Physicochemical Measurements at High Temperatures

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PREFACE

THE concept of the present book originated in 1952 during discussions between J. O'M. Bockris and J. W. Tomlinson, whilst these authors were working at the Imperial College of Science and Technology, London. The transfer of Bockris to the University of Pennsylvania in the following year reduced the potentialities of the originally intended co-authorship. With the kind collaboration of the publishers, it was agreed to change the character of the book to that of a co-operative effort by leading workers who had made contributions to the field of high temperature physical chemistry, and to the technique of the measurements involved. The present editors are all formerly of the same high temperature physicochemical research group at Imperial College, so that a degree of continuity with the original work has been retained.

The need for the existence of a book of this type is manifestly clear to anyone who, trained in physical chemistry, takes up fundamental investigations of phenomena occurring at high temperatures. His only source in respect of experimental technique is the literature, and although reference to the original papers is always necessary for research workers utilizing or developing a known technique, it is highly advantageous if he has available under one cover a presentation, critical discussion, and comparison, of the various methods available for the measurement of a property. The combined experience and, to some extent, distilled wisdom of some twenty chemists and metallurgists who have contributed to the high temperature field, offers in addition a picture of the experimental side of high temperature measurements as known at the present time. This fact may give the book a secondary purpose as a source for those who, in increasing numbers, teach courses concerning high temperature work.

The role of physicochemical measurements at high temperatures in the chemistry of the future is likely to be a rapidly increasing one, firstly because of the importance which such measurements have in freeing chemistry from the limitations in knowledge involved in studies of the properties of matter and of chemical changes when the thermal energy is approximately that of room temperature, and secondly, because of the many technological applications. Thus, a principal limitation to the development of the practical use of nuclear power lies in the present lack of knowledge of the properties of materials at high temperatures (specifically, in respect of heat transfer systems, where the higher the temperature, the greater the efficiency). The recent developments in rocket technology demand rapid advance in respect of materials for components such as combustion chambers and nose cones. Furthermore, innumerable actual and potential chemical processes exist, e.g. the production of many metals, of glasses, of diamonds, and of refractory materials such as boron nitride, in which high temperatures are involved.

In the present book, the stress is upon the technique of fundamental investigations, namely those which are the necessary precursors of the

technological developments which inevitably follow from advances in basic research. The book will be of maximum use to those in universities, research institutions, and the fundamental research laboratories of industrial organizations. The chapters have been arranged with an eye to the fact that all investigations at high temperatures involve decisions such as how to obtain and control the temperature concerned, how to measure it, and how to contain the system under examination. Chapters concerning these matters, together with the introductory notes of Chapter 1, in which the aim is to give some perspective to the following material, take up the first four chapters. In each following chapter, techniques for investigating a given type of property are discussed.

The editors' viewpoint has been that their tasks were not only to invite the right authors to contribute the right kind of chapters, as well as to carry out the tasks common to all editors of scientific books. They have attempted carefully to review, or have reviewed, most of the chapters; they have entered into discussion (sometimes prolonged) with many of the contributing authors concerning the substance and detail of what was presented. They have attempted, in this way, to bring about the presentation of material which contained the essence of what present and future chemists need at the beginning of, and during, experimental investigations of physicochemical behaviour at high temperatures. They have also tried to bring about some uniformity in the method of presentation—it is desirable that the work be a *book*, not a collection of papers—and to reduce repetition and duplication among the various chapters to a minimum.

2 April, 1959

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GENERAL ASPECTS OF PHYSICOCHEMICAL
RESEARCH AT HIGH TEMPERATURES

J. O'M. BOCKRIS

INTEREST in fundamental physicochemical research at high temperatures springs basically from the primary position of temperature in the equation of state of materials; and in respect of its effects upon the structure of matter and the velocity of chemical reactions. The corresponding applied interest is very great. Thus, many inorganic materials of use are fabricated at high temperatures, and interest in extra-terrestrial systems underlines the increasing value of a knowledge of properties at high temperatures. In published quantitative physicochemical research, such temperatures are generally above 500°C and below 2500°C.

Chemical research at high temperatures has been pursued for many years. For example, melting points of certain silicates in the region of 1000°C were recorded by Hautefeuille and Perry in 1888; arc furnaces were discussed comprehensively by Moissan in 1897, and used much earlier; Lorenz published the first edition of his well-known book 'Die Elektrolyse geschmolzener Salze' in 1900; and in the same year, Le Chatelier and Boudouard published a book on the measurement of high temperatures. Metal oxides, particularly MgO, were being used as elements in resistance furnaces by Nernst before 1903, and the volatilization of graphite at over 3000°C was described by Moissan in 1905. Ruff, Pirani, Tammann and von Wartenburg carried out extensive work at temperatures in the region of 2000°C some 40 years ago. However, much of this early work consisted of preparative inorganic chemistry and electrochemistry and the measurements of the simpler physicochemical properties, such as melting and boiling points. Systematic thermodynamic and kinetic studies of systems at temperatures over 1000°C date largely from the early 1930s, and this type of research was seldom extended to temperatures above 1650°C before about 1945.

Physicochemical behaviour at high temperatures is characterized by the fact that the exponential dependence of reaction rate on temperature causes a reduction in the primacy of chemical reaction rate as the more important factor in the determination of a reaction. Consequently, greater reliance can be placed on thermodynamic equilibrium calculations for the determination of the actual state of a reacting system. Thus, $\Delta G°$, rather than $\Delta G°^{\ddagger}$, determines not only the possibility but also the practicability of a reaction. In those systems at high temperatures in which equilibrium is not rapidly attained, diffusion, rather than a chemical reaction, is usually the rate-determining step of the process concerned. Conversely, experimental measurements are characterized by great difficulties which centre upon the attackability of container materials and which concern, for example, the

problem of attaining zones of uniform temperature in the experimental vessel. Not least of the practical difficulties of physicochemical work at high temperatures is its high cost.

A primary aspect of experimental technique at high temperatures is the measurement of the temperature. This measurement is not made easier by fundamental difficulties connected with the experimental basis of the agreement of various temperature scales, particularly above about 1100°C. Differences of temperature scales used in various laboratories and absence of satisfactory compensation for the non-black body nature of systems are potent sources of discrepancies between the results of independent experimenters. Conversely, the instrumentation involved has been substantially developed in recent times. For example, until the early years of this decade, it was standard practice to use optical pyrometers at temperatures above about 1500°C, but more recently it has been possible to extend the range in which thermocouples can be accurately used up to some 2400°C (e.g. with the Ir/Ir–10 Ru couple).

Methods of attaining temperature, particularly in physicochemical measurements, depend largely upon resistance and inductive heating, and the choice will depend upon the requirements of temperature uniformity and temperature control to be judged anew for each experimental application. Resistance heating is generally the more satisfactory method, because of the greater ease of temperature control which it allows. Its greatest disadvantage, the need of a controlled atmosphere in the use of refractory metals such as tungsten, is rapidly being overcome by the development of oxide elements.

The design of any actual heating arrangement must always be a compromise between power input, insulation and cooling, and the optimum position has usually had to be reached empirically. This situation is improved by a mode of calculation reported for the first time in this book. Mention may also be made of less conventional methods for attaining high temperatures, which have come more recently to prominence, e.g. the use of arcs, electron bombardment and solar furnaces.

The most frequently occurring difficulty of making measurements at high temperature is that of attack on refractories. The choice of refractory material should be preceded by careful consideration of available thermodynamic data on reactions which may take place between the experimental object and its container or atmosphere. Attack by a melt usually involves the penetration of a solid container by intergranular solution processes, and the rate of this attack depends primarily upon kinetic factors, e.g. diffusion and viscosity. In practice, especially at temperatures in excess of 1600–1700°C, it is usually relevant only to demand that the rate of attack be sufficiently slow for negligible effect on the property under examination. This can, however, be an exacting condition, particularly when a surface property, e.g. an electrode process, is being measured. There is a particularly pressing need for greatly increased research efforts in this field of the stability of refractory materials. Among more recently investigated systems, the carbides, nitrides, sulphides, and silicides seem promising.

The choice of subject matter in this book is based upon the viewpoint that the most frequent aim of fundamental physicochemical work at high temperatures is the detailed elucidation of the constitution of the material

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concerned. Pursuit of better techniques, without a reasoned aim for their application, is hardly likely to give rise to significant contributions to chemistry. An example of enhanced progress in the understanding of structure, arising from the reasoned development of high temperature techniques, is given by work upon glassy and liquid silicates. Thus, after the classical work of Zachariasen (1932), little progress was made in the understanding of the structure of these liquids, partly because experimental work was concentrated upon vitreous materials at room temperatures. There, the material is not in equilibrium, and its properties are affected by kinetic factors, e.g. annealing, thermal history, etc. More rapid progress became possible, when, as from about 1946, work was commenced upon the corresponding liquids at high temperatures, where they are in equilibrium. Firstly, electrochemical measurements were made to verify the ionic nature of the materials by means of conductance measurements and an examination of the degree of applicability of Faraday's laws. Thereafter, an examination of viscous flow was carried out, to obtain evidence on the general nature of the anions present. Densitometry was later applied to enable a comparison with experiment to be made of the space requirements of various possible anionic structures. Further studies were carried out on the diffusion velocity of the anionic components, to obtain detailed information on the size and shape of the particles present. Such high temperature investigations have given rise to a workable model of the liquid silicates.

The various properties of interest in physicochemical investigations at high temperatures may be mentioned as follows.

The measurements of the equilibrium constants of chemical reactions, of phase equilibria, and of calorimetry, are the basic thermodynamic measurements of high temperature physical chemistry, and the relevant techniques have reached a comparatively advanced stage of development. At high temperatures, the advantage exists that a reaction will be more likely to go to completion (cf. the corresponding difficulty when this is not so, e.g. in low temperature calorimetry).

Liquid densitometry is of importance because it leads to partial molar volumes, which, e.g. in some molten electrolyte systems, give rise to information concerning the nature of the groups which make up the liquid; and also because knowledge of density is needed in the evaluation of certain parameters, e.g. equivalent conductance from specific conductance. Most methods for the high temperature liquids are Archimedean, and all involve measurements of weight, length, or volume made relative to a reference solid in thermal equilibrium with a liquid. They are generally very precise. The eventual limitation to accuracy lies in knowledge of the thermal expansion of the reference solid. A problem of great importance in high temperature densitometry is the change in volume of a substance upon fusion, which provides direct evidence of the difference between the (usually known) structure of the solid and that of the liquid. This is a difficult measurement to make directly, owing to the difficulty of obtaining the volume of the solid, exclusive of air bubbles, in a vessel in which it can be fused. Density measurements on both sides of the melting point, by

means of independent techniques, may be a more suitable approach in some systems.

Knowledge of interfacial free energy is of value in applications of certain theories of liquids and also for many applied problems, e.g. the foaming of blast furnace slags. Several well-known methods for the measurement of surface tension at room temperature have been successfully modified for use at high temperatures. Thus, the maximum bubble pressure method is suitable for molten salts, the pendant drop for molten glasses, and the sessile drop for the metal–silicate interface. The principal difficulty with all such methods is their sensitivity to contamination with impurities arising from the container–melt reaction.

Vapour pressure measurements are used to obtain heats of vaporization, from which it is possible to gain qualitative knowledge concerning the strength and type of binding between entities in the liquid (cf. the heat of activation in viscous flow). Methods are available which allow evaluation of vapour pressures over the range $5 \cdot 10^{-15}$ mm Hg to 1 atm. In more normal pressure ranges (1 mm Hg and above) reproducibility can usually be obtained to about $\pm$ 2 per cent. In spite of this, a much greater discrepancy often exists between the work of independent authors (amounting often to $\pm$ 50 per cent), and this is doubtless due to container interaction problems together with inadequate assumptions, such as those concerning the means of escape of atoms from a Knudsen cell, and the molecular species involved.

Substantial progress has been made during the last decade in techniques dealing with electrochemical measurements at high temperatures. Such measurements yield, for example, information on the nature of the conducting species, on the standard free energy change in chemical reactions, on the relation of surface tension to potential, and the resulting knowledge of the charge at the metal–melt interface. Transport measurements usually call for non-conducting containers, so that metals such as Mo, which is particularly resistant to the attack of, e.g. high melting silicates, cannot often be used. The applicability of Faraday's laws is also frequently an important piece of knowledge to obtain in respect of a molten liquid. Here, because of the ease of attackability of electrodes with evolved gases at high temperatures, and the ease of dissolution of deposited metals into the melts, it may be found better to allow such attack to occur and to attempt to obtain the needed information by measuring its products.

Optical and sonic measurements at high temperatures have been commenced only in recent years. The optical measurements are of particular value because they give rise (e.g. from Raman spectra) to knowledge on the nature of the bonds formed between ions in molten salts, and therefore of the complexes present. Special caution is needed in respect of contaminants, such as dissolved SiO_2, which may set up Raman lines competing with those of the molten test substance. Sonic measurements give thermodynamic and structural information concerning molten electrolytes because they lead to the adiabatic compressibility of the liquid and to its free volume, which quantities act as excellently informative goals for absolute calculations in terms of alternative models of the melt. The temperature at which such measurements can be carried out is limited at the present time

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to about 1400°C, above which temperature the rods carrying the sound from sources outside the hot system begin to absorb too large a portion of it for accurate measurements to be practicable.

Diffusion and viscosity studies likewise yield structural information. Diffusion measurements are also important in respect to rate control in high temperature reactions (as in metal–molten silicate reactions). In the liquid state, they are difficult to make, largely because of the tendency of convective processes to interfere and the difficulties associated with the density changes on freezing. Viscosity measurements give rise to information on the nature of the flowing unit and its ease of movement. The technique of viscosity measurements at high temperature is now rather satisfactorily developed. For metals, where the viscosity is low, an oscillating crucible technique is of optimum value; the classical Poiseuille method can be applied satisfactorily to molten salts; and for molten silicates and glasses, where the major difficulty is that the viscosity involved varies over several powers of ten with composition and temperature, a new version of the rotating crucible method, in which the spindle is kept from deflection by a variable magnetic torque (the current controlling which can easily be altered over several powers of ten), has proved to be of wide applicability.

These brief notes on some general aspects of physicochemical measurements at high temperature cannot be completed without mention of the potential field of thermal reactions at temperatures and pressures above those now commonly available. This field would seem to promise to the chemist a considerable extension of his power to bring about desired chemical changes. Were applicable heat to grow cheaper with increasing time, preparative metallurgy might thereby undergo something of a revolution. In the thermodynamic and kinetic possibilities of chemical reactions at temperatures above some 1500°C, there promises to arise a new phase of exploration in physical and inorganic chemistry.

TEMPERATURE MEASUREMENT

JOHN L. MARGRAVE

I. INTRODUCTION

IN MODERN laboratories one can find systems under study from 10^{-5} to $10^8\,°K$. Although the range of temperatures used in experimental measurements has been greatly increased in recent years, the concept of temperature is not greatly different from that developed in the early 1800s by the founders of classical thermodynamic theory.

Temperature and temperature measurement have been discussed recently by various authors[1].

II. THEORY

1. *Definitions of Temperature*

Early observers of natural phenomena made a qualitative distinction between 'hot' and 'cold' objects on the basis of the ability of a 'hot' object to lose heat to a 'cold' object. Two bodies are said to be in thermal equilibrium if they are brought into thermal contact and allowed to exchange heat until no further heat flow occurs. The basis for the concept of temperature is the *zeroth* law of thermodynamics[2], which states that two bodies in thermal equilibrium with a third are in equilibrium with each other. The three bodies then have a common property, designated as the temperature, which signifies that they are in thermal equilibrium with each other. The recording of the temperature of a system may be made in terms of the physical properties of a standard reference body brought into thermal equilibrium with the system. Such properties as the physical state, thermal expansion, electrical resistance, crystal form, etc., are the basis for many empirical temperature scales.

The reference standards for early temperature determinations were the human body itself and a certain mixture of snow, salt and sal ammoniac which fixed the temperatures on the Fahrenheit scale devised in 1714. Later, Celsius made use of the freezing point and boiling point of water as standards of temperature, and divided the interval between into 100 units or degrees. These definitions of temperature scales do not have theoretical significance in the field of thermodynamics.

(i) *Thermodynamic temperature*

The thermodynamic temperature scale may be defined in various ways. One of the most familiar is that involving a reversible cycle for an ideal Carnot engine[3], suggested by Kelvin in 1848[4]. In this cycle a frictionless, perfect engine takes heat from a reservoir at a high temperature, T_1, and

returns all the heat not transferred into work to another reservoir at a lower temperature, T_2, in a series of equilibrium steps. By applying the second law of thermodynamics to this cycle, it follows that the efficiency of the Carnot engine is independent of the working substance[2] and depends only on the temperatures of the two reservoirs, i.e.

$$\frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = f(T_1, T_2) \tag{1}$$

where W is the work performed by the engine, Q_1 is the heat extracted from the high temperature reservoir, Q_2 is the heat rejected to the low temperature reservoir, and f is an unknown function of the temperatures T_1 and T_2. Rearranging equation (1),

$$\frac{Q_1}{Q_2} = g(T_1, T_2) \tag{2}$$

where g is also an unknown function. A similar relation holds for another Carnot engine operating between T_2 and T_3 and utilizing the heat Q_2 rejected at T_2 by the first engine,

$$\frac{Q_2}{Q_3} = g(T_2, T_3) \tag{3}$$

These engines working together constitute a third Carnot engine for which

$$\frac{Q_1}{Q_3} = g(T_1, T_3) \tag{4}$$

Combining equations (2), (3) and (4),

$$g(T_1, T_2) = \frac{g(T_1, T_3)}{g(T_2, T_3)} \tag{5}$$

Since the temperature T_3 is arbitrary and does not appear on the left hand side of equation (5), the ratio on the right hand side must be independent of T_3. Thus

$$\frac{Q_1}{Q_2} = \frac{\phi(T_1)}{\phi(T_2)} \tag{6}$$

From equation (6) actual temperature scales may be obtained by arbitrary definition of the function ϕ. The 'thermodynamic temperature scale' is established by a choice such that

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2} \tag{7}$$

This scale, historically chosen by Kelvin, is also called the Kelvin, or 'absolute', temperature scale.

The efficiency of the first Carnot engine is then given by

$$\frac{W}{Q_1} = \frac{T_1 - T_2}{T_1} \tag{8}$$

To define the zero of temperature on the thermodynamic (Kelvin) scale let $T_2 \to 0$, so $W/Q_1 \to 1$; thus, the zero on this scale is that temperature at which a heat engine is capable of completely converting heat into work. The definition of the thermodynamic scale is completed by one of two methods: (i) by assigning a numerical value in °K to one fixed point, or (ii) by specifying the number of degrees between two fixed points (*see* p. 12).

Of the various empirical temperature scales, the most important is that based on the properties of an ideal gas, defined by Boyle's law and Joule's law as follows:

$$PV = F(T) \tag{9}$$

$$\left(\frac{\partial E}{\partial V}\right)_T = 0 \tag{10}$$

The absolute gas scale assigns numerical values to the empirical temperature θ by the relation

$$\theta = a \lim_{P \to 0} (PV) \tag{11}$$

where the constant a is determined as above, by assigning a numerical value to a fixed point or by specifying the number of degrees between two fixed points. One may employ an ideal gas as the working substance in a Carnot cycle of four reversible stages: (a) isothermal expansion at θ_1 from V_1 to V_2, (b) adiabatic expansion to θ_2 and V_3, (c) isothermal compression at θ_2 to V_4, and (d) adiabatic compression to θ_1 and V_1. The work done in this cycle is given by

$$W = \frac{(\theta_1 - \theta_2)}{a} \ln \frac{V_2}{V_1} \tag{12}$$

and the heat absorbed in step (a) is

$$Q_1 = \frac{\theta_1}{a} \ln \frac{V_2}{V_1} \tag{13}$$

Thus the efficiency is given by

$$\frac{W}{Q_1} = \frac{\theta_1 - \theta_2}{\theta_1} \tag{14}$$

Since the efficiency is also given by equation (8), one concludes that $\theta = $ constant $\times\ T$, and, if the gas scale and the thermodynamic scale are defined by assigning the same numerical values to the fixed points, then $\theta = T$, and the scales are identical.

From a rigorous mathematical viewpoint the thermodynamic temperature can be regarded as the reciprocal integrating factor for converting an inexact differential, δQ, into an exact differential, dS, the entropy increase in a reversible process.

(ii) *Kinetic interpretation of temperature*

An ideal gas may be regarded as consisting of molecules which are moving randomly and colliding in perfectly elastic collisions. From such a picture and the laws of classical mechanics comes the kinetic theory of gases and the ideal gas law, $PV = nRT$, in which temperature is defined in terms of the energies of the molecules of a gas. From a consideration of momentum transfer on collision with the walls of a container, the pressure exerted by a mole of ideal gas is $P = Nm\bar{c}^2/3V = 2E_K/3V$, where $N =$ Avogadro's number, $m =$ the mass of the molecule, $\bar{c}^2 =$ the mean square of the molecular velocities, and $E_K =$ the average kinetic energy of the molecules mole^{-1}.

Since heating a gas increases E_K, $E_K = f(T)$ and, if $PV = nRT$, then $E_K = 3/2\ RT$. Hence, the ideal gas scale temperature defined in this way is proportional to the average translational kinetic energy of the gas molecules.

(iii) *Radiation and temperature*

A fundamental law connected with radiation is Kirchoff's law[5] which states that for total radiation from an opaque body, the total emittance, ϵ, is equal to its total absorptance, α, for radiation from a black body at the same temperature. In this law,

$$\epsilon = \frac{\text{rate of emission of radiant energy per unit area from a non-black body at T°K}}{\text{rate of emission of radiant energy per unit area from a black body at T°K}} \quad (15)$$

One may also state Kirchoff's law in terms of spectral emittances and absorptances; thus at each wavelength,

$$\epsilon_\lambda = \alpha_\lambda \quad (16)$$

Kirchoff defined the ideal 'black body' as an object which absorbs all incident radiation without reflection. Since no known material has these properties, an ideal black body may be approached by use of an enclosure in which a small hole allows the escape of very nearly black-body radiation. The multiple reflections and emissions as indicated in *Figure 1*, each resulting in partial reflection of the incident radiation, give a 99·9 per cent black-body radiation for a Cu cavity after 45 reflections, for a W cavity after 12 reflections and for a C cavity after only 3 reflections. Thus, in a satisfactory black-body cavity no details of the interior are observable through the hole.

The quantities emittance, absorptance and reflectance are characteristics of the nature of the surface of the non-black bodies as well as of the materials composing them. Worthing and Halliday[6] have expressed the relevant characteristics of materials as the emissivity, ϵ', the absorptivity, α, and the reflectivity, ρ', determined under the conditions that (i) the body is of uniform composition, (ii) it is opaque, and (iii) its surface is highly polished.

The quantitative relationship between the electromagnetic radiation from hot objects and their temperature was stated by Stefan[7], and derived by Boltzmann[8], and is known as the Stefan–Boltzmann law, i.e.

$$J = \sigma T^4 \quad (17)$$

where J is the total energy radiated per unit area per second and T is the Kelvin temperature. The constant σ is given by

$$\sigma = \frac{2\pi^5 k^4}{15c^2 h^3} = 5\cdot6685 \times 10^{-5} \text{ erg cm}^{-2}\text{sec}^{-1}\text{deg}^{-4} \qquad (18)$$

where k is the Boltzmann constant, c is the velocity of light, and h is Planck's constant.
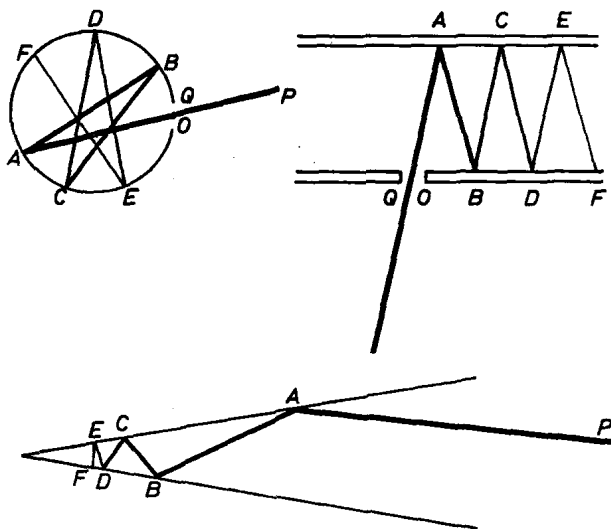

Figure 1. Laboratory methods for attaining black-body radiation by multiple reflexions

Experimental work on radiation from hot bodies was carried out by Lummer and Pringsheim[9], and others in the later 1880s and 1890s. The main object of their work was to establish, experimentally, the nature of the variation of intensity of radiation with wavelength. From thermodynamics, Wien[10] deduced the displacement law which related the wavelength for the maximum of radiant intensity, λ_{max}, and the absolute temperature by the equation

$$\lambda_{max} = \frac{K}{T} \qquad (19)$$

where K is a constant. Wien also developed a more general law for the relationship between the rate of radiation from a hot object, and wave length and temperature:

$$J_\lambda = \frac{c_1}{\lambda^5 e^{c_2/\lambda T}} \qquad (20)$$

where J_λ is the energy radiated per unit area per second at the wave length λ. However, this law did not fit the experimental data at long wave lengths and low temperatures. Another radiation law was developed by Rayleigh[11] and Jeans[12], but it did not fit the experimental data at short wave lengths

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