(\gamma/\gamma - 1)$ where $\gamma = C_p/C_v$, P_2 = absolute discharge pressure, and P_1 = absolute upstream pressure. For example, the values of r_c for air and superheated steam are 0.53 and 0.55, respectively. Thus, temperature may be determined by measuring upstream pressure provided that an equation of state, molecular weight, and the ratio C_p/C_v are known as a function of temperature. Such probes require a rather large amount of gas and may be operated at either sonic or sub-sonic velocity. Warshawsky and Kuhns[77] have given a comprehensive account of the theory and historical development of this probe and have included an extensive bibliography. Land and Barber described a commercial instrument[78] used to measure temperatures to 1600°C. Specially designed probes may be used to measure higher temperatures.

Spectroscopic observation of gases permits one simultaneously to measure temperature and to identify the constituents which comprise the gas mixture. The power of the method as a high temperature research tool is evidenced by the great amount of knowledge which has been obtained from such studies on flames and plasmas. While it is true that the sample is a cylindrical disc observed edge-on, methods have been developed to convert these data into radial intensity for the case of cylindrical symmetry.[79, 80] The special advantage of the spectrographic method is that no perturbation is introduced into the system being studied; i.e. the system is its own thermometer.

The determination of accurate temperatures from spectroscopic observations requires considerable insight and experience due to the complications brought about by the presence of several species, i.e. molecules, atoms, positive and negative ions, and electrons, which may be created by various physical processes to yield different distributions of energy over the various degrees of freedom, i.e. translation, vibration, rotation, and electronic, which may not be in equilibrium with each other and which may not be Boltzmann in character. The usual approach is to assume equilibrium as predicted by the Boltzmann equation and to calculate electronic, vibrational or rotational temperatures in chemical flames or to assume that the Saha equation holds and utilize the Griem modification of the Holtzmark theory of Stark-effect broadening of spectral lines[81] to yield temperatures in partially-ionized gases (plasmas). Deviations from ideality and coulombic effects may also be considered quantitatively by a Debye–Huckel type of treatment.[82]

Spectroscopic methods applied to gas temperature measurement have been covered in comprehensive fashion in the International Conference on Combustion series, and books by Penner,[83] Gaydon and Wolfhard,[84] Gaydon,[85] Lewis and von Elbe,[86] Ladenburg, Lewis, Pease and Taylor,[87] Wolfe,[88] and Dickerman.[37b] For work above 4000°K the review article of Lochte–Holtgreven is especially well-done.[89] Recent work in the field is covered in the NBS "Bibliography of Temperature Measurement" and its supplements.[90]

The sodium line reversal method has been used more successfully than any other optical method of gas temperature measurement. Techniques to achieve time resolutions of the order of a few tenths of a microsecond have been described by Penner.[91] In addition to measuring temperature, Bundy and Strong[92] also estimated pressure and gas velocity from the line broadening and Doppler shift, respectively, of the Na-D lines.

The precision of the line reversal method is estimated[93] to be about 5°K at 1500°K and approximately 10°K at 2300°K. A comparison of self-balancing pyrometer line reversal temperatures of various probes was made by Buechele.[94] A recording line reversal pyrometer has also been described by Brobeck, Clemsen, and Voreck.[95]

In addition to the sodium lines, characteristic lines of Li, K, Rb, and Tl as well as the 2.7 μ-band of H_2O and 4.4 μ-band of CO_2 have been used for line reversal studies.[96] The CH and the C_2 bands present in the reaction zone of flames possess abnormal excitation and cannot be reversed and are, therefore, not usable for temperature measurements by this method.

The observed changes in the emission spectrum of a gas may be used to determine temperatures to 10^{6}°K. Line broadening, line intensity, and continuum intensity measurements have been most used for the measurement of the highest temperatures. The choice of the method to be used can only be determined after a comprehensive analysis of the nature of the spectral emission of the particular system whose temperature is sought. It is usually possible to satisfy the optical requirements either by adding a small amount of H_2, He, or other indicator gas, or by selecting an atomic emission line of one of the components or a natural impurity which is in an optically clear region of the spectrum and is not affected by self absorption.

As the temperature of a gas is increased above 4000°K, the spectroscopic changes which occur may be described as follows: (1) rotation-vibration transitions disappear below 10^{4}°K, (2) with increasing temperature, atomic lines broaden, some to a far greater extent than others, (3) all lines first increase in intensity and then decrease in intensity with increasing temperature, (4) the intensity of background continuum radiation increases in proportion to line intensities with increasing temperature, (5) atomic lines are slightly shifted towards the red at higher temperatures, (6) the continuum series limit becomes diffuse and shows an apparent shift towards the red.

All of these changes are related to temperature or heat content and may be used to estimate ion and electron concentrations from which the gas temperatures may be computed using the Saha equation. For these calculations, it is usually assumed that the particles comprising the plasma possess Maxwell velocity distributions and Boltzmann population distributions among the excited states.

Line broadening of the H_β line at 4861 Å has been widely used for temperature measurements in astrophysics, shock tubes, and arc plasmas. The other lines of the Balmer series, H_α, H_γ, and H_δ have received the same theoretical study and understanding; however, the H_β line is more convenient experimentally and is the one most often used to measure temperatures in the range 7000–30,000°K. Higher temperatures may be measured by choosing a line corresponding to a higher energy level, i.e. lower principal quantum number. For measuring temperatures above 100,000°K, a recent review by Griem[97] may be consulted.

The theoretical and historical development of line broadening has been covered in comprehensive fashion in a recent book by Breene.[98] In the original Holtsmark[99, 100] theory of Stark line broadening, the radiating atom is supposed always to be surrounded by a fluctuating microfield due to the presence of plasma ions and dipole and quadrupole interactions. With this assumption, Holtsmark calculated, as a function of time, the probability of the existence of a field strength F at the radiating atom. The probability is normalized in terms of a normal field strength F_0 which depends only upon the number of ions per cc and is given by the equation

$$F_0 = 2.61\, eN^{2/3}$$

where e is the charge of the electron, and N is the number of ions per cc.

In the Holtsmark theory, the field strength probability distribution is independent of the ion density and, as the line broadens, its intensity increases and the line shape does not change. Schmaljohann[101] using the Holtsmark theory has calculated the theoretical intensity profiles of the H_α, H_β, H_γ, and H_δ Balmer lines in terms of the distance from the center of the emission line, $\Delta\lambda$, and the normal field strength F_0. Thus in order to measure temperature, it is only necessary to assume values of F_0 and calculate the intensity of the H_β line which has the same half-width as the experimentally observed line. From this value of F_0, N may be calculated and, in turn, the temperature may be determined by application of the Saha equation,

$$\frac{(N_+)(N_e)}{N_0} = f(T)$$

where N_+, N_e, and N_0 are the numbers of ions, electrons, and neutral atoms. If there are several atomic species contributing to the ion and electron concentrations, then one can write a Saha equation for each component and solve the set of equations simultaneously with the help of Dalton's law and equations for charge and mass balance.

Kolb[102] and Griem, Kolb, and Shen[103] have calculated corrections to be applied to the Holtsmark theory in order to include the effect of electrons on line broadening; however, the agreement between theory and observed line profile is still not perfect. The accuracy of this method of determining electron concentrations is of the order of 10% and Lochte–Holtegreven suggests that the Holtsmark theory holds pretty well up to $n_e = 18 \times 10^{16}$ at 15,000°K for the H_β line. For higher temperatures, the narrower lines of H_α and He^+ may be used in conjunction with the Holtsmark theory to determine electron densities to 4×10^{16}/cc.

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