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TRANSLATION

THERMODYNAMIC RESEARCH BY THE METHOD OF EXPLOSION AND COMPUTATION OF COMBUSTION PROCESSES

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By A. M. Gurvich, Yu. Kh. Shaulov

September 1959

181 Pages

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PREPARED BY
LIAISON OFFICE
TECHNICAL INFORMATION CENTER
MCLTD
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

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A. M. GURVICH AND YU. M. SHAVLOV

TERMODINAMICHESKIYE ISSLEDOVANIYA METODOM VZRYVA I RASCHETY PROTSESSOV GORENIYA

Publishing Office
Izdatel'stvo Moskovskogo Universiteta

1955

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Published by resolution of the
Council of Editors and Publishers
of Moscow University

Dedicated to the unfading memory of
Professor Andrey Vladimirovich Frost

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FOREWORD

This book is closely related to the previously published books Statisticheskiye Metody rascheta termodinamicheskikh velichin (Statistical Methods of Computation of Thermodynamic Quantities) by V. M. Gryaznov and A. V. Frost, and Svobodnyye energii organicheskikh soyedineniy (The Free Energies of Organic Compounds) by V. V. Korobov and A. V. Frost. It is a result of the great theoretical and pedagogic work conducted in the Department of Physical Chemistry of MGU (Moscow State University) under the guidance of Professor A. V. Frost. Regrettably, the untimely death of A. V. Frost made it impossible for him to participate in the preparation of this book which was written after his death. The book contains an outline of the methods of computation of the characteristics of combustion processes on the basis of thermodynamic functions and equilibrium constants, the computation procedures for which were analyzed in the two above-mentioned books. At the same time, the book is so compiled that the knowledge acquired within the scope of the physical chemistry curricula for university students in departments of chemistry is sufficient for its understanding and no preliminary perusal is required of the books by Gryaznov and Frost or Korobov and Frost. For this purpose, in particular, Appendix I was incorporated at the end of this book; there we find a brief review of the statistical methods of computation for thermodynamic quantities (to the approximation of harmonic oscillator - - rigid rotator), as well as a calculation of equilibrium constants.

The fundamental principles of the computation methods outlined in the book are described in the monographs by Zel'dovich and Polyarny, Vanichev, and Lewis and Elbe. The authors introduced a series of improvements into these methods, consolidated the computation procedures for constant volume and constant pressure, and made an effort to present them formally and at the same time sufficiently graphically. The derivations of a considerable number of formulas recorded in the book constitute something original. Several simple formulas were developed to facilitate a check on the accuracy of the initial stages of calculation, in the course of which -- as it is evidenced in practice -- errors are often committed which nullify all the subsequent highly laborious work. Chapter IX contains the methods developed by the authors for the calculation of the correction pertaining to the maximum explosion pressure for the temperature gradient in the products of combustion, and for the computation of temperature distribution in the mixture of combustion products depending on the distance from the center of the explosion vessel.

A simple method is also given for the computation of thermal capacities of the combustion products according to experimental values of maximum explosion pressure. All calculations related to thermodynamic research by method of explosion are brought into conformance with the consolidated methods of computation of combustion at constant volume and at constant pressure, as outlined in Chapters V and VI.

The examples of thermodynamic research by the method of explosion and the calculations connected therewith -- which are analyzed in Chapter IX on the basis of all the material contained in the preceding chapters and in the appendixes -- are designed, apart from their direct object, to facilitate a more critical approach by the reader to the evaluation of the accuracy of calculations required in every given case, in particular, with respect to the required precision for calculation of the thermodynamic functions of substances by statistical methods, which is a matter of special importance in view of the labor-consuming character of this operation.

The methods and computation procedures incorporated in the book are illustrated by means of a considerable number of examples. The reader will easily perceive a definite system in the selection of these examples and the relationship of some of them to each other. All examples are computed by the authors.

The methods of calculation are presented in such a manner as to facilitate their utilization by a wide circle of research workers and professional engineers engaged in work involving combustion processes. This fact constitutes the great practical significance of this book.

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Chapter I

INTRODUCTION

Very high temperatures develop as a result of combustion of gaseous explosive mixtures. It is natural to assume that, in view of the great progress rate of reactions under these conditions, the system arrives at a state of chemical equilibrium by the moment combustion is terminated. Owing to the speed of burning, the heat losses into the ambient space are, as a rule, small. These circumstances make possible the application of thermodynamics to calculations of such quantities as maximum pressure of explosion, degree of expansion, combustion temperature, and so on.

Through a corresponding experimental setup, heat losses, as a matter of fact, may be reduced to insignificantly small values. In this manner, it becomes possible under definite conditions to obtain good agreement between the experimental values of the combustion characteristics and their values calculated on the basis of the application of thermodynamic laws. But in this case the experiment in turn makes it possible to calculate the unknown thermodynamic quantities included in the calculation scheme of this or that quantity observed experimentally. For this purpose, use is ordinarily made of the method of explosion in a closed spherical vessel (bomb) with central ignition. In such a vessel, the flame comes into contact with the walls of the bomb simultaneously over their entire surface as a result of total combustion of the explosive mixture. Up to this moment, which coincides with maximum pressure in the vessel, the heat losses for rapidly burning mixtures are negligible. The maximum explosion pressure is measured by means of special pressure indicators. This method, initially suggested by Bunsen, was employed after a number of technical difficulties were overcome by Pier (52, 53) --by a number of researchers for the determination of the mean specific heat of gases and for other purposes. It is possible to record a considerable number of examples in which this method was successfully used for the determination of thermodynamic quantities at high tempera-

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tures (61, 47), to define more precisely the data on the structure of molecules (46), for the study of the combustion process itself (63, 21, 62) and the determination of the possible degree of useful utilization of the energy contained in explosive mixtures. Other experimental methods of thermodynamic research, though sometimes even more accurate than the method of explosion, do not permit research to be conducted at high temperatures on the order of the combustion temperature of explosive gas mixtures.

We refrain entirely from dealing here with the matter of the feasibility of quantitative thermodynamic investigations based on the comparison of the measured detonation rates with those calculated theoretically. Such investigations were carried out by Zel'dovich and Ratner (17) and a few other researchers. Computation in this case is similar to that for adiabatic explosion in a closed vessel. This method allows us to study the thermodynamic properties of gases at even higher temperatures than this is possible by the method of explosion in a bomb.

For the study of combustion at constant pressure, a method is applied which roughly consists of the following. An explosive mixture is ignited by a spark in the center of a soap bubble (57) or a spherical film of thin transparent rubber (54). The flame, while travelling in such a "constant pressure bomb", retains its spherical form with the change of diameter being registered on a moving photographic film. In this manner one can determine the degree of expansion, i.e., the ratio between the ultimate volume of combustion products at constant pressure and the initial volume of the original mixture.

The most reliable method of the flame temperature measurement is the reversal of spectral lines (21). The light from an incandescent wire passes through the flame, colored by traces of sodium. With the rise of the wire temperature, the bright lines of sodium radiation change into black absorption lines at the moment when the temperature of the wire becomes equal to that of the flame.

The satisfactory coincidence of the experimental values of combustion characteristics obtained, by the mentioned methods, with the theoretical values confirms the

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validity of the basic postulates and the initial data supporting thermodynamic calculations. Thus, we have a fairly reliable method of computation of combustion processes for industrial purposes. Selection of fuel (37) and material for the manufacture of equipment (3) evaluation of the effect which the composition of the initial mixture may produce on these by other characteristics of various processes (37, 26), determination of the possible degree of utilization of the chemical energy of fuel for the performance of certain work (26), calculation of the technical characteristics of all types of engines (16, 2, 41, 42), solution of various problems in metallurgy (23), in the field of welding and in processes of fuel gasification -- all this constitutes a far from complete list of the fields of possible application of thermodynamic computation of combustion processes.

For these calculations, use is made of thermodynamic quantities computed b the statistical method on the basis of data on molecular and atomic structure obtained mainly by means of spectroscopic and electron diffraction studies. It is in this manner that a "mathematical bridge" is built from experiments pertaining to the determination of microscopic quantities to experiments intended to define the macroscopic quantities providing direct characteristics of the real processes.

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Chapter II

EXPERIMENTAL DETERMINATION OF MAXIMUM EXPLOSION PRESSURE

The problem of measuring the maximum explosion pressure with accuracy satisfactory for scientific purposes is quite complex. The experimental equipment used will be described briefly here in order to furnish a real physical basis for the thermodynamic calculations of combustion processes, the methods for which are analyzed in detail below.

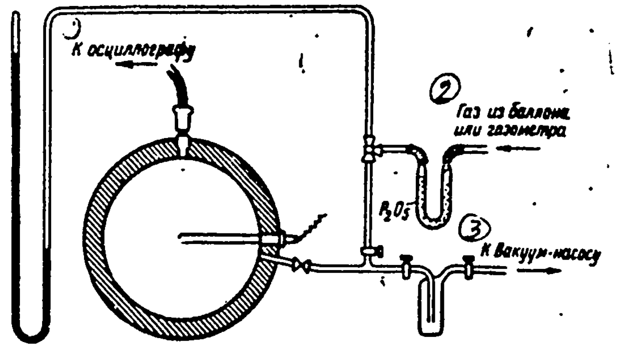

Figure 1a. Diagram of spherical bomb and auxiliary equipment.

(1) To oscillograph; (2) gas from flask or gasmeter; (3) to vacuum pump.

Such an assembly (Figure 1a) consists of an explosion vessel -- a bomb with equipment for its evacuation, inlet of gases and vapors, and the ignition of the mixtures -- and a diaphragm pressure indicator * to register the change in pressure during explosion in relation to time. The unit may be also provided with other devices and apparatuses in accordance with the research objectives.

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* Indicators of the piston type cannot be used for accurate measurements because of high inertia.

The history of pressure indicator development for thermodynamic research by the method of explosion in a bomb is to be found in the book by Bone and Townend(27).

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Section 1. The Bomb

The bomb (Figure 1b) constitutes a steel vessel whose inner hollow space has a strictly spherical shape. It consists of two sections fastened together by means of massive bolts and a gasket of soft metal. This arrangement assures the possibility of inspection and cleaning of the bomb and at the same time provides for sufficiently tight sealing.

The spark electrodes are so mounted as to make sure that the gap between them is right in the center of the sphere.

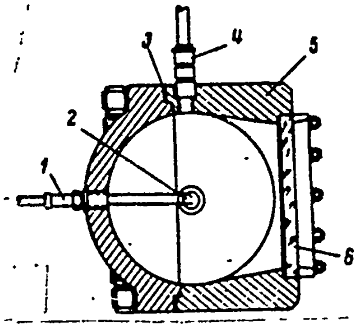

Figure 1b. Cross-section of the spherical bomb.

(1) two-point spark plug; (2) quartz window; (3) gasket; (4) condenser pickup; (5) bomb body; (6) window for photographing of flame propagation.

To permit photographing of the flame propagation—which, in particular, is important to check that the flame reaches the walls of the vessel simultaneously at all points -- the bomb is provided with a window in the form of a narrow slit covered by thick glass. The flame is photographed on a motion picture film fixed on a rotating drum whose axis runs parallel to the slit. A typical recording of the flame propagation is shown in Figure 2.

Different researchers used bombs with volumes ranging from 3.5 to 35 liters (53, 47). Bombs of small size are disadvantageous because the eccentricity of the spark gap in them may be relatively large (47). Besides, the larger the bomb, the smaller is the surface-volume ratio and the smaller, therefore, are the heat losses through the walls. However, an increase of the explosion vessel radius facilitates

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detonation, which entails a narrowing of the range of the initial mixture concentrations that may be utilized for thermodynamic research by the method of explosion in a bomb.

The fuel mixture is prepared either in the bomb itself (53, 62) by means of alternate introduction of gases, or in special mixing containers (37) sufficiently large to permit the preparation of a mixture for a number of experiments. On their way to the bomb, the gases pass through a drying system. To assure a complete mixing of the mixture components, and in order to communicate to them the temperature of the atmosphere surrounding the bomb, a certain period of time must be permitted to elapse between the filling of the bomb and the explosion. This period depends on the density of the mixture gases and the order of their introduction into the bomb or the mixing container.

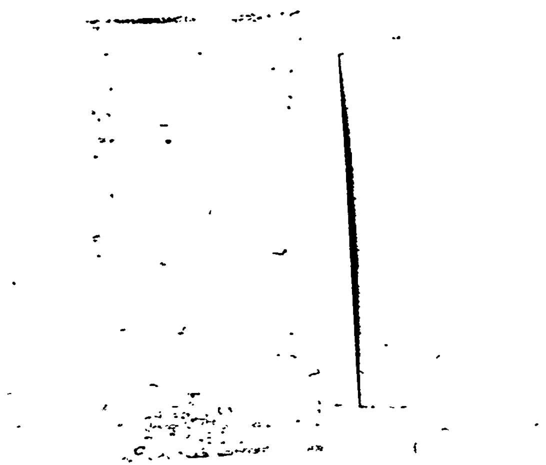

Figure 2. Photorecording of flame propagation in a spherical vessel with central ignition (Fiok and King).

To introduce water vapor into the explosion vessel, a corresponding amount of water is vaporized in a special test tube (37), or, alternatively, prior to the inlet of gases into the bomb, the gases are saturated by water vapor at a definite temperature. If experiments are to be conducted with a considerable content of H_2O in the initial mixture, then use is made of an explosion vessel with a steam jacket (37, 31). Since at constant volume and constant temperature, the molar concentra-

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tions of gases are proportional to their partial pressures, it suffices, for the preparation of a mixture of a given composition, to measure the partial pressures during the alternate introduction of the mixture components. For the measurement of pressure, use is made of a mercury manometer with cathetometer. Whenever the initial pressure exceeds 1 atm, a reference manometer of the 02 class may be utilized.

For gases with a relatively high critical temperature, such as HCl or Cl_2 the deviation from the ideal gas state should be calculated while determination is being made of their initial quantities on the basis of partial pressures. From the Van der Waals equation we derive:

$$pv^3 - (bp + RT)v^2 + av - ab = 0, \qquad \text{(II.1)}$$

where v is the volume of one mole of gas and p is its partial pressure,

$$b = \frac{R}{8}\cdot\frac{T_k}{p_k}; \quad a = \frac{27}{64}\frac{R^2\cdot T_k^2}{p_k}. \qquad \text{(II.2)}$$

In working out equation (II.1) by the approximation method with application of graphic interpolation (22), we find the volume v of one mole of the given gas.

From the Clapeyron equation, we calculate the partial gas pressure p* which it should have had, had it conformed to the law of ideal gases

$$p^* = \frac{RT}{v}. \qquad \text{(II.3)}$$

In summing up the partial pressures of the initial mixture components reduced to the state of ideal gases, we obtain a corrected initial pressure of the mixture P_1^*.

Example. The partial pressure of chlorine p = 663,9 mm Hg, the temperature of the mixture T = 291° K, the critical temperature of chlorine T_{cr} = 417,2° K, the critical pressure p_{cr} = 76,1 atm.

From equation (II.2), we determine

$b = 0,05623 \qquad a = 6,496$

By substituting the numerical values of p (in atm), a,b,R (in $\frac{\text{1-atm}}{\text{deg.}}$) and T in equation (II.1), we find

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$$0{,}8738\, v^3 - 23{,}9257\, v^2 + 6{,}496\, v - 0{,}37 = 0$$

On solving this equation by the approximation method, we determine that

$$v = 27{,}114 \text{ lit}$$

whence

$$p^* = 0{,}8806 \text{ atm} = 669{,}3 \text{ mm Hg}.$$

For $p = 241{,}0$ mm, we find $p^* = 241{,}7$ mm by similar procedure.

Analogous considerations exist also for water vapor. If a considerable quantity of water vapor is to be introduced into the mixture, then experimental data on its compressibility should be utilized.

Section 2. Pressure Indicators

The pressure indicators consist of two basic parts: the sensitive element (pickup) receiving pressure, and the recording unit. The existing indicators may be divided into three groups: mechanical, optical, and electric indicators. The two latter groups are most suitable for precise measurements.

In optical and electric indicators, the main pickup element is the diaphragm which responds directly to pressure. The deflection of the optical indicator diaphragm causes the mirror, which is connected thereto, to turn, entailing a deviation of the reflected light beam which is registered on a moving photofilm. In electric indicators, the shifting of the diaphragm is translated into a change of one or another parameter of the electric circuit registered by the oscillograph.

Of a number of different types (4, 14) of electric indicators, we shall consider the two most suitable ones for accurate measurement: the condenser and piezoelectric indicators.

A pressure indicator used for thermodynamic investigations by the method of explosion must record rapid changes in pressure with the greatest possible precision and the least possible delay. For this purpose, it should be characterized by small inertia and small hysteresis, while being sufficiently stable in operation and depending as little as possible on temperature in its recordings. To obviate the

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possibility of a resonance with the fluctuations of the measured pressure, the diaphragm must have its own high frequency. The indicator diaphragm must be at one level with the inner surface of the bomb.

(1) Optical Pressure Indicators

This type of indicator is widely used in thermodynamic research by the explosion method, since it is relatively simple and assures considerable accuracy of measurement. The diaphragm of the optical indicator is connected to the mirror by means of a flexible system. A voltaic arc serves as the source of illumination. The beam of light reflected by the mirror is focused by the objective of the photographic recorder onto a sensitive film fixed to a rotating drum, and shifts proportionally to the magnitude of the diaphragm deflection (if it is not too large), while tracing the pressure-time curve, i.e., the indicator diagram (Figure 9a). This gives us more than 1,000-fold magnification. By measuring the height of the sharp maximum on the indicator diagram, the corresponding pressure increment ΔP is determined (data on the calibration of indicators will be found below). By adding ΔP to the initial pressure P_i, we get the maximum value of explosion pressure P_e (experiment) $= P_i + \Delta P$.

Figure 3 illustrates the diaphragm indicator proposed by Lewis and Elbe (45). The characteristic feature of this indicator is that the diaphragm is not clamped in the supporting frame (as this is the case with most diaphragm indicators), but constitutes one solid piece with it. This insures the stability of the diaphragm's zero position and the absence of an apparent hysteresis caused by the inelastic nature of its attachment. The measurement accuracy exceeds 0.1% of the magnitude of maximum pressure (26). Optical indicators used by other investigators showed an accuracy of the order of 0,1 - 0,2% (61). Discrepancies between the results of individual measurements range within the limits of 0,2 - 0,8% (46, 47, 61).

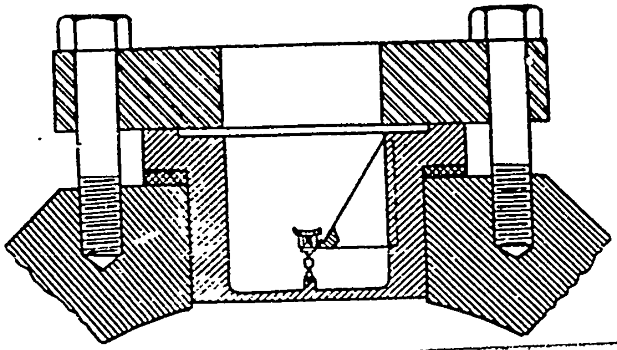

Figure 3. Pickup of optical pressure indicator developed by Lewis and Elbe.

(2) Condenser Pressure Indicators

The diaphragm of a condenser indicator is one of the plates of the adjustable capacitor-condenser pickup (Figure 4), whose second plate is insulated from the indicator body and connected with an amplifier.

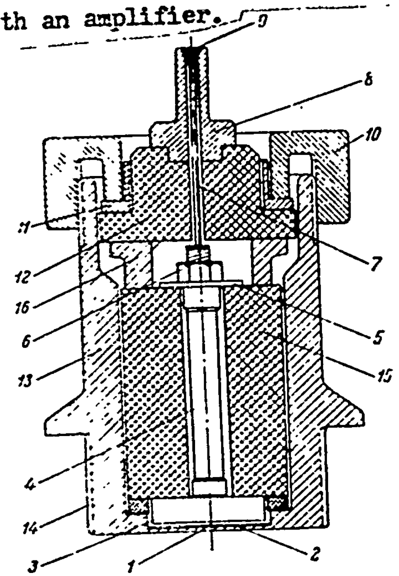

Figure 4. Condenser pickup.

1- diaphragm; 2- mica gasket; 3- fixed lining; 4- rod; 5- washer; 6- nut; 7- conductor; 8- terminal block; 9 - conductor seal-in; 10- shaped nut; 11- packing block; 12- insulating bush; 13- housing; 14- thread for housing fitting; 15- ebonite sleeve; 16- support bush.

The small capacitance variations of the pickup resulting from diaphragm deformation under the influence of pressure cause almost linear changes of the voltage supplied after amplification to the vertical scanning plates of the cathode-ray

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oscillograph. Saw-tooth voltage is delivered to the plates of horizontal scanning. During explosion, the luminous point on the electron-ray tube screen traces a pressure-time curve which may be photographed.

The response of the pickup to pressure variations increases as the superficial area of the diaphragm (and the fixed lining) increases; it decreases as the distance between the pickup linings decreases. At the same time, this distance must be large in comparison to its changes under the influence of pressure, so as to assure the linearity of the pickup characteristics*. This may be achieved through the use of a relatively thick diaphragm, characteristic for small values of deflection, which in turn enables the pickup linings to be placed close to each other. A thick membrane is more advantageous than a thin diaphragm, in that its zero position has greater stability and that it has a smaller hysteresis (60). The diaphragm is made of stainless steel or special alloys (elinvar, mnimonica).

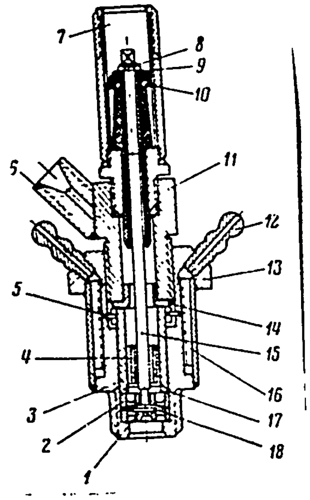

Figure 5. Single-contact pickup.

1- separator, lower; 2- separator, upper; 3- packing block; 4- perforated insulator; 5- packing block; 6- gas inlet tube; 7- contact guide; 8- cap nut; 9- contact washer; 10- insulating washer; 11- upper housing; 12- water inlet pipe; 13- lower housing; 14- packing sleeve; 15- regulated contact; 16- water jacket; 17 - packing washer; 18- diaphragm.

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* It should be borne in mind that condenser pressure indicators are usually characterized by a linear relationship between the point displacement on the diagram and the pressure only over a relatively narrow range (49).

For the determination of the indicator diagram scale -- provided the indicator characteristic, which is checked by calibration, is linear -- it is sufficient to have two points on the curve for which the corresponding pressure values are known. One of these points is the point of ignition -- the basis of the rising branch of pressure curve. This point corresponds to the initial pressure of the mixture. The second calibration point may be plotted on the indicator diagram with the aid of a single-contact pickup (Figure 5), which, when a definite pressure is reached in the bomb, produces a pip in the form of a bright point on the steep left-hand branch of the diagram. The single-contact pickup (26) has a diaphragm and a contact screw between which there is a small gap, if pressure on both sides of the diaphragm is equal. The difference in pressure required to press the membrane to the contact is being measured before each test ("correction for back pressure" -Δp_{back}). Prior to the explosion, a definite pressure ("back pressure" - p_{back}) is applied to the pickup diagram from the side of the contact screw. When the pressure in the bomb, affecting the inner face of the diaphragm, exceeds back pressure by the quantity Δp_{back}, the circuit closes and a bright point appears on the indicator diagram.

Time is plotted on the diagram by means of a special device. The entire system of instruments is synchronized, ignition of the mixture, registration of pressure, and, whenever needed, the photographing of flame propagation, are affected by a single depression of the push-button.

(3) Piezoelectric Pressure Indicators (5).

The diaphragm of a piezoelectric indicator activates a quartz crystal on whose surface there appears an electric charge during compression (this is known as the piezoelectric effect). The charge magnitude is proportional to crystal deformation. Through an electric converter, the pickup is connected with the oscillograph, by means of which the pressure-time variation is registered.

The advantages of the piezoelectric indicator are the absence of hysteresis and independence of registration from temperature. The short-comings of this type of

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indicators, as of any electric pressure indicators in general, are the relative complexity of their construction and of their operation.

(4) Calibration of Pressure Indicators.

There are two types of pressure-indicator calibration. We have static calibration, in the process of which a known pressure is applied to the diaphragm gradually, and we have dynamic calibration, when the diaphragm is subjected to rapid loading. Dynamic calibration corresponds to the unit's operating conditions during explosion and should therefore be given preference. However, in case of total absence of hysteresis, both methods should produce coinciding results.

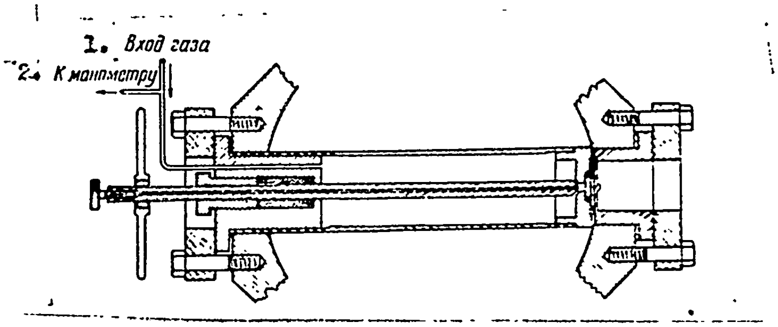

Figure 6. Instrument for dynamic calibration of optical pressure indicator (Lewis and Elbe).

(1) Gas inlet; (2) to manometer.

During static calibration (37, 59) the bomb is filled with air or any other gas, for instance, nitrogen or carbon dioxide, up to different values of pressure measured by manometer so as to assure the greatest possible precision.

For dynamic calibration, use is made of special cylinders or flasks filled with gas. One of such units is shown in Figure 6 (45). The calibration cylinder is placed inside the bomb. Between it and the diaphragm of the pickup, screwed into the opening in the explosion vessel, there is a small space isolated from the remaining bomb space by a rubber ring. Pressure is applied to the diaphragm by means of a swift turn of the screw. The time of pressure growth comprises approximately 0,01 sec.

On the basis of the indicator calibration data, a diagram is constructed for the dependence of the height of the indicator diagram on pressure. If the characteristic of the indicator is linear, the graph has the form of a straight line.

In summing up this short description of the equipment for the measurement of maximum explosion pressure, it should be noted that these measurements may be sufficiently reliable for the determination of thermodynamic quantities by the method of explosion (47) -- if use is made of carefully calibrated pressure indicators of good design and capable of satisfying the above mentioned requirements; if the inner surface of the bomb has a strictly spherical shape and there are no "dead spaces" outside of this surface; if the bomb volume is sufficiently large to assure a precise central position of the spark gap; and if the experimental unit permits us to reduce the heat losses to a minimum before the flame has reached the walls of the bomb. If all these requirements are duly observed when use is made of rapidly burning mixtures, indicator diagrams with a sharp maximum may be produced. This maximum corresponds to the moment when the spherical flame makes contact with the inner surface of the bomb.

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Chapter III

HEAT LOSSES AND THE DEGREE TO WHICH EQUILIBRIUM IS ACHIEVED DURING EXPLOSIONS IN SPHERICAL VESSELS WITH CENTRAL IGNITION

1. Phenomena Arising in the Bomb during Explosion

During ignition of an explosive mixture of gases in the bomb, the flame travels from the spark gap in all directions. The transformation of the initial mixture into combustion products takes place in the reaction zone which constitutes a thin spherical layer whose surface is called the flame front. The reaction zone separates the dark region of the unburned mixture from the luminous region of combustion products which are in a state of chemical equilibrium. The spherical shape of the vessel with central ignition assures the preservation of the sphericity of the flame front and its simultaneous reaching of the bomb walls at all points, provided the rate of combustion is sufficiently high (see Figure 7).

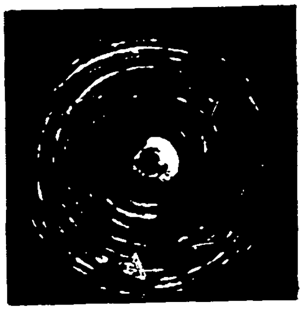

Figure 7. Instantaneous photos of the flame propagating in a spherical glass vessel with central ignition (Ellis).

At the expense of heat released during combustion, the transformation products remaining behind the reaction zone expand due to strong heating and compress the unburned gas. As a result of this, pressure increases continuously. Moreover, in view of the fact that flame velocity is low as compared to the speed of sound, it is possible to consider, without too much of an error, that pressure is even within the

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whole volume of the vessel at any moment in time, with the exception of those cases when the combustion rate is very high (29, 56). At the same time, the flame fails to heat up the unburned mixture in any appreciable way, so that, before it reaches the walls of the bomb, the latter are in contact only with the gases faintly heated in consequence of compression. This assures the almost totally adiabatic character of combustion.

Experiments show (40, 34) that at the moment when the maximum explosion pressure is reached, the temperature at the center of the bomb, near the ignition point, exceeds the gas temperature at its walls by several hundred degrees. This fact can be explained as follows (13, 18, 21, 38, 40, 50). Let the volume of the vessel be mentally divided into a number of thin spherical layers with a common center at the ignition point. In practice, each such elementary layer, whose volume comprises but an insignificant part of the total gas volume, burns up at constant pressure. Thus, the volume element situated at the center burns at initial pressure P_i, whereby the pressure performs the work of expansion. Later on, it is compressed almost to its initial volume* by pressure which rises continuously from P_i to maximum pressure P_e grad, i.e., on an average, by a pressure considerably greater than P_i, as a result of which fact it initially releases less energy than is reabsorbed by it at a later time. As to the volume element which burns the last, i.e., practically at P_e grad. pressure, the situation is reversed. Consequently, at the moment when the maximum explosion pressure is reached, the temperature at the center of the vessel turns out to be higher than at the walls.

Since the specific heat of gases grows with rising temperature, it is reasonable to expect that, during temperature equalization without heat losses, the pressure of the mixture of combustion products must increase. Let us assume, for example, that the vessel is divided into two parts, containing equal masses of gas at

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* At the same time we must bear in mind that the described effect constitutes a secondary effect as compared with the thermal effect of combustion which is the primary factor responsible for the general increase of temperature. Let it be noted that, in the qualitative explanations provided herein, the dissociation of combustion products has so far not been taken into account.

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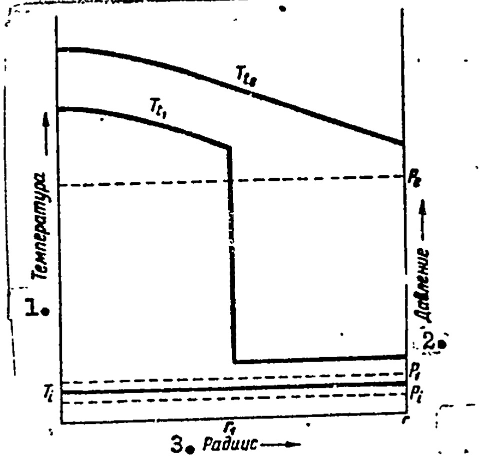
different temperatures. With the establishment of an even temperature distribution, one part would have absorbed the same amount of energy as was lost by the other, but its temperature, at the same time, would have grown in a higher measure than would have been the drop of temperature in the other part. In the absence of dissociation of combustion products, pressure is directly proportional to temperature. Hence, in the first part of the vessel it would also have grown to a greater extent than it would have slackened in the second part. Consequently, during its equalization, a higher pressure would have been registered than that which corresponds to the initial, uneven distribution of temperature.

The dissociation of gases, which increases with rising temperature, accelerates the growth of pressure with temperature. Therefore, in its presence the mentioned effect of pressure growth with temperature equalization will be somewhat leveled down.

In addition to this, dissociation as an endothermic process should reduce the temperature gradient (in comparison with what it would have been in the absence of dissociation). Figure 8 shows the distribution of temperature and pressure in the bomb for three time instants: before the commencement of burning, at moment t_1, when the flame attains the sphere with radius r_1, and at the moment when combustion ends t_e. Throughout the entire process of combustion, the temperature at the ignition point is at the maximum. In the reaction zone it drops sharply. In the region of unburned mixture, it is uniform though rising somewhat with time.

The increase in steepness of the rising branch of the indicator diagram (Figure 9a) as the maximum is approached evidences the growth of the rate of transformation. However, since the flame surface grows proportionally to the square of the radius, the speed at which the flame front moves in the direction of the normal to its surface (the so-called, spatial flame velocity), not only fails to increase as the flame approaches the walls of the bomb, but even diminishes somewhat. This may be seen from the generatrix of the cone on photographs of flame propagation in spherical vessels (Figure 2).



<u>Figure 8.</u> Variation of pressure and temperature during explosion in a spherical vessel

(1) Temperature; (2) pressure; (3) radius;

After the flame has come in contact with the bomb walls, the cooling of the mixture of combustion products begins, as a result of which a drop in pressure is to be registered. Minor cambers, which sometimes may be observed on the drooping branch of the pressure diagram (Figure 9b), are to be attributed to temporary retardation of cooling in consequence of heat influx from the bomb center (21, 47).

In the case of rapidly burning mixtures, pressure sometimes fails to equalize and compression waves -- shock waves -- are being formed. This provokes powerful diaphragm vibrations which usually arise toward the end of the combustion process when the transformation rate reaches the minimum. The indicator diagrams resulting therefrom are unsuitable for purposes of thermodynamic research. Consequently, such mixtures are being exposed to flegmatization through dilution by one of their principle components taking part in the reaction, or by some inert gas. Dilution with inert gas allows us to maintain the required proportion among the reacting substances, and at the same time permits us to shift the region of experiments, capable of being processed, toward higher temperatures than those registered in a case where we have an excess of one of the principal components (63).

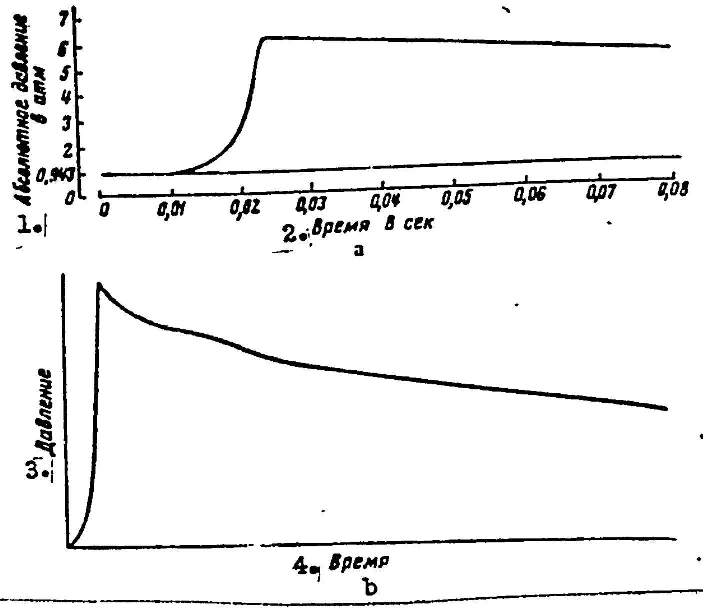


Figure 9. (a) Indicator diagram. (b) Effect of the temperature gradient on the shape of the curve of cooling (Lewis and Elbe).

(1) Absolute pressure in atm; (2) time in sec; (3) pressure; (4) time.

Apart from compression waves, several researchers were able to observe also other types of vibrations in rapidly burning mixtures, for example, fluctuations in certain slowly burning mixtures arising long before the maximum pressure is attained, irregular fluctuations in hydrogen-oxygen mixtures at low temperatures (63), and other types. The causes of these phenomena are not in all cases sufficiently firmly established.

Section 2. Degree of Equilibrium Attained during Explosions.

In computations of combustion processes connected with thermodynamic research by means of explosion and in other cases, as well as in general calculations of parameters characterizing any physical phenomena, it is customary to proceed from some definite simplifying assumptions which are apt to idealize somewhat the true conditions of experimentation. To assure correct deductions made on the basis of these calculations and comparisons of the computed quantities with those observed,

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it is important to know to what extent do these assumptions correspond to reality.

First of all, our calculations will be based on the supposition that combustion leads to the establishment of equilibrium in the mixture of combustion products behind the reaction zone. The high development rate of reactions thermodynamically possible in gases at high temperatures provides a basis for such assumptions. The fact that combustion, in case of sufficiently rapidly burning mixtures, stops instantaneously and completely is evidenced by a sharp break in the indicator graph at the point of transition from the pressure growth curve to the curve of cooling. Had the chemical changes not been termintaed by that moment, the maximum of the pressure diagram would have been rounded off. Some investigators (26, 34, 35) are inclined to interpret the secondary glow at the ignition point -- observed by a number of authors at the end of the combustion process -- as a proof that the processes do not reach equilibrium in the reaction zone. However, this point of view runs into a number of objections (18, 21, 47). In particular, it is believed that this phenomenon may be attributed to the existence of a temperature gradient.

The degree to which the postulates, on which calculations are based, correspond to the actual conditions of experimentation is often checked by comparison of the observed data on maximum explosion pressure with those calculated on the basis of thermochemical, spectroscopic, and thermodynamic constants whose certainty is beyond question. The underrated experimental values of maximum explosion pressure as compared with those obtained by calculation are usually attributed to heat losses, whose sources will be discussed in Section 3 (some authors (26) explain them by the incompleteness of chemical changes; see above). The (sometimes by a few percent) overrated experimental values of maximum pressure -- which are to be observed, for instance, in mixtures of hydrocarbons and H_2 with oxygen, with excess of the latter -- are ascribed to a delay in excitation of vibrational energy levels of certain molecules (21, 63). As a result of this, the energy initially is distributed mostly according to the progressive and rotary degrees of freedom, and the thus arising excess of forward-motion energy leads to a rise in pressure as compared to that

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which would have been registered in case of equilibrium distribution of energy according to the degrees of freedom. It should be observed here that this is not an unquestionable explanation.

Section 3. Heat Losses in Explosions in Bombs with Central Ignition

Since it is impossible to determine the precise magnitude of heat losses, experiments are carried out under such conditions when the losses of heat during the period of pressure rise are insignificantly small.

The most important source of heat losses, which may not be disregarded in case of slowly burning mixtures, is constituted by the convective upward motion of the hot combustion products (Figure 10). As a result of this, the flame initially comes in contact with the upper section of the bomb wall, which results in strong losses of heat even before the maximum explosion pressure has been reached. In this case, heat losses make the burning of the last portion of gas ineffective and the maximum of the indicator diagram therefore becomes smoother.

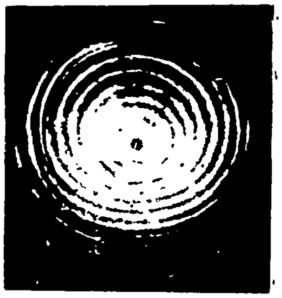

Figure 10. Convective upward motion of a slow flame (Ellis).

Heat losses through the wall, resulting from the heating of unburned mixture owing to adiabatic compression, are minor -- first of all, because the rise of temperature of gases at the wall is consequently small (see Table 17, Chapter IX), and, second, because it occurs mainly at the end of the process of combustion (37).

During the period of pressure growth, the surface of the spark electrodes (of the plug) -- which right from the moment of ignition remains in direct contact with the burning gases -- may become a substantial source of heat losses. Consequently, the ignition device should have the least possible surface and be manufactured from

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a material with the least possible heat conductivity. It should be mentioned in passing that the margin of the spark energy is too small to produce a substantial effect on the maximum pressure of explosion.

Finally, radiation constitutes an important source of heat losses. In order to reduce heat losses caused by radiation to the minimum, the internal surface of the bomb should possess a good reflecting power. Wohl and Elbe (62) explain the reduction in heat losses -- observable after the introduction of a small quantity (<1.3 mm Hg) of water vapors into the initial mixture -- by the suppression of luminescent radiation of such molecules as H_2O and OH during collisions with the unexcited molecules of water vapor. An increase of the initial pressure of the original mixture also facilitates radiation suppression.

Another explanation for the reduction of heat losses upon introduction of steam into the original mixture is based on the assumption (49) that the film of water, which may form on the inner surface of the wall in consequence of unburned gas compression, hinders a rapid recombination of hydrogen atoms which diffuse in considerable quantities from the reaction zone into the unburned gas.

Practical conclusions from the experimental material reviewed here will be drawn in Chapter IX.

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Chapter IV

GENERAL PRINCIPLES OF THERMODYNAMIC COMPUTATION OF COMBUSTION PROCESSES.

Let the state of the initial fuel-oxidizer mixture be set. Under the definite conditions (precisely those which interest us now) there will develop reactions in the system leading it to a state of equilibrium. Our task is to define this equilibrium state of the system, i.e., its chemical composition, temperature, and pressure (if combustion takes place at constant volume), or volume (if the pressure is constant). We shall set aside the question as to the manner in which this final state or that pertaining to the mechanism of combustion may be arrived at. Important is only the fact that the system is conservative and that equilibrium in it was fully established. In other words, we assume that the system is thermally totally insulated, that the distribution of temperature and pressure in the mixture of the combustion products is uniform, and that chemical equilibrium, as well as an equilibrium distribution of energy according to the degrees of freedom, are fully attained. In our calculations we shall consider also that the gaseous products of combustion behave like ideal gases. The validity of this assumption is confirmed by the analysis of equation (II.1) for T values of the order of temperatures of combustion for explosive gaseous mixtures, and for P values not exceeding 200 atm. (Calculations of explosions in which higher pressures are achieved are not discussed here.) In this case, the laws of matter conservation, energy conservation, and mass action fully determine the state of the system. The temperature calculated on the basis of these assumptions will be referred to as maximum theoretical temperature of combustion products (or briefly, combustion temperature), while pressure calculated on the same basis will be called the maximum explosion pressure.

The conditions enumerated above, in case of combustion at a constant volume, are best fulfilled in a spherical vessel with central ignition at the moment when

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the flame reaches the walls of the vessel, after the mixture has already burned out but has not yet engaged in appreciable quantities in heat exchange with the surrounding space (see Chapter III). In case of combustion at constant pressure, these conditions are observed best of all during explosions in soap bubbles. Consequently, it is precisely these methods that are being used in thermodynamic research. The computed combustion characteristic of the rapidly burning mixtures closely approach the real ones. Thus, if we are far from the ignitability limit, the calculations for assumed adiabatic burning usually amount to a sufficiently good approximation.

If the combustion temperature does not exceed 1,600-1,800° K, which in the case of ordinary fuel burning may occur under conditions of strong dilution by air or inert gas, then dissociation may be disregarded. In the simplest instance, when isomolecular exchange reactions of the type of water vapor reaction are absent, all the heat released during burning is used for the heating of combustion products. Their composition is thereby easily determined by stoichiometric equation, i.e., on the basis of the law of matter conservation, while the temperature may be computed from the heat balance equation, which in the case of burning at constant volume has the form

$$(-\Delta U^{\circ}_{T_i})_{comb.} = \sum_{k} m_k \, (U^{\circ}_{T_e} - U^{\circ}_{T_i})_k, \qquad \text{(IV.1)}$$

where $(-\Delta U^{\circ}_{T_i})_{comb.}$ - heat liberated during combustion;

$(U^{\circ}_{T_e} - U^{\circ}_{T_i})_k$ - heat of inner energy of one mole of the k-th product of combustion during its heating from temperature T_i of the initial mixture to combustion temperature T_e;

m_k - the number of moles of the k-th component in that quantity of mixture for which the calculation is made (for example, in 1 kg).

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Since

$$\frac{U_{T_e} - U_{T_i}}{T_e - T_i} = \overline{C}_v^{T_e - T_i},$$

where $\overline{C_v}^{T_e - T_i}$ - average molar thermal capacity over the range from T_i to T_e at constant volume, the heat balance equation may be written also in the form resolved with respect to temperature

$$T_e = T_i + \frac{(-\Delta U_{T_i})_{comb.}}{\sum_k n_k \overline{C}_{vk}^{T_e - T_i}} \qquad \text{(IV.2)}$$

But since average specific heats are functions of temperature, the magnitude of T_e should be found by the method of selection. The combustion temperature in the analyzed simplest case is determined by analogous equations in which the inner energy is replaced by enthalpy.

The requirement that dissociation be calculated for temperatures above 1,600-1,800°K, and the requirement for exchange reactions of the water vapor type greatly complicates computations. In this case the composition of the combustion products mixture is determined not only by the law of matter conservation alone, but simultaneously also by the law of mass action and the law of energy conservation, and depends on temperature, whereas in the absence of dissociation and exchange reactions it is independent of temperature. The mixture composition obtained in the presence of dissociation of pure carbon dioxide and water vapor at 1 atm pressure is represented in Figures 11 and 12*, respectively. The volume or pressure thus increases at high temperatures not only owing to the heating of gases, but also due to dissociation.

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* It should be noted that, contrary to the previously held views, dissociation of water into hydrogen and oxygen is not at all predominant as compared with dissociation with hydroxyl formation. From the very beginning, hydrogen and hydroxyl are present in the gas almost in equal quantities.

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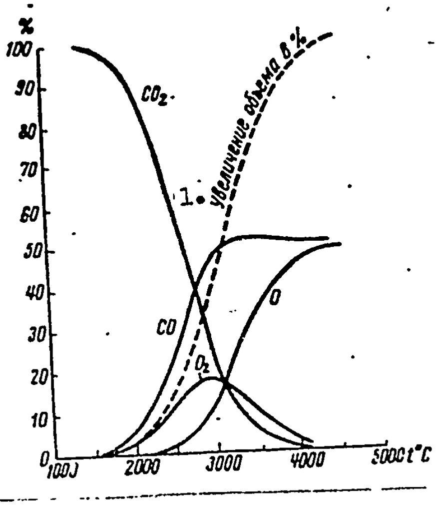

Figure 11. Composition of CO_2 dissociation products (Fehling)

(1) Volume growth in %.

Since dissociation is an endothermic process, the quantity of chemical energy changing into thermal energy decreases and the energy balance equation for the case of combustion at constant volume will assume the aspect of:

$$(-\Delta U^{\circ}_{T_i})_{\text{comb.}} = \sum_k m_k (U^{\circ}_{T_e} - U^{\circ}_{T_i})_k + \sum_j \alpha_j (\Delta U^{\circ}_{T_i})_{\text{diss } j}, \qquad \text{(IV.3)}$$

where $(\Delta U^{o}_{T_i})_{\text{diss } j}$ - heat of the j-th dissociation reaction or exchange reaction, while α_j is the coefficient determining the degree of its progress. In future we shall use a heat-balance equation of another type more convenient for calculations, but formulas (IV.1), (IV.2), and (IV.3) illustrate the principle of calculation in a more graphic way.

The substances which compose the gaseous mixture of combustion products will henceforth be referred to as mixture components. To determine the state of such a mixture of n components means to determine n+1 unknown quantities: the combustion temperature T_e, the pressure (or volume), and n-1 unknown partial pressures (or concentrations).

Hence, it is necessary to produce a system of n+1 equations. In view of the complexity of this system, it is more convenient to solve it by the method of selection, in setting different temperature values and seeking that value which satisfies the energy balance equation.

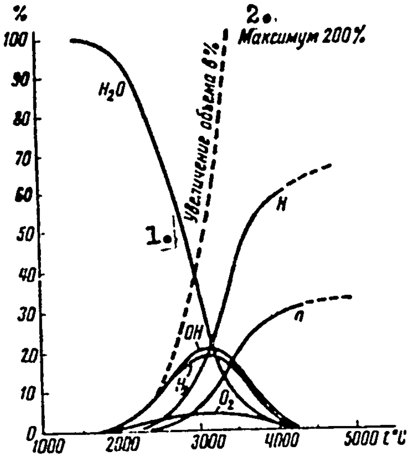

Figure 12. Composition of H_2O dissociation products (Fehling).
(1) Volume growth in %; (2) maximum 200%.

The calculation for each set temperature is made in two stages: (1) calculation of the composition, which for the given temperature is determined by equilibrium constants and equations of material balance for each element, and (2) calculation of intrinsic energy (or enthalpy) of the combustion products mixture. It is in this plane that analysis will be made below of the computation methods in the case of constant volume and constant pressure.

Here we should emphasize the importance of a rough preliminary evaluation of the composition of the combustion products with a view to ascertaining what components of the mixture should be taken into consideration in precise calculations. Such preliminary calculations may be made, for example, by the method of successive approximations (see Chapter VIII, Section 1) for all substances, whose heats of formation and the thermodynamic functions are known, or may be computed, from molecular constants (see Appendix 1).

The freely expanding flames perform work against external pressure, whereby a proportion of heat is being additionally consumed. Consequently, combustion temper-

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ature at constant pressure must be lower than combustion temperature at constant volume of the same initial mixture if all other initial conditions are identical. Let it be noted, that thermodynamic calculation of combustion at constant pressure is more complex than computation of combustion at constant volume.

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Chapter V

CALCULATION OF COMBUSTION PROCESSES AT CONSTANT VOLUME

Let the composition of the initial mixture, its pressure, and temperature T_1 be set. Our task is to determine the equilibrium state of the given system which will be attained by it at constant volume. For reasons previously given, it is more expedient first to consider the problem pertaining to the determination of the state of mixture at the fixed temperature. For this purpose it suffices to determine only n unknown quantities: n-1 partial pressures (or concentrations) and the total pressure of the system. From now on we shall consider the n partial pressures as independent variables, while total pressure $P = \sum_{k=1}^{n} p_k$ will be assumed as a dependent quantity.

Section 1. Determination of the Composition of the Mixture of Combustion Products at a Given Temperature

(1) Chemical Equilibrium Constants

Ya. B. Zel'dovich was able to prove in a general form that for a mixture of reacting gases the system of equations ensuing from the law of mass action, together with superimposed conditions of matter conservation, when the values of T and V or T and P are given, always has only one positive material solution (15). In other words, the composition of the mixture, i.e., the n partial pressures (or n concentrations) of its components are unambiguously determined by the law of matter conservation and the law of mass action. If the mixture is formed by m chemical elements, the law of matter conservation produces m equations of material balance for each of the elements. Moreover, the quantity of each of them is determined by the composition of the initial mixture. The remaining n-m equations, necessary for the determination of the n unknown quantities, may be produced on the basis of the law of mass action in the form of equilibrium equations. Consequently, it is necessary

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to know n-m unknown equilibrium constants. It is obvious, too, that on their basis any other equilibrium constants may be found for the determination of the ratio between the partial pressures (or concentrations) of the mixture components. But this is tantamount to an assertion that there exist but n-m equations of reactions which in the thermodynamical sense may be regarded as independent. Equations for any other reactions* imaginable for this system may be derived from these n-m independent equations. This, in turn, means that it suffices to know the heat content changes in n-m reactions in order to be able to calculate the thermal effect of any conceivable reaction in the system formed by these elements. Thus, we obtain a simple rule:

The number of independent reaction equations in a closed system remaining in the state of chemical equilibrium, equal to the number of independent equilibrium constants and equal to the number of independent thermal effects of reactions, is equal to the number of components, less the number of elements composing this system**.

Let us, for example, assume that we have a system formed by two elements -- hydrogen and oxygen. We shall write down all the possible reactions, which are conceivable for the state of equilibrium, and their corresponding chemical equilibrium constants***, while maintaining the designations adopted by us:

$$(1)\ H_2O \rightleftarrows H_2 + \frac{1}{2} O_2 \qquad K_2 = \frac{p_{H_2} \sqrt{p_{O_2}}}{p_{H_2O}}$$

$$(2)\ H_2O \rightleftarrows OH + \frac{1}{2} H_2 \qquad K_3 = \frac{p_{OH} \sqrt{p_{H_2}}}{p_{H_2O}}$$

$$(3)\ H_2 \rightleftarrows 2H \qquad K_4 = \frac{p_H^2}{p_{H_2}}$$

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* We are not going into the question as to the extent to which these or other reactions are realistic from the point of view of their mechanism.

** An exception to this rule is constituted by the case when two elements making part of the one and same component are not included in any other component of the system. However, such exceptions are fairly seldom encountered in combustion calculations.

*** The numerical values of equilibrium constants and their logarithms are to be found in Appendix IV (tables II and III).

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(4) $O_2 \rightleftarrows 2O$ $\quad K_5 = \frac{p_O^2}{p_{O_2}}$

(5) $H_2O \rightleftarrows H_2 + O$ $\quad K_9 = \frac{p_{H_2} \cdot p_O}{p_{H_2O}}$

(6) $H_2O \rightleftarrows 2H + \frac{1}{2} O_2$ $\quad K_{16} = \frac{p_H^2 \cdot \sqrt{p_{O_2}}}{p_{H_2O}}$

(7) $H_2O \rightleftarrows OH + H$ $\quad K_{17} = \frac{p_{OH} \cdot p_H}{p_{H_2O}}$

(8) $H_2O \rightleftarrows 2H + O$ $\quad K_{18} = \frac{p_H^2 \cdot p_O}{p_{H_2O}}$

(9) $H_2O + \frac{1}{2} O_2 \rightleftarrows 2OH$ $\quad K_{19} = \frac{p_{OH}^2}{p_{H_2O} \sqrt{p_{O_2}}}$

(10) $OH \rightleftarrows O + H$ $\quad K_{20} = \frac{p_O \cdot p_H}{p_{OH}}$

We have two elements -- hydrogen and oxygen -- and six components: H_2O, H_2, O_2, OH, H, O. Consequently, only 6-2 = 4 reaction equations are independent. Of course, none of the four equations of the recorded series form a system of independent equations. For instance, among equations (2), (3), (4) and (7), equation (7) is a consequence of (2) and (3), whereas equation (4) is composed of components which are not included in any of the remaining equations. At the same time (1), (2), (3), (4); (1), (2), (3), (5); (1), (3), (4), (7) constitute systems of independent equations. Assuming as independent the equilibrium constants of reactions (1), (2), (3), and (4) -- K_2, K_3, K_4, and K_5 -- we may derive from them the equilibrium constants for all the remaining reactions

$$K_9 = K_3 \sqrt{K_5}, \quad K_{18} = K_2 \cdot K_4 \sqrt{K_5},$$
$$K_{16} = K_3 \cdot K_1, \quad K_{19} = \frac{K_3^2}{K_3},$$
$$K_{17} = K_3 \sqrt{K_1}; \quad K_{20} = \frac{K_3 \sqrt{K_4 \cdot K_5}}{K_3}.$$

Thus, on the basis of thermodynamic functions and thermal effects only, n-m independent equilibrium constants should be calculated. The selection of equilibrium constants for the computation of the composition of the mixture of combustion products is determined by considerations of mathematical expediency and may be changed from case to case.

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Normally, the state of ideal gas at 1-atm pressure is taken for standard state and in conformance therewith the equilibrium constants are expressed through partial pressures. It is, of course, possible to assume for standard state the state of ideal gas with 1 mole/cm^3 concentration, and calculate K_c instead of K_p, but this is less convenient. Henceforward, we shall exclusively use constants expressed through partial pressure and denote them simply by the letter K.

(2) Material-Balance Equations

The number of atoms (gram-atoms) of a given element l, contained in any substance forming part of a closed system, is equal to the number of its atoms in a molecule of this substance, multiplied by the number of molecules (gram-molecules) of substance k in the given system. The number of gram-atoms of an element in the system, (m) , is equal to the sum of the number of its gram-atoms in all substances constituting the system:

$$[m]_l = \sum_k l_k m_k, \qquad (V.1)$$

where l_k is the number of atoms of the l-th element in the k-th component, m_k is the number of moles of the k-th component in the system.

If, for instance, H_2O, CO_2, H_2, O_2, OH, H, O, CO are the components of the system, then

$$\left.\begin{aligned} [m]_C &= m_{CO_2} + m_{CO}; \\ [m]_H &= 2m_{H_2O} + 2m_{H_2} + m_{OH} + m_H; \\ [m]_O &= m_{H_2O} + 2m_{CO_2} + 2m_{O_2} + m_{OH} + m_O + m_{CO}. \end{aligned}\right\} \qquad (V.2)$$

In a closed system, the number of atoms of each of the elements composing the system and, consequently, also the number of its gram-atoms, remains unaltered during all chemical changes (law of conservation of matter).

By virtue of this we have:

$$\sum_k l_k m_{ek} = \sum_j l_j m_{ij}, \qquad (V.3)$$

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where ℓ_k and ℓ_j are the numbers of atoms of the ℓ-th element in the k-th component of the combustion product mixture, and in the j-th component of the initial mixture, respectively; m_{ek} and m_{ij} are the numbers of moles of the k-th component of the equilibrium mixture and of the j-th component of the initial mixture, respectively.

It is convenient to pass from molar concentrations to partial pressures, since it is precisely through them that we express the equilibrium constants used, and, in addition to this, the composition of the initial mixture is also given in partial pressures of the substances of which it is composed. If instead of the number of moles of the components it is desired to record their partial pressures in the left-hand side of equation (V.3) a factor $\frac{P_e}{\Sigma m_e}$ must be introduced, where P_e is the total pressure in the system at state of equilibrium, while Σm_e is the total number of moles of all components. This gives us:

$$\sum_k l_k p_k = \frac{P_e}{\Sigma m_e} \sum_j l_j m_{ij}. \qquad (V.4)$$

Since the volume of system V = const,

$$\frac{P_e}{\Sigma m_e} = \frac{P_i}{\Sigma m_i} \cdot \frac{T_e}{T_i}, \qquad (V.5)$$

and insofar as

$$m_{ij} \frac{P_i}{\Sigma m_i} = p_{ij},$$

we finally produce (25):

$$\sum_k l_k p_{ek} = \frac{T_e}{T_i} \sum_j l_j p_{ij}. \qquad (V.6)$$

Thus, equations of material balance expressed through partial pressures are composed according to the same rule as the equations expressed through molecular concentrations, with the sole difference that the partial pressures of the initial substances are multiplied by ratio $\frac{T_e}{T_i}$, where T_e is the temperature at which the composition of the combustion products mixture is calculated.

Let, for example, the initial mixture be composed of methane and oxygen in quantities of m_{iCH_4} and m_{iO_2} moles, respectively. In this case:

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$$[m]_C = m_{iCH_4};\quad [m]_H = 4m_{iCH_4};\quad [m]_O = 2m_{iO_2}. \tag{V.7}$$

If, while burning, this mixture comes into the state of equilibrium, then, as we can see from the comparison of equations (V.7) and (V.2), we will have the following relationships:

$$\left.\begin{aligned} m_{CO_2} + m_{CO} &= m_{iCH_4};\\ 2m_{H_2O} + 2m_{H_2} + m_{OH} + m_H &= 4m_{iCH_4};\\ m_{H_2O} + 2m_{CO_2} + 2m_{O_2} + m_{OH} + m_O + m_{CO} &= 2m_{iO_2}. \end{aligned}\right\} \tag{V.8}$$

In passing on to partial pressure, we produce by the method described above:

$$\left.\begin{aligned} p_{CO_2} + p_{CO} &= p_{iCH_4}\cdot\frac{T_e}{T_i};\\ 2p_{H_2O} + 2p_{H_2} + p_{OH} + p_H &= 4p_{iCH_4}\cdot\frac{T_e}{T_i};\\ p_{H_2O} + 2p_{CO_2} + 2p_{O_2} + p_{OH} + p_O + p_{CO} &= 2p_{iO_2}\cdot\frac{T_e}{T_i}. \end{aligned}\right\} \tag{V.9}$$

This expression may be readily obtained on the basis of equation (V.6).

Let us introduce the following designations:

$$\left.\begin{aligned} p_{iCH_4}\cdot\frac{T_e}{T_i} &= \{p\}_C;\\ 4p_{iCH_4}\cdot\frac{T_e}{T_i} &= \{p\}_H;\\ 2p_{iO_2}\cdot\frac{T_e}{T_i} &= \{p\}_O; \end{aligned}\right\} \tag{V.10}$$

in general

$$\frac{T_e}{T_i}\sum_j l_j p_{ij} = \{p\}_l, \tag{V.11}$$

and call $\{p\}_C$, $\{p\}_H$, $\{p\}_O$, $\{p\}_l$ the conditional partial pressures of atomic concomponents. The meaning of these expressions may be grasped from the following considerations. Let the substances, which compose the initial mixture, become decomposed totally down to the atoms. Since V = const, T = const $\frac{P}{\sum m}$ = const, i.e., in the process of dissociation the pressure pertaining to one gram-molecule, or one

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gram-atom, does not change. Hence, from equation (V.7) for pressures of atomic gases in case of total dissociation at temperature T_i, we shall obtain the following expressions:

$$\{p_i\}_C = p_{i\,CH_4};\quad \{p_i\}_H = 4p_{i\,CH_4};\quad \{p_i\}_O = 2p_{i\,O_2}.$$

If the gas dissociated to atoms should be now heated up to temperature T_e, the atomic components of the mixture would have pressures determinable by formulas (V.10). Hence, $\{p\}_C$, $\{p\}_H$, $\{p\}_O$ are the pressures which the atomic gases C, H, and O would have at temperature T_e, if all the substances of the system had been decomposed to atoms.

(3) Calculation of the Partial Pressures of the Products of Combustion

To calculate the partial pressures of n components formed by m elements, it is necessary to solve a system of n equations: m equations of material balance, and n-m equilibrium equations. If, by way of successive exclusion of the unknown quantities, the system is reduced to one equation, we would get a high-degree equation whose solution in general form is impossible (see Chapter VIII, Section 4). It is often possible -- by means of arbitrary setting of partial pressure of one of the components -- to break the system of equations up into a series of "subsystems" which, upon successive solution, lead to equations of a degree not higher than second. By changing the partial pressure set, we may select those of its value at which all equations of the system will be satisfied with required precision*.

We shall analyze this method by taking a system formed by carbon, hydrogen, and oxygen as an example. Let some hydrocarbon, or, say, a mixture of hydrocarbons, burn in oxygen. The following eight gases **: CO_2, CO, H_2O, H_2, O_2, OH, H and O would then constitute the products of combustion forming an equilibrium mixture at high temperature.

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* Other methods of solution of this type of system of equations are considered in Chapter VIII.

** Here, and further on, we shall restrict our analysis to the case when $(m)_O > (m)_C$. When $(m)_O < (m)_C$, account should be taken of the formation of compounds of the C_mH_n type and of free carbon. Incidentally, if at the same time the upper limit of ignition turns out to be close, additional difficulties arise which are connected, as certain investigators believe (44), with the low rate of carbon condensation, but which very possibly also be related to other phenomena which hinder the establishment of a thermodynamic equilibrium.

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Hence, to determine the partial pressures of the mixture components it is necessary to compose a system of eight equations. We have three equations of material balance:

$$p_{CO_2}+p_{CO}=\{p\}_C; \qquad (V.12)$$

$$2p_{H_2O}+2p_{H_2}+p_{OH}+p_H=\{p\}_H; \qquad (V.13)$$

$$2p_{CO_2}+p_{CO}+p_{H_2O}+2p_{O_2}+p_{OH}+p_O=\{p\}_O. \qquad (V.14)$$

For all cases, with the exception of that when there is a great excess of oxygen, it is most convenient to select as independent equilibrium constants the following five.

$$K_6=\frac{p_{CO_2}\cdot p_{H_2}}{p_{CO}\cdot p_{H_2O}}; \qquad (V.15)$$

$$K_7=\frac{p_{H_2}^2\cdot p_{O_2}}{p_{H_2O}^2}; \qquad (V.16)$$

$$K_8=\frac{p_{OH}\sqrt{p_{H_2}}}{p_{H_2O}}; \qquad (V.17)$$

$$K_9=\frac{p_H}{\sqrt{p_{H_2}}}; \qquad (V.18)$$

$$K_9=\frac{p_{H_2}\cdot p_O}{p_{H_2O}}. \qquad (V.19)$$

If constants $K_1 = \frac{p_{CO}\sqrt{p_{O_2}}}{p_{CO_2}}$, K_2, K_3, K_4 and K_5 are calculated on the basis of thermodynamic functions and thermal effects (see above), K_6, K_7, K_8, and K_9 may be determined from formulas:

$$\left.\begin{aligned} \lg K_6 &= \lg K_2 - \lg K_1; \\ \lg K_7 &= 2\lg K_3; \\ \lg K_8 &= \frac{1}{2}\lg K_1; \\ \lg K_9 &= \lg K_2 + \frac{1}{2}\lg K_5. \end{aligned}\right\} \qquad (V.20)$$

If we set the value of the partial pressure of one of the eight components, only seven equations will be required for the determination of the remaining unknown. The eighth, for example (V.14) -- the most cumbersome of the balance equations -- could be used to check the accuracy of selection of the arbitrarily set value of partial

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pressure.

We shall fix the magnitude of p_{H_2}*. Then

$$p_{H} = K_8 \sqrt{p_{H_2}}. \qquad (V.21)$$

Furthermore, in solving the system composed of equations (V.13) and (V.17), we obtain:

$$p_{H_2O} = \frac{\{p\}_H \quad p_H - 2p_{H_2}}{2 + \frac{K_3}{\sqrt{p_{H_2}}}}; \qquad (V.22)$$

$$p_{OH} = p_{H_2O} \cdot \frac{K_3}{\sqrt{p_{H_2}}} = \{p\}_H - p_H - 2p_{H_2} - 2p_{H_2O}. \qquad (V.23)$$

We further have

$$p_0 = K_9 \cdot \frac{p_{H_2O}}{p_{H_2}}; \qquad (V.24)$$

$$p_{O_2} = K_7 \left(\frac{p_{H_2O}}{p_{H_2}}\right)^2. \qquad (V.25)$$

Finally, in solving the system of equations (V.12) and (V.15), we find:

$$p_{CO} = \frac{\{p\}_C}{1 + K_6 \cdot \frac{p_{H_2O}}{p_{H_2}}}; \qquad (V.26)$$

$$p_{CO_2} = \left(K_6 \cdot \frac{p_{H_2O}}{p_{H_2}}\right) p_{CO} = \{p\}_C - p_{CO}. \qquad (V.27)$$

The value of p_{H_2} is varied in such a manner that the difference between the right-hand side and the left-hand side of equation (V.10)

$$D_0 = (2p_{CO_2} + p_{CO} + p_{H_2O} + 2p_{O_2} + p_{OH} + p_0) - \{p\}_0 \qquad (V.28)$$

should tend to zero. At the same time it is advisable that a D_0 to p_{H_2} curve be constructed which would permit a more rapid approach to the true value of p_{H_2} by means of interpolation. In most cases it suffices to fulfill the condition:

$$|D_0| \leqslant 0{,}001 \{p\}_0. \qquad (V.29)$$

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*The calculation scheme of partial pressures reviewed here was borrowed from the work by Zel'dovich and Polyarny (16).

For technical calculations of combustion at high temperature, such accuracy is often even superfluous.

The accuracy up to three to four decimals is usually sufficient for partial pressures of components when P_e is of the order of 10-20 atm. It should, however, be noted that excessive rounding off of figures in the process of calculation of partial pressures may lead to irregular fluctuations which will prevent us from attaining the precision determined by condition (V.29). If we use the same scheme in case of a large excess of oxygen, the accuracy of the intermediate operations should be greater, since D_o becomes very sensitive to the changes of p_{H_2}.

In those cases when -- apart from C, H, and O -- nitrogen is also present in the system, three more components -- N_2, NO, and N -- must be added to the said eight components if the temperatures are high. Correspondingly, the system of equations must be supplemented by three new equations: the balance equation for nitrogen

$$2p_{N_2}+p_{NO}+p_N=\{p\}_N$$

and two equilibrium equations. By way of the latter, in cases when the system of equations is to be solved by method of p_{H_2} selection, it is convenient to take

$$\frac{p_{H_2}\cdot p_{NO}}{p_{H_2O}\cdot\sqrt{p_{N_2}}}=K_{15};\qquad \frac{p_N}{\sqrt{p_{N_2}}}=K_{14}.$$

Besides, in the balance equation for oxygen, there will appear a new member, i.e., p_{NO}.

The partial pressures of N_2, NO, and N are determined by formulas:

$$p_{N_2}=\left(\frac{\sqrt{\left(K_{14}+K_{15}\cdot\frac{p_{H_2O}}{p_{H_2}}\right)^2+8\{p\}_N}-\left(K_{14}+K_{15}\cdot\frac{p_{H_2O}}{p_{H_2}}\right)}{4}\right)^2;$$

$$p_{NO}=K_{15}\cdot\frac{p_{H_2O}}{p_{H_2}}\sqrt{p_{N_2}};$$

$$p_N=K_{14}\sqrt{p_{N_2}}.$$

Since p_{NO} and p_N are usually small as compared with p_{N_2}, the method of successive approximations, outlined in Chapter VIII, Section 1, may also be applied for their determination.

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When there is an excess of oxygen, it is often convenient to make use of another scheme, in arbitrarily fixing the value of p_{O_2} and in utilizing the following equilibrium constants to compose the system of equations.

$$K_1 = \frac{p_{CO}\sqrt{p_{O_2}}}{p_{CO_2}}; \qquad (V.30)$$

$$K_2 = \frac{p_{H_2}\sqrt{p_{O_2}}}{p_{H_2O}}; \qquad (V.31)$$

$$K_{10} = \frac{p_{OH}}{\sqrt{p_{H_2O}}\sqrt[4]{p_{O_2}}}; \qquad (V.32)$$

$$K_{11} = \frac{p_H\sqrt[4]{p_{O_2}}}{\sqrt{p_{H_2O}}}; \qquad (V.33)$$

$$K_{12} = \frac{p_O}{\sqrt{p_{O_2}}}. \qquad (V.34)$$

Constants K_{10}, K_{11}, and K_{12} may be calculated from constants K_2, K_3, K_4, and K_5 on the basis of formulas:

$$\left.\begin{aligned} \lg K_{10} &= \lg K_3 - \frac{1}{2}\lg K_2; \\ \lg K_{11} &= \frac{1}{2}(\lg K_3 + \lg K_4); \\ \lg K_{12} &= \frac{1}{2}\lg K_5. \end{aligned}\right\} \qquad (V.35)$$

The partial pressures of the products of combustion may be calculated as follows:

$$p_O = K_{12}\sqrt{p_{O_2}}; \qquad (V.36)$$

$$p_{CO_2} = \frac{\{p\}_C}{1 + \frac{K_1}{\sqrt{p_{O_2}}}}; \qquad (V.37)$$

$$p_{CO} = \frac{K_1}{\sqrt{p_{O_2}}} \cdot p_{CO_2} = \{p\}_C - p_{CO_2}; \qquad (V.38)$$

$$p_{H_2O} = \left(\frac{\sqrt{f^2 + 4h\{p\}_H} - f}{2h}\right)^2, \qquad (V.39)$$

where

$$f = \frac{K_{11}}{\sqrt[4]{p_{O_2}}} + K_{10}\sqrt[4]{p_{O_2}}, \quad h = 2\left(\frac{K_2}{\sqrt{p_{O_2}}} + 1\right). \qquad (V.40)$$

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The accuracy of p_{O_2} value selection is checked by equation (V.28).

If nitrogen is present -- and if the system of equations is handled on the basis of the method of p_{O_2} selection -- the following equations must be added to the five independent equilibrium equations (V.30) to (V.34):

$$\frac{p_{NO}}{\sqrt{p_{N_2}}\sqrt{p_{O_2}}} = K_{13}; \quad \frac{p_N}{\sqrt{p_{N_2}}} = K_{14}.$$

The partial pressures N_2, NO and N can be determined by the formulas:

$$p_{N_2} = \left(\frac{\sqrt{(K_{13}\sqrt{p_{O_2}} + K_{14})^2 + 8\{p\}_N} - (K_{13}\sqrt{p_{O_2}} + K_{14})}{4}\right)^2;$$

$$p_{NO} = K_{13}\sqrt{p_{O_2}}\sqrt{p_{N_2}};$$

$$p_N = K_{14}\sqrt{p_{N_2}}.$$

Although this scheme is more cumbersome than the preceding one, it permits us to select immediately a value for p_{O_2} fairly closely approaching to the final value in the case where we have a considerable excess of oxygen. If, for instance, hydrocarbon C_nH_m burns in excess oxygen with excess coefficient α (constituting the ratio of the quantity of oxygen taken to stoichiometric oxygen), the reaction equation might be written in the form

$$C_nH_m + \alpha\left(n + \frac{m}{4}\right)O_2 = nCO_2 + \frac{m}{2}H_2O + (\alpha - 1)\left(n + \frac{m}{4}\right)O_2 \qquad (V.41)$$

(with $\alpha > 1$).

It follows that, had there been no dissociation, the partial pressure of oxygen in the mixture of combustion products at temperature T_e would have been

$$p_{O_2} = \frac{\alpha - 1}{\alpha} p_{iO_2} \cdot \frac{T_e}{T_i}. \qquad (V.42)$$

This value actually may be assumed as initial for calculations when there is a considerable excess of oxygen.

Besides, D_0 proves to be considerably less sensitive to the changes in p_{O_2}, than to those of p_{H_2}.

Section 2. Determination of Combustion Temperature and Maximum Pressure of Explosion

We can visualize that the initial mixture may burn up at starting temperature

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T_i. Thereupon dissociation of combustion products takes place and exchange reactions develop which lead the system to a composition corresponding to equilibrium at combustion temperature T_e, whereby part of the heat released in combustion is being consumed. After this the mixture is heated to temperature T_e. The corresponding thermal-balance equation looks like equation (IV.3). Moreover, the coefficient α_j, determining the degree of the j-th reaction development, may be computed if the equilibrium composition of the combustion products is known.

Yet, a separate consideration of physical heat and chemical energy is inconvenient in computations. To consider simultaneously the entire energy, it is necessary to stipulate the beginning of the scale for its recording.

(1) Selecting the origin of the scale for reading energy

For calculation of thermodynamic quantities, the zero level of the molecule of a given substance is taken as the zero of energy level. The increment of intrinsic energy or enthalpy is calculated for different temperatures in relation to this level. The experimental values of thermal effects of reactions permit us to compute the difference between the zero-level energies of different types of molecules, or, in other words, the difference between the values of intrinsic energy of different substances. The variation of the intrinsic energy of a system in the process of reaction, extrapolated to absolute zero, is in essence the difference in chemical energy reserves between the products of reaction and the initial substance.

As was shown previously, when n components formed by m chemical elements, are present in the system, there are but n-m independent equations and n-m independent heats of reactions accordingly. We can therefore, compose only n-m equations to determine the absolute values of the intrinsic energy or enthalpy of n substances. Consequently, the values of inner energy or enthalpy of m components must be fixed arbitrarily. The enthalpy of the m elements themselves is often set equal to zero at the temperature of 298.16° K. Then the "absolute" enthalpy of any substance at this temperature will be equal to the heat of formation of this substance from the

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element at constant pressure and the same temperature. But for our purposes it is more convenient (16) to take for the beginning of the energy scale the energy at absolute zero of the m most "exothermic" substances, i.e., the m-number of those components whose formation from the other components of the given system proceeds with liberation of heat and, consequently, toward the formation of which a shift is to be registered of chemical equilibrium during the cooling of the gas mixture containing an excess of oxygen. Owing to this selection of the energy scale zero, the "absolute" values of intrinsic energies and enthalpies of all substances forming a given system turn out to be not negative at any temperature.

By way of an example, we shall consider a system made up of carbon, hydrogen, and oxygen. As we stated above, such a system at a high-temperature equilibrium is composed of eight components. Pursuant to the adopted rule for the selection of the energy scale zero, the intrinsic energy at 0° K ($U_0^0 = H_0^0$) of gaseous water, carbon dioxide, and oxygen will be set equal to zero. The inner energy of the remaining five components at 0° K is calculated on the basis of the thermal effect values of the five "independent" reactions* extrapolated to absolute zero. The following will be considered as such**

$$(1)\quad CO_2 \rightleftarrows CO + \frac{1}{2} O_2; \qquad \Delta H^{\bullet}_{01} = 66{,}760;$$

$$(2)\quad H_2O \rightleftarrows H_2 + \frac{1}{2} O_2; \qquad \Delta H^{\bullet}_{02} = 57{,}113;$$

$$(3)\quad H_2O \rightleftarrows OH + \frac{1}{2} H_2; \qquad \Delta H^{\bullet}_{03} = 63{,}000;$$

$$(4)\quad \frac{1}{2} H_2 \rightleftarrows H; \qquad \Delta H^{\bullet}_{08} = 51{,}241;$$

$$(5)\quad \frac{1}{2} O_2 \rightleftarrows O; \qquad \Delta H^{\bullet}_{012} = 58{,}680.$$

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* Namely the reactions whose gross equations are independent. The method of extrapolation of the experimentally observed thermal effects to absolute zero is outlined in Appendix I.

** We adopted the same values of thermal effects here as those on the basis of which the tables of equilibrium constants and enthalpies were prepared; see Appendix IV.

We have:

$$\Delta H^{\circ}_{01} = H^{\circ}_{0\mathrm{CO}} + \frac{1}{2} H^{\circ}_{0\mathrm{O}_2} - H^{\circ}_{0\mathrm{CO}_2},$$

and since it was agreed that $H^{o}_{0}O_2 = 0$ and $H^{o}_{0}CO_2 = 0$,

$$H^{\circ}_{0\mathrm{CO}} = \Delta H^{\circ}_{01} = 66{,}760.$$

Further

$$\Delta H^{\circ}_{02} = H^{\circ}_{0\mathrm{H}_2} + \frac{1}{2} H^{\circ}_{0\mathrm{O}_2} - H^{\circ}_{0\mathrm{H}_2\mathrm{O}},$$

and because

$$H^{\circ}_{0\mathrm{H}_2\mathrm{O}} = 0, \quad \text{TO} \quad H^{\circ}_{0\mathrm{H}_2} = \Delta H^{\circ}_{02} = 57{,}113.$$

We further have:

$$\Delta H^{\circ}_{03} = H^{\circ}_{0\mathrm{OH}} + \frac{1}{2} H^{\circ}_{0\mathrm{H}_2} - H^{\circ}_{0\mathrm{H}_2\mathrm{O}},$$

whence

$$H^{\circ}_{0\mathrm{OH}} = \Delta H^{\circ}_{03} - \frac{1}{2} H^{\circ}_{0\mathrm{H}_2} = 34{,}444.$$

In a similar way we get:

$$H^{\circ}_{0\mathrm{H}} = \Delta H^{\circ}_{08} + \frac{1}{2} H^{\circ}_{0\mathrm{H}_2} = 79{,}797;$$

$$H^{\circ}_{0\mathrm{O}} = \Delta H^{\circ}_{012} = 58{,}680.$$

While having the "absolute" enthalpy values of the components at 0° K at out disposal, we may calculate their absolute enthalpies at any given temperature according to formula:

$$H^{\circ}_{T} = H^{\circ}_{0} + (H^{\circ}_{T} - H^{\circ}_{0}). \qquad \text{(V.43)}$$

Quantities $H^{o}_{T} - H^{o}_{0}$ are calculated by the methods of statistical thermodynamics (see Appendix I). Tables of "absolute" molar enthalpies of certain substances composed in this manner are to be found in Appendix IV.

The enthalpy of initial substances is calculated in a similar way from the same zero. For enthalpy calculation of fuel we may use either the data on the heat of combustion or the data on the heat of its formation from the elements. The values of these quantities, as recorded in manuals, are as a rule related to 25° C (298.16° K) with the heat of combustion being usually given in terms of liquid water formation whose enthalpy may be computed in the following manner:

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$H_2O(liq) \rightleftarrows H_2O(gas)$; $\Delta H^o_{208.16}$ steaming = 10,520 $\frac{Kcal}{mole}$[20].

Whereupon:

$$H^\circ_{298.16\,H_2O\,(l.)} = H^\circ_{298.16\,H_2O\,(g)} - \Delta H^\circ_{298.16}\text{steam} = 2{,}365 - 10{,}520 = -8{,}155\,\frac{Kcal}{mole}.$$

If we use this quantity and the data of Table 1 and Appendix IV, we can determine the enthalpy at temperature T of any fuel composed of elements C, H, O, and N by solving equation (V.44) in relation to the enthalpy of the corresponding substance:

$$(-\Delta H^\circ_T)_{fuel} = \sum_j \nu_j H^\circ_{Tj} - \sum_k \nu_k H^\circ_{Tk}. \qquad (V.44)$$

Here ν - stoichiometric coefficients; index j refers to the initial substances and index k refers to products of combustion. Values of $(-\Delta H^o_T)$ comb. for hydrocarbons may be found, for instance, in symposium (19).

Table 1

Substance	Enthalpy at 298.16° K
Carbon (β-graphite) Hydrogen, H_2 (gas) Oxygen, O_2 (gas) Nitrogen, N_2 (gas)	94,220 59,128 2,070 2,072
Cargon dioxide, CO_2 Water vapor, H_2O	2,238 2,365

For the calculation of the enthalpy of a substance according to the heat of its formation from elements, use should be made of equation (V.45):

$$H^\circ_{T\,subst.} = \sum \nu_{el} H^\circ_{T\,el} + \Delta H^\circ_{form}. \qquad (V.45)$$

The values of H^o_T el for T = 298.16° K are recorded in Table 1. The enthalpy of β-graphite is calculated on the basis of its heat of combustion at 298.16° K (20). The values of $H^o_{298.16} - H^o_0$, used for the calculation of the data, and recorded in Table 1, are borrowed from the article by Wagman, Kilpatrick, et al. (58).

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The values of intrinsic energy may be computed from formula $U^{o}_{T} = H^{o}_{T} - RT$. However, the use of the enthalpy table may be considered as quite sufficient.

(2) Energy-Balance Equation

Having selected the energy-scale zero point by arbitrarily fixing the intrinsic energy values for a definite number of components, equal to the number of elements forming the given system, we obtain, for the case of combustion at constant value, an energy-balance equation of the type (compare with IV.3) of:

$$U_{T_e\,\text{prod}} = U_{T_i}\,\text{init.} \qquad \text{(V.46)}$$

where U_{T_e} prod is the intrinsic energy of the mixture of combustion products at combustion temperature T_e, U_{T_i}init is the intrinsic energy of the initial mixture at starting temperature T_i. Let it be noted that U_{T_i} init includes the heat of combustion of the initial mixture, while U_{T_e} prod includes the heat of the combustion products heating to T_e and the energies of dissociation reactions and endothermic exchange reactions.

The inner energy of a definite quantity of a mixture of substances may be found by several methods.

(a) Let us calculate the inner energy of G grams of mixture. We have:

$$U_T = \sum_k m_k U^{\circ}_{Tk} \qquad \text{(V.47)}$$

or

$$U_T = \sum_k m_k H^{\circ}_{Tk} - \left(\sum m\right) RT, \qquad \text{(V.48)}$$

where $U^{o}_{T}k$ and $H^{o}_{T}k$ - "absolute" value of the molar intrinsic energy, or , respectively, of the k-th substance enthalpy, m_k - number of the k-th substance moles in G grams of mixture (this quantity will from now on also be referred to as molar concentration), $\sum m$ - total number of moles of all substances forming a given system in G grams of mixture.

The molar composition of a given quantity of fuel mixture is calculated on the basis of the following considerations. Let the mixture be composed of substances

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A_1, A_2, A_3, ... A_n. It is necessary to determine their molar concentrations m_{A_1}, m_{A_2}, m_{A_3}, ... m_{A_n} in G grams of mixture. We shall introduce designations:

$$\frac{m_{A_2}}{m_{A_1}} = a_1, \quad \frac{m_{A_3}}{m_{A_1}} = a_2, \ldots, \quad \frac{m_{A_n}}{m_{A_1}} = a_{n-1}. \qquad (V.49)$$

The magnitude of these ratios may be easily computed from the initial conditions. For example, if hydrocarbon C_nH_m is the fuel, then, at excess oxygen coefficient α,

$$\frac{m_{iO_2}}{m_{iC_nH_m}} = \alpha\left(n + \frac{m}{4}\right). \qquad (V.50)$$

The number of such ratios is one unit smaller than the number of the unknown molar concentrations. Besides, we have the condition:

$$m_{A_1}\mu_{A_1} + m_{A_2}\mu_{A_2} + m_{A_3}\mu_{A_3} + \ldots + m_{A_n}\mu_{A_n} = G \qquad (V.51)$$

where μ_{A_1}, μ_{A_2}, μ_{A_3}, ...μ_{A_n} - molecular weights of substances A_1, A_2, A_3, ...A_n.

In solving (V.51) together with equations (V.49) recorded above, we obtain

$$m_{A_1} = \frac{G}{\mu_{A_1} + a_1\mu_{A_2} + a_2\mu_{A_3} + \ldots + a_{n-1}\mu_{A_n}} \qquad (V.52)$$

The molar concentrations of the remaining substances are computed from equations (V.49).

(b) Let us now replace the molar concentrations in the formula for intrinsic energy of mixture by partial pressures. We have:

$$\sum_k m_k\mu_k = G.$$

It follows from equation (V.47) that

$$U_T = G\frac{\sum_k m_k U_{Tk}}{\sum_k m_k\mu_k}. \qquad (V.53)$$

Since $p_k = \frac{m_k}{\sum m} P$, where P is the pressure of the mixture of combustion products, we shall -- in order to pass on to partial pressure -- multiply the numerator and the denominator of the right-hand side of equation (V.53) by $\frac{P}{\sum m}$. Finally, this yields

$$U_T = G\frac{\sum_k p_k U^{\circ}_{Tk}}{\sum_k p_k \mu_k} \qquad (V.54)$$

or

$$U_T = G\frac{\sum_k p_k H^{\circ}_{Tk} - P\cdot RT}{\sum_k p_k \mu_k}. \qquad (V.55)$$

Inasmuch as μ_k are expressed in $\frac{g}{mole}$, G should be taken in grams. The U_T values will be expressed in the units of the same system as $H^{o}_{T}k$, for example, in Kcal, if $H^{o}_{T}k$ values are taken in $\frac{Kcal}{mole}$.

Below we shall often make our calculations per 1 kg of mixture (G = 1000).

(c) Let us now derive still another equation for the intrinsic energy of a mixture of substances, which in a number of cases proves to be the most convenient.

Since

$$m_k = \frac{p_k V}{RT},$$

therefore

$$\sum_k m_k U_T^{\circ k} = \frac{V}{RT}\sum_k p_k U_T^{\circ k}, \qquad (V.56)$$

whence, for the inner energy of unit volume of mixture, we obtain:

$$U_T = \frac{1}{RT}\sum_k p_k U_T^{\circ k}. \qquad (V.57)$$

In view of the fact that it is not the increment of intrinsic energy from 0° K to the given temperature, but rather the increment of enthalpy that is computed directly in statistical calculations, it is more convenient to express U_T through "absolute" molar enthalpies. Thus, we have:

$$U_T = \frac{1}{RT}\sum_k p_k\,(H_T^{\circ k} - RT);$$
$$U_T = \frac{1}{RT}\sum_k p_k H_T^{\circ k} - P, \qquad (V.58)$$

where $P = \sum_k p_k$. The gas constant R and molar enthalpies must be expressed in the

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units of the same system, for instance, in $\frac{\text{Kcal}}{\text{mole deg.}}$ and $\frac{\text{Kcal}}{\text{mole}}$, respectively. Then the value of U_T will be in $\frac{\ell - \text{atm}}{\ell}$. In order to express U_T in $\frac{\text{Kcal}}{\ell}$, the right-hand side of equation (V.58) should be multiplied by $24.2 \cdot 10^{-3}$.

For the calculation of the intrinsic energy of the initial mixture, we shall use mainly equations (V.58) and (V.48), while for computations of the intrinsic energy of the mixture of combustion products use will be made of expressions (V.58) and (V.55).

The problem here is this: we must find the kind of temperature T_e at which equation (V.46) can be satisfied.

It should not be forgotten that under the term of "combustion temperature" we understand the maximum theoretical temperature of the combustion products and that, in the case of burning at constant volume, this quantity is to a certain degree conditional in view of what was said in Section 1, Chapter III (see also Section 2, Chapter IX).

(3) Determination of Combustion Temperature and Maximum Explosion Pressure

Thus we obtain the following scheme for the calculation of combustion temperature T_e. For temperature T, which is supposedly close to T_e, we calculate the composition of equilibrium mixture of combustion products, as was described in Section 1, and its pressure P. From formula (V.58) we determine the inner energy $U_{T\text{prod.}}$ of the unit volume of this mixture and compare it with the value of intrinsic energy $U_{T_i\text{init.}}$ of the initial mixture, calculated on the basis of an analogous formula. If $U_{T\text{prod.}} < U_{T_i\text{init.}}$, the computation must be repeated for a higher temperature, and vice versa. $U_{T\text{prod.}}$ should be calculated no less than three times, for three temperature values with an interval of 200° C, in such a way as to assure that $U_{T\text{init.}}$ will be located between the extreme values of $U_{T\text{prod.}}$. Thereafter the combustion temperature is determined graphically (see Figure 13) or by analytical interpolation proceeding from the condition (V.46).

Analytical interpolation may be best accomplished through the use of the

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parabolic interpolating function.

Let U_1, U_2, U_3 be the intrinsic energy values of a unit volume of equilibrium mixture of the combustion products, corresponding to the equidistant (with intervals ΔT) temperature values T_1, T_2, T_3. U_e is the intrinsic energy of a unit volume of this mixture at combustion temperature T_e equal to the inner energy of a unit volume of the initial mixture at temperature T_i, calculated by formula (V.58).

Let us prepare a table of differences for U and T according to the following scheme:

$$\begin{array}{lll} U_1 & & \\ & \Delta U_1 & \\ U_2 & & \Delta^2 U_1 \\ & \Delta U_2 & \\ U_3 & & \end{array}$$

where $\Delta U_n = U_{n+1} - U_n$ - differences of the first order, or first differences, $\Delta^2 U_n = \Delta U_{n+1} - \Delta U_n$ - differences of the second order, or second differences, and so on.

It is assumed that the dependence of the inner energy of the equilibrium mixture of the combustion products on the temperature may be expressed by a polynomial of the second degree of the type of

$$U = a + bT + cT^2. \tag{V.59}$$

Coefficients a, b, and c are determined from the following system of equations:

$$\left.\begin{array}{l} a + bT_1 + cT_1^2 = U_1, \\ a + bT_2 + cT_2^2 = U_2, \\ a + bT_3 + cT_3^2 = U_3. \end{array}\right\} \tag{V.60}$$

In solving this system (while considering the equalities ΔT_1 and ΔT_2), we obtain:

$$c = \frac{\Delta^2 U_1}{\Delta^2 (T_1^2)}; \tag{V.61}$$

$$b = \frac{\Delta U_1 - c \cdot \Delta (T_1^2)}{\Delta T_1}; \tag{V.62}$$

$$a = U_1 - bT_1 - cT_1^2. \tag{V.63}$$

Let us note that

$$\Delta^2 U_1 = U_3 - 2U_2 + U_1; \tag{V.64}$$

$$\Delta^2 (T_1^2) = 2(\Delta T)^2; \tag{V.65}$$

$$\Delta (T_1^2) = (2T_1 + \Delta T)\Delta T. \tag{V.66}$$

The value of combustion temperature T_e may be found from equation

$$a + bT_e + cT_e^2 = U_e$$

as per formula

$$T_e = \frac{-b + \sqrt{b^2 - 4c(a - U_e)}}{2c}. \tag{V.67}$$

The maximum explosion pressure may now be calculated on the basis of the known combustion temperature T_e also by means of graphic (Figure 13) or analytical interpolation, while using one of the following four formulas 92 which we cut short with the third term:

(1) Newtonian formula for forward interpolation:

$$\left. \begin{aligned} P_e &= P_1 + S\Delta P_1 + \frac{S(S-1)}{2!}\Delta^2 P_1 + \dots, \\ \text{where } S &= \frac{T_e - T_1}{\Delta T}. \end{aligned} \right\} \tag{V.68}$$

(2) Newtonian formula for back interpolation:

$$\left. \begin{aligned} P_e &= P_3 - S\Delta P_2 + \frac{S(S-1)}{2!}\Delta^2 P_1 - \dots, \\ \text{where } S &= \frac{T_3 - T_e}{\Delta T}. \end{aligned} \right\} \tag{V.69}$$

(3) Gaussian formula for forward interpolation:

$$P_e = P_2 + S\Delta P_2 + \frac{S(S-1)}{2!}\Delta^2 P_1 + \dots \text{ where } S = \frac{T_e - T_2}{\Delta T}. \tag{V.70}$$

(4) Gaussian formula for back interpolation:

$$P_e = P_2 + S\Delta P_1 + \frac{(S+1)S}{2!}\Delta^2 P_1 + \dots \text{ where } S = \frac{T_e - T_2}{\Delta T}. \tag{V.71}$$

The ratio of the number of moles $\sum m_e$ in the mixture of combustion products at combustion temperature to the number of moles $\sum m_i$ in the initial mixture is determined by the laws of ideal gases

$$\frac{\Sigma m_e}{\Sigma m_i} = \frac{P_e}{P_i} \cdot \frac{T_i}{T_e}. \qquad (V.72)$$

The number of moles in a unit volume of the initial mixture is calculated according to formula:

$$\sum m_i = \frac{P_i}{RT_i}.$$

Similarly:

$$\sum m_e = \frac{P_e}{RT_e}.$$

On the basis of combustion equation (see, for example (V.41), and also Section 2, Chapter VII), it is easy to calculate the number of moles $\sum m$ of combustion products in the assumption that there is no dissociation. Thereupon, it becomes possible to compute the value of $\zeta_e = \frac{\sum m_e - \sum \overline{m}}{\sum m}$, which characterizes the growth of the number of moles as a result of dissociation of combustion products at T_e, and the corresponding growth of pressure.

Example 1. A mixture of methane with oxygen burns at constant volume in an enclosed space; $\alpha = 0.8$, initial pressure $P_i = 1$ atm, initial temperature $T_i = 25^\circ C = 298.16^\circ K$. Calculate the maximum pressure of explosion.

We shall write down the equation for methane combustion

$$CH_4 + 2O_2 = CO_2 + 2H_2O. \qquad (V.73)$$

Since $\alpha = 0.8$, the ratio of the number of oxygen moles to the number of methane moles in the initial mixture is not equal to two, but to 1.6. Hence:

$$p_{i\,CH_4} = \frac{1}{2{,}6} \text{ atm} \quad p_{i\,O_2} = \frac{1{,}6}{2{,}6} \text{ atm}$$

Let us now calculate the intrinsic energy of a unit volume of the initial mixture. The heat of combustion of methane at $25^\circ C$ $(-\Delta H^0_{298.16})_{comb} = 212.798 \frac{Kcal}{mole}$ (19).

From equations (V.44) and (V.73) it follows that

$$\Delta H^\circ_{T_i\,comb\,CH_4} = H^\circ_{T_i\,CO_2} + 2H^\circ_{T_i\,H_2O\,(ж)} - H^\circ_{T_i\,CH_4} - 2H^\circ_{T_i\,O_2}.$$

Whence, in using the data in Section 2, we obtain:

$$H^{\circ}_{298,16\,CH_4} = 194,586\ \frac{Kcal}{mole}$$

From formula (V.58) we shall find

$$U^{\bullet}_{T_i\,init} = 127,464\ \frac{\ell\text{-atm}}{\ell}$$

Supposing the temperature of combustion is equal to 3,600° K, then according to formulas (V.10), we shall have:

$$|p|_C = 4,6439; \quad |p|_H = 18,5758; \quad |p|_O = 14,8603.$$

Let is be assumed that the partial pressure of H_2 in combustion products is equal to 2 atm*.

The partial pressures of other components will be computed from formulas (V.21) - (V.27). If computations are made with a calculating machine, it is more convenient to use the expanded working table (see Table 2). The results of calculations -- based on the assumption that $p_{H_2} = 2.0$ -- are recorded in the second column of Table 2. Further, while making $p_{H_2} = 2.1$, we complete a second series of computations. The next value of p_{H_2} is computed on the basis of the first two in the assumption that there is a linear relationship between p_{H_2} and D_o. In the given case this leads to satisfactory results right away, since the first two values of p_{H_2} were close to its true value. (In less fortunate cases, this process must be continued until condition (V.29) is fulfilled. However an experienced calculator seldom needs to repeat computations according to the scheme in Section 1 more than four to five times.)

Assuming the values of partial pressures of the third approximation to be identical to the true values, we calculate P = 16.543 atm. On the basis of formula (V.58) we find the value of the intrinsic energy of a unit volume of the mixture of

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* For the determination of the order of magnitude of the varying partial pressure, one could use the method of successive approximations (Chapter VIII, Section 1).

combustion products*. We obtain:

$$U_{prod.} = 137.205 \frac{\text{lit - atm}}{\text{lit}}$$

Table 2

	1st Approximation	2nd Approximation	3rd Approximation	Final Result
1) p_{H_2}	2,0000	2,1000	2,0900	2,090
2) $\sqrt{p_{H_2}}$	1,4142	1,4491	1,4457	
$p_H = K_8\sqrt{p_{H_2}}$	1,0902	1,1171	1,1145	1,115
3) $\{p\}_H - p_H - 2p_{H_2}$	13,4856	13,2587	13,2813	
$K_3/\sqrt{p_{H_2}}$	0,4421	0,4314	0,4325	
$p_{H_2O} = \frac{\{p\}_H - p_H - 2p_{H_2}}{2 + (K_3/\sqrt{p_{H_2}})}$	5,5221	5,4531	5,4599	5,460
4) $p_{OH} = p_{H_2O}(K_3/\sqrt{p_{H_2}})$	2,4413	2,3525	2,3614	2,361
5) p_{H_2O}/p_{H_2}	2,76105	2,5967	2,6124	
$p_O = K_9(p_{H_2O}/p_{H_2})$	0,4589	0,4316	0,4342	0,434
6) $(p_{H_2O}/p_{H_2})^2$	7,6234	6,7429	6,8246	
$p_{O_2} = K_7(p_{H_2O}/p_{H_2})^2$	0,4900	0,4334	0,4386	0,439
7) $K_6(p_{H_2O}/p_{H_2})$	0,3206	0,3015	0,3033	
$p_{CO} = \frac{\{p\}_C}{1 + K_6(p_{H_2O}/p_{H_2})}$	3,5165	3,5681	3,5632	3,563
8) $p_{CO_2} = p_{CO} \cdot K_6(p_{H_2O}/p_{H_2})$	1,1274	1,0758	1,0807	1,081
9) $p_{H_2O} + p_{OH} + p_O + 2p_{O_2} + p_{CO} + 2p_{CO_2} = \Sigma O$	15,1736	14,8237	14,8573	
$D_O = \Sigma O - \{p\}_O$	+0,3133	- 0,0366	- 0,0030	

(* Footnote on bottom of next page)

Since $U_{prod} > U_{T_i init.}$; the same calculations should be made as for 3,400° K. Calculation results for three temperature values are to be found in Table 3**.

In carrying out an interpolation with the aid of formulas (V.61) - (V.67) we find

$$T_e = 3,520.6^\circ \text{ K.}$$

Table 3

T	3400°K	3600°K	3800°K
$\{p\}$ C	4,3859	4,6439	4,902
$\{p\}$ H	17,5438	18,5758	19,608
$\{p\}$ O	14,0347	14,8603	15,686
P	14,659	16,363	18,351
U_{prod} $\left(\frac{\text{lit-atm}}{\text{lit}}\right)$	117,085	134,863	155,453

To calculate the maximum explosion pressure, use will be made of the Newtonian formula for forward interpolation (V.68). This yields

$$P_e = 15.65 \text{ atm.}$$

(The same result could be obtained directly with the help of the parabolic function of the (V.59) type. Graphic interpolation (Figure 13) also permits us to determine T_e and P_e with sufficient accuracy.)

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* In calculating enthalpy and entropy and in a number of other cases, we encounter expressions of the type of $\sum a_i b_i$. Such addition of pair-by-pair products may be most easily accomplished with the help of a computer in one single operation, without copying each product separately. To do so, it is only necessary that intermediate results not be cancelled. Then each successive product will be added to the preceding one. If the product has a minus sign, the computer handle should be rotated in the inverse direction ("negative multiplication"). To avoid any confusion in the order of figures, it is expedient to take all the a_i and also all the b_i values with the same number of decimals.

** Here -- as in other examples of methane-oxygen mixtures, with the exception of example 7 -- we used the data from (7, 20, 58, 1), which differ somewhat from those recorded in Appendix IV. Examples 2, 4, 6, 7, 9, 10, 11, 12 and 13 were calculated entirely on the basis of the tables contained in Appendix IV.

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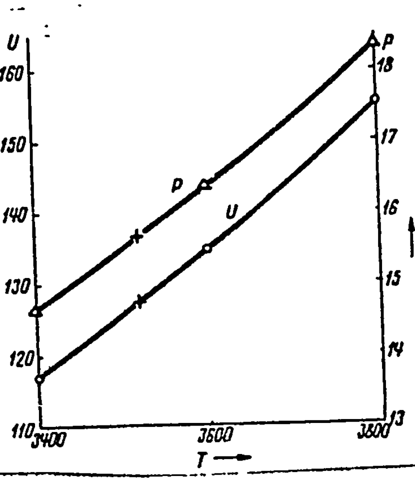

Figure 13. On the determination of combustion temperature and maximum explosion pressure on the basis of curves U(T) and P(T).

We shall now calculate the growth of the number of moles as a result of dissociation. According to formula (V.72)

$$\frac{\Sigma m_e}{\Sigma m_i}=1{,}3256.$$

Let us write down the equation for methane combustion in oxygen with $\alpha = 0.8$, while assuming that the composition of the combustion products corresponds to equilibrium of the system at low temperatures (see Section 2, Chapter VII):

$$CH_4+1{,}6O_2=CO_2+1{,}2H_2O+0{,}8H_2.$$

It may be seen from this that

$$\frac{\Sigma \bar{m}}{\Sigma m_i}=\frac{3{,}0}{2{,}6}=1{,}1538\,^*.$$

Consequently

$$\frac{\Sigma m_e}{\Sigma \bar{m}}=\frac{1{,}3256}{1{,}1538}=1{,}149;$$

$$\zeta_e=\frac{\Sigma m_e}{\Sigma \bar{m}}-1=0{,}149.$$

Example 2. In a bomb with central ignition a burning mixture is characterized by the following values of partial pressures: $p_iH_2 = 0.2015$ atm, $p_iO_2 = 0.1197$ atm,

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* Below, pp. 70-74, formulas common for hydrocarbon C_nH_m mixtures with oxygen will be derived for the calculation of $\frac{\Sigma \bar{m}}{\Sigma m_i}=\frac{\Sigma m''}{\Sigma m_i}$.

$p^*_iH_2O = 0.0272$ atm, $p_iHe = 0.5442$ atm, $P^*_i = 0.8926$ atm**. The initial temperature of the starting mixture $T_i = 302.8^\circ$ K. Determine the theoretical value of the maximum pressure of explosion.

The calculation will be made for 1 kg of the initial mixture.

By linear interpolation according to the data in Table IV, Appendix IV, we get

$$H^\circ_{302,8\,H_2} = 59,168; \quad H^\circ_{302,8\,O_2} = 2,102;$$
$$H^\circ_{302,8\,H_2O} = 2,410; \quad H^\circ_{302,8\,He} = 1,504\ ^{***}.$$

Upon substitution of the determined values of m_{ij} and $H^\circ_{T,j}$ in equation (V.55) we find: $U_{T_i\,init.} = 1,813.35\ \frac{Kcal}{kg}$.

From formula (V.11) we obtain

$$\{p\}_H = (2p_{iH_2} + 2p^*_{iH_2O})\,\frac{T_e}{T_i} = 1,51057 \cdot 10^{-3} \cdot T_e. \qquad (V.74)$$

$$\{p\}_O = (2p_{iO_2} + p^*_{iH_2O})\,\frac{T_e}{T_i} = 0,88045 \cdot 10^{-3} \cdot T_e. \qquad (V.75)$$

$$\{p\}_{He} = p_{iHe} \cdot \frac{T_e}{T_i} = 1,79723 \cdot 10^{-3} \cdot T_e. \qquad (V.76)$$

The balance equations have the aspect

$$2p_{H_2O} + 2p_{H_2} + p_{OH} + p_H = \{p\}_H; \qquad (V.77)$$
$$p_{H_2O} + 2p_{O_2} + p_{OH} + p_O = \{p\}_O; \qquad (V.78)$$
$$p_{He} = \{p\}_{He}. \qquad (V.79)$$

The partial pressure of helium p_{He} is determined right from equation (V.79). For the determination of partial pressures of the remaining six components of the mixture of combustion products H_2, H, H_2O, OH, O and O_2, a system of six equations is composed: two balance equations, i.e., (V.77) and (V.78), and four equilibrium equations, i.e., (V.16), (V.17), (V.18), and (V.19). To solve this system, we shall use formulas (V.21) - (V.25).

** Asterisks denote pressures corrected for deviations from the ideal gas state (see p. 7).

*** The enthalpy of helium and two other inert gases is equal to $\frac{5}{2}$ RT.

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The results of calculation of the composition of the mixture of combustion products for three temperatures, 2,600, 2,800, and 3,000° K are recorded in Table 4.

Table 4

Order No.	Component	Partial Pressures		
		2600°K	2800°K	3000°K
1	H_2	0,04800	0,10900	0,20700
2	H	0,00904	0,02892	0,07657
3	H_2O	1,83500	1,86241	1,81996
4	OH	0,15243	0,25785	0,40121
5	O	0,00929	0,02266	0,05071
6	O_2	0,14615	0,16057	0,18544
7	He	4,67280	5,03224	5,39169
	D_o	- 0,00015	- 0,00120	+ 0,00141
	P	6,87271	7,47365	8,13258
	$\sum_k p_k \mu_k$	59,2884	63,8324	68,4350
	$U_{T prod}$ $(\frac{Kcal}{kg})$	1539,13	1799,96	2136,70

For the same temperature values, using equation (V.55), we calculate $U_{T prod}$ and on the basis of formula (V.67) find $T_e = 2,808.9°$ K. Here, by way of interpolation with the help of equation (V.70), we determine:

$$P_e = 7.502$$

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Chapter VI

COMPUTATION OF COMBUSTION PROCESSES AT CONSTANT PRESSURE -- DIRECT METHOD OF CALCULATION

Let us assume that we have the composition of the initial mixture, its starting temperature T_i, and the pressure P_0 at which combustion is taking place. The problem is to calculate the equilibrium state of the system which is attained by it at constant pressure. Let it be mentioned here that the rule for the determination of the number of unknown reaction equations and all ensuing consequences, considered in Sections 1 and 2 of the preceding chapter, remain in force for this case.

The principles of the computation method reviewed here are outlined by A. P. Vanichev in his monograph (2).

Section 1. Determination of the Composition of the Mixture of Combustion Products at Given Temperature

(1) Equations of Material Balance

The equations of material balance -- expressed through molecular concentrations-- of the type of equations (V.1) - (V.2), naturally remain the same as in the case of combustion at constant pressure, since they express the law of conservation of matter in a closed system in which there are no nuclear transformations. Since in this case the pressure which is applied to one gram-molecule does not remain unchanged in the system in the process of transformation at constant temperature, we get -- in passing on from molecular concentrations to partial pressures -- more complicated balance equations than for a system in which combustion develops at constant volume. For example, in order to pass from molar concentrations of components to their partial pressures in the left-hand part of the first of the three (V.2) equations, it is necessary to multiply both parts of this equation by $\frac{P_0}{\Sigma m_e}$. We obtain:

$$p_{CO_2} + p_{CO} = m_{iCH_4} \cdot \frac{P_0}{\Sigma m_e}.$$

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But the magnitude of $\sum m_e$ is unknown; the magnitude of ratio $\sum m_e/\sum m_i$* is also unknown.

We therefore proceed as follows. We divide the second of the three (V.2) equations by the first:

$$\frac{2m_{H_2O}+2m_{H_2}+m_{OH}+m_H}{m_{CO_2}+m_{CO}}=\frac{[m]_H}{[m]_C}. \qquad (VI.1)$$

Upon multiplication of the numerator and denominator of the left part of equation (VI.1) by $\frac{P_0}{\sum m_e}$ we get:

$$\frac{2p_{H_2O}+2p_{H_2}+p_{OH}+p_H}{p_{CO_2}+p_{CO}}=\frac{[m]_H}{[m]_C}. \qquad (VI.2)$$

In a similar manner we derive:

$$\frac{p_{H_2O}+2p_{CO_2}+2p_{O_2}+p_{CO}+p_{OH}+p_O}{p_{CO_2}+p_{CO}}=\frac{[m]_O}{[m]_C}. \qquad (VI.3)$$

The third balance equation is produced from the condition of pressure constancy:

$$p_{CO_2}+p_{CO}+p_{H_2O}+p_{H_2}+p_{O_2}+p_{OH}+p_H+p_O=P_0. \qquad (VI.4)$$

We introduce the designations:

$$\frac{[m]_H}{[m]_C}=a, \quad \frac{[m]_O}{[m]_C}=b.$$

After simple transformations, we obtain from equations (VI.2) and (VI.3), respectively:

$$2p_{H_2O}+2p_{H_2}+p_{OH}+p_H-ap_{CO_2}-ap_{CO}=0. \qquad (VI.5)$$

$$p_{H_2O}+2p_{O_2}+p_{OH}+p_O-(b-2)p_{CO_2}-(b-1)p_{CO}=0. \qquad (VI.6)$$

It is the balance equations (VI.4), (VI.5), and (VI.6) that we shall use henceforward for the calculation of equilibrium in the system formed by carbon, hydrogen, and oxygen.

Knowing the initial mixture composition, it is easy to calculate the values of

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* The same difficulty is also encountered when, on leaving the balance equations (V.1)-(V.3) unchanged, we replace partial pressures by molar concentrations in expressions for equilibrium constant K_p (21).

a and b. For example, the left side of the equation for hydrocarbon C_nH_m combustion in oxygen has the form

$$C_nH_m+\alpha\left(n+\frac{m}{4}\right)O_2.$$

Hence

$$a=\frac{m}{n};\ b=\frac{2\alpha\left(n+\frac{m}{4}\right)}{n}. \qquad \text{(VI.7)}$$

Everything we have said so far about the composition of balance equations in a system formed by carbon, hydrogen, and oxygen illustrates in a sufficient measure the general rule for the composition of such equations: if the number of elements is equal to m, then out of m equations of material balance, expressed through molecular concentrations, m-1 relationships may be composed. Moreover, the molecular concentrations of components are replaced by their partial pressures. The m-e balance equation expresses the constancy condition of the system's total pressure which is equal to the sum of partial pressures of its constituent components.

(2) Calculation of partial pressures of the Combustion Products

Balance equations for constant pressure -- such as (VI.4)-(VI.6) -- include a greater number of terms than balance equations for constant pressure as, for instance, (V.12)-(V.14). Consequently, the solutions of the system of equations for the determination of partial pressures of combustion products in this case turns out to be more complicated. Generally speaking, various methods of approximate solution may be applied here (see Chapter VIII). In this chapter we shall analyze the method of selection of the value for one of the unknown partial pressures by using the example of an equilibrium system composed by carbon, hydrogen, and oxygen. We used this example in Section 1, Chapter V, in application to a similar system at constant pressure. If the partial pressure of hydrogen p_{H_2} is selected as the arbitrarily fixed quantity, then, in the given case, the task of solving an equation of an order higher than the second becomes inevitable. We shall therefore, fix the value of p_{O_2} both for the case of excess of oxygen as well as for the case of its shortage.

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To serve as five independent equilibrium constants, we select those constants which were used to construct the system of equations for the case of hydrocarbon combustion in considerable oxygen excess at constant volume.

Thus the system of equations which must be solved to determine the partial pressures of combustion products consists of equations (VI.4)-(VI.6) and (V.30)-(V.34).

If we arbitrarily fix the value of p_{O_2} and substitute the values of p_{CO}, p_{H_2}, p_{OH}, p_H, and p_O from equations (V.30)-(V.34) in balance equations (VI.5 and VI.6), we shall obtain a system of equations with two unknowns, i.e., p_{H_2O} and p_{CO_2}; in solving these equations by the ordinary method, we get:

$$p_{H_2O}=\left(\frac{-r-\sqrt{r^2-4qs}}{2q}\right)^{2*}, \qquad \text{(VI.8)}$$

where

$$q=[K_1(2+a-2b)+K_3(4-2b)]\frac{1}{\sqrt{p_{O_2}}}+ +K_1K_3(2-2b)\frac{1}{p_{O_2}}+(4+a-2b); \qquad \text{(VI.8a)}$$

$$r=K_{10}(2+a-b)\sqrt[4]{p_{O_2}}+[K_1K_{10}(1+a-b) + K_{11}(2-b)]\frac{1}{\sqrt[4]{p_{O_2}}}+K_1K_{11}(1-b)\frac{1}{(p_{O_2})^{3/4}}; \qquad \text{(VI.8b)}$$

$$s=2ap_{O_2}+a(K_{12}+2K_1)\sqrt{p_{O_2}}+aK_{12}K_1. \qquad \text{(VI.8c)}$$

Furthermore:

$$p_{H_2}=\frac{K_2}{\sqrt{p_{O_2}}}\cdot p_{H_2O}; \qquad \text{(VI.9)}$$

$$p_{OH}=K_{10}\sqrt[4]{p_{O_2}}\sqrt{p_{H_2O}}; \qquad \text{(VI.10)}$$

$$p_H=\frac{K_{11}}{\sqrt[4]{p_{O_2}}}\cdot\sqrt{p_{H_2O}}; \qquad \text{(VI.11)}$$

$$p_O=K_{12}\sqrt{p_{O_2}}; \qquad \text{(VI.12)}$$

$$p_{CO_2}=\frac{2p_{H_2O}+2p_{H_2}-p_{OH}+p_H}{a\left(1+\frac{K_1}{\sqrt{p_{O_2}}}\right)}; \qquad \text{(VI.13)}$$

$$p_{CO}=\frac{K_1}{\sqrt{p_{O_2}}}\cdot p_{CO_2}. \qquad \text{(VI.14)}$$

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* For the solution to acquire a physical meaning, condition: $\sqrt{p_{H_2O}}=\frac{-r\pm\sqrt{r^2-4qs}}{2q}>0$, must be fulfilled. The analysis, whose details will be omitted here, shows that only that of the two values of $\sqrt{p_{H_2O}}$ satisfies this condition in which a minus sign stands in front of $\sqrt{r^2-4qs}$.

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The correctness of p_{O_2} value selection is checked on the basis of equation (VI.4), in a way similar to the one in the case of earlier partial pressure calculations for combustion products at constant volume. In most cases it suffices to fulfill condition

$$|D_p| = |\sum_k p_k - P_0| \leqslant 0{,}001\ P_0. \qquad \text{(VI.15)}$$

In the case of excess fuel, the quantity p_{O_2} becomes small as compared with partial pressures of other components, while the difference D_p turns out to be quite sensitive to changes of p_{O_2}. Consequently, the accuracy requirements should be increased.

Section 2. Determination of Combustion Temperature and the Degree of Expansion

(1) Energy-Balance Equation

By analogy with equation (V.46) we obtain for the case of combustion at constant volume:

$$H_{T_e}\ \text{prod} = H_{T_i}\ \text{init} \qquad \text{(VI.16)}$$

The enthalpy of G grams of substance mixture may be determined by formulas:

$$H_T = \sum_k m_k H^{\circ}_{Tk} \qquad \text{(VI.17)}$$

or

$$H_T = G\frac{\sum_k p_k H^{\circ}_{Tk}}{\sum_k p_k \mu_k}, \qquad \text{(VI.18)}$$

which are perfectly similar to formulas (V.47) and (V.54) for intrinsic energy. Equation (V.57) cannot be applied because, in consequence of expansion, the quantity of substance per unit volume does not remain constant.

In the future we shall use formula (VI.17) for calculations of enthalpy of the initial mixture and formula (VI.18) mainly for enthalpy calculations of the mixture of combustion products.

(2) Determination of Combustion Temperature and the Degree of Expansion

Combustion temperature may be determined from condition (VI.16) by way of

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interpolation in the same way as this was done in the case of combustion at constant volume.

In order to determine the degree of expansion E, it is necessary to compute the total number of moles ($\sum m_e$) of combustion products in a definite amount of mixture G which is adopted as a unit for calculation. We shall refer to

$$\mu = \frac{G}{\Sigma m} \tag{VI.19}$$

as apparent molecular weight of the system. Since $G = \sum m_k \mu_k$,

$$\sum \frac{m_k}{\Sigma m} \mu_k = \mu$$

and since $\frac{m_k}{\sum m} = \frac{p_k}{P}$,

$$\frac{1}{P} \sum_k p_k \mu_k = \mu. \tag{VI.20}$$

From formula (VI.19) it follows that

$$\sum m_e = \frac{G}{\mu_e}. \tag{VI.21}$$

Since $\sum_k p_k \mu_k$ results from enthalpy calculation of combustion products, there is no difficulty in determining μ from formula (VI.20).

Knowing the values of μ for three temperatures, and having determined combustion temperature T_e, we can, on the basis of interpolation formulas (V.68)-(V.71), calculate the apparent molecular weight μ_e of the mixture of combustion products at T_e. At the same time, the number of moles of combustion products in G grams of mixture may be found from formula (VI.21). Knowing the number of moles of the initial substance $\sum m_i$ in the same quantity of their mixture, we can calculate the ratio $\frac{\sum m_e}{\sum m_i}$ and find from it also the degree of expansion

$$E = \frac{V_e}{V_i} = \frac{\Sigma m_e}{\Sigma m_i} \cdot \frac{T_e}{T_i}. \tag{VI.22}$$

The quantity ζ_e, which characterizes the growth of the number of moles in consequence of dissociation, and the corresponding volume increment may be calculated in the same way as in the case of combustion at constant volume.

Example 3. A mixture of methane and oxygen burns at constant pressure $P_0 = 1$ atm; $\alpha = 0.8$; initial temperature $T_i = 298.16°$ K. Calculate the combustion temperature and the degree of expansion.

We have:

$$\frac{m_{iO_2}}{m_{iCH_4}} = 1,6.$$

On the basis of formula (V.52), assuming G = 1,000, we get:

$$m_{iCH_4} = 14,8717 \ \frac{\text{mole}}{\text{kg}} .$$

Consequently,

$$m_{iO_2} = 23,7947 \ \frac{\text{mole}}{\text{kg}} .$$

According to formula (VI.17) we shall determine

$$H_{T_i \text{ init}} = 2,943.1 \ \frac{\text{Kcal}}{\text{kg}} .$$

Further, on the basis of (VI.7) we find

$$a = 4; \qquad b = 3.2$$

These values are now introduced into equations (VI.8a)-(VI.8c):

$$q = 1,6 - (0,4K_1 + 2,4K_2)\frac{1}{\sqrt{p_{O_2}}} - 4,4K_1K_2\frac{1}{p_{O_2}} \qquad \text{(VI.8a')}$$

$$r = 2,8K_{10}\sqrt[4]{p_{O_2}} + (1,8K_1K_2 - 1,2K_{11})\frac{1}{\sqrt[4]{p_{O_2}}} - 2,2K_1K_{11} \cdot p_{O_2}^{-\frac{3}{4}} \qquad \text{(VI.8b')}$$

$$s = 8p_{O_2} + 4(K_{12} + 2K_1)\sqrt{p_{O_2}} + 4K_{12}K_1. \qquad \text{(VI.8c')}$$

We shall first determine the state of the equilibrium mixture of combustion products at 3,000° K, while assuming this temperature to be close to that of combustion. In using formulas (VI.8a')-(VI.8c') according to the scheme contained in Section 1 of this chapter, we determine the mixture composition. On the basis of formula (VI.18) we calculate the enthalpy of the mixture of combustion products at 3,000° and obtain:

$$H_{3,000\text{prod}} = 2,870.9.$$

On comparing this quantity with the value of $H_{T_i \text{ init}}$, we come to the conclusion that the combustion temperature lies above 3,000° K. We then repeat the calculation along the same pattern for 3,200 and 2,800° K and incorporate the results in Table 5. After interpolation with the aid of formulas (V.61)-(V.67), we find:

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$$T_e = 3{,}023.7^\circ \text{ K}$$

Table 5

T	2800° K	3000° K	3200° K
μ	21,0902	19,8487	18,0891
H_{prod} $(\frac{Kcal}{kg})$	2390,6	2870,9	3582,4

Since $P_0 = 1$ atm, $\mu = \sum_k p_k \mu_k$; this quantity was calculated in computing the enthalpy of combustion products. Its values for three temperatures are recorded in Table 5. In using the Gaussian formula for back interpolation (V.71), we obtain

$$\mu_e = 19.6674.$$

From this, according to formula (VI.21), we get

$$\sum m_e = \frac{1000}{19{,}6674} = 50{,}8456.$$

At the same time

$$\sum m_i = m_{i\,CH_4} + m_{i\,O_2} = 38{,}6664.$$

Hence,

$$\frac{\sum m_e}{\sum m_i} = 1{,}3150.$$

On the basis of formula (VI.22), we calculate the degree of expansion:

$$E = 13{,}335$$

Let us now determine the growth of the number of moles owing to dissociation. Here, as in Example 1, we have

$$\frac{\sum \overline{m}}{\sum m_i} = \frac{3{,}0}{2{,}6} = 1{,}1538.$$

Hence,

$$\frac{\sum m_e}{\sum \overline{m}} = \frac{1{,}3150}{1{,}1538} = 1{,}1397$$

and $\zeta_e = 0.1397$.

It should be noted here that, for purposes of comparison of the calculation results for constant volume and constant pressure, the initial mixture we took in Examples 1 and 3 had the same composition for the same initial conditions (T_i and P_i).

Example 4. A mixture of the same composition as in Example 2, i.e., whose component molar concentrations in $\frac{\text{mole}}{\text{kg}}$ comprise:

$$m_{iH_2} = 29{,}1815;$$
$$m_{iO_2} = 17{,}3338;$$
$$m_{iH_2O} = 3{,}9395;$$
$$m_{iHe} = 78{,}8192,$$

burns at constant pressure P_0 = 2,674.25 mm Hg (3.51876 atm). The starting temperature of the mixture, T_i = 484° K. Determine the combustion temperature.

By numerical interpolation on the basis of the data of Table IV, Appendix IV, we find:

$$H^\circ_{484\,H_2} = 60{,}430;\quad H^\circ_{484\,O_2} = 3{,}404;\quad H^\circ_{484\,H_2O} = 3{,}895;\quad H^\circ_{484\,He} = 2{,}403.$$

From formula (VI.17) we determine

$$H_{T_i\ \text{init}} = 2{,}027.9\ \frac{\text{Kcal}}{\text{kg}}$$

(the same value of $H_{T_i\ \text{init}}$ would have been produced had we used a formula similar to (VI.18).

The balance equations look something like this:

$$\frac{2p_{H_2O} + 2p_{H_2} + p_{OH} + p_H}{p_{H_2O} + 2p_{O_2} + p_{OH} + p_O} = \frac{[m]_H}{[m]_O} = a,$$
$$\frac{p_{He}}{p_{H_2O} + 2p_{O_2} + p_{OH} + p_O} = \frac{m_{He}}{[m]_O} = b,$$
$$\sum_k p_k = P_0.$$

Computation formulas for partial pressures at given temperature are derived in the same way as was done above for the system formed by carbon, hydrogen, and oxygen. We fixed the value of p_{O_2} arbitrarily.

Further,

$$p_{H_2O} = \left(\frac{-r - \sqrt{r^2 - 4qs}}{2q}\right)^2.$$
$$q = a - 2 - \frac{2K_2}{\sqrt{p_{O_2}}} = -\left(0{,}28432 + 2\frac{K_2}{\sqrt{p_{O_2}}}\right),$$
$$r = (a-1)K_{10}\sqrt[4]{p_{O_2}} - \frac{K_{11}}{\sqrt[4]{p_{O_2}}} = 0{,}71568K_{10}\sqrt[4]{p_{O_2}} - \frac{K_{11}}{\sqrt[4]{p_{O_2}}},$$
$$s = 2ap_{O_2} + aK_{12}\sqrt{p_{O_2}} = 3{,}43136p_{O_2} + 1{,}71568p_O.$$

The values of p_{OH}, p_H, p_{H_2}, p_O will be found according to formulas (VI.9)-(VI.12),

$$p_{He} = b(2p_{O_2}+p_O+p_{H_2O}+p_{OH}) = 2{,}04126(2p_{O_2}+p_O+p_{H_2O}+p_{OH}).$$

Table 6

	1st Approximation	2nd Approximation	Final results
p_{O_2}	0,077100	0,078950	0,078997
p_O	0,000790	0,000799	0,000799
p_{H_2O}	0,971376	0,994599	0,995185
p_{OH}	0,026944	0,027426	0,027138
p_H	0,000402	0,000105	0,000105
p_{H_2}	0,004306	0,004357	0,004358
p_{He}	2,354206	2,410165	2,411578
Σp_k	3,435124	3,516701	3,518760
$\Sigma p_k - P_0$	− 0,083636	− 0,002059	0,000000

The correctness of selection of p_{O_2} values is checked by condition $\sum_k p_k = P_0$. Partial pressure calculation for combustion products in this case is facilitated by the existence of an almost linear relationship between their values corresponding to the given values of p_{O_2} and the respective values of $\sum p_k$ or $\sum_k p_k - P_0$. This allows the use of linear interpolation and extrapolation. A calculation of the composition of the mixture of combustion products at 2,200° K (Table 6), whose final result is produced by extrapolation, is given here as an illustration. The fulfillment of condition $\sum_k p_k = P_0$ with a precision exceeding $10^{-4}\%$ P_0 bears witness to the high accuracy of this extrapolation.

Table 7 contains the results of calculations of the composition and enthalpy of the mixture of combustion products at 2,200, 2,400, and 2,600° K. By interpolation from condition (VI.16), we find $T_e = 2{,}491°$ K.

Table 7

Seq. Nos.	Component	2200°K	2400°K	2600°K
		Partial Pressures		
1	H_2	0,00136	0,01364	0,03345
2	H	0,00040	0,00201	0,00779
3	H_2O	0,99818	0,96820	0,91911
4	OH	0,02744	0,05359	0,09147
5	O	0,00080	0,00253	0,00668
6	O_2	0,07900	0,07632	0,07551
7	He	2,41158	2,40247	2,38475
	Σp_k	3,51876	3,51876	3,51876
	H_T prod	1681,44	1907,41	2181,37

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Chapter VII

COMPUTATION OF COMBUSTION PROCESSES AT CONSTANT PRESSURE -- APPROXIMATION METHOD OF CALCULATION (16)

The above discussions show us that the calculation of the composition of an equilibrium mixture of gases presents the most laborious operation in computing the processes of adiabatic combustion. Moreover, in the case of combustion at constant pressure, it is more complex than in cases when changes occur at constant volume. It is so even for relatively simple systems formed by three chemical elements carbon, hydrogen, and oxygen. For more complex systems, it often becomes impossible to apply the method of partial-pressures-value selection for one of the products of combustion at constant pressure. If the combustion temperature is high, it is also impossible to use the method of successive approximations which is outlined in Section 1, Chapter VIII. Meanwhile, the selection of partial-pressure values for more than one component is a highly cumbersome operation in a general case.

Very often a substantial simplification may be achieved through application of the Zel'dovich - Polyarny method of approximation. This method makes possible the application of the scheme of computation of partial pressures of combustion products at constant volume to calculations for the case of constant pressures.

The temperature of combustion is determined as above (Chapter VI) by selection of the system's enthalpy from the condition of constancy (VI.16). For the calculation of enthalpy for each given temperature value, use is made of the procedure -- widely utilized in the field of thermodynamics -- which consists of the arbitrary selection of the method whereby the system is brought into the state of equilibrium. Let us assume that this state may be attained in three stages. (1) First of all, the system is brought into a state at which its composition and enthalpy correspond to equilibrium at high pressure totally suppressing dissociation, and to the given temperature T (this state is taken as the first approximation for calculations of

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the actual state of the system). (2) Thereafter, the pressure is reduced to P_0, whereupon the mixture is exposed to dissociation at constant volume and given temperature T, until such time as that equilibrium state is reached which corresponds to these conditions (second approximation). The equilibrium pressure of the system, P', will thereby be greater than P_0. (3) Finally, the mixture is reversibly and isothermically expanded until pressure is reduced to P_0. In this process, dissociation will increase. The equilibrium state of the system at pressure P_0 and the given temperature T is precisely the state for which we must calculate the enthalpy of combustion products.

For purposes of comparison of the Zel'dovich-Polyarny method with the direct method of calculation, an analysis will be made of the three stages of calculations corresponding to the adopted conditional mechanism. For this operation, we will use a model system formed by carbon, hydrogen, and oxygen, although no obvious advantages are to be derived from the application of the approximation method to this relatively simple case.

Section 1. Calculation of the State of Combustion Products in the Assumed Absence of Dissociation

The first stage of computations consists in calculation of the final state which the mixture of combustion products tends to attain when pressure is indefinitely increased. In cases where it is impossible to develop isomolecular reactions of the water-vapor type in the system, the composition of the mixture of combustion products at high pressure and any given temperature coincides with its equilibrium composition at low temperatures. We shall therefore begin with an analysis of calculations pertaining to the composition corresponding to the low temperatures.

(1) Calculation of Composition Corresponding to Low Temperatures

The equation of C_nH_m hydrocarbon combustion in oxygen when $\alpha = 1$ looks like this:

$$C_nH_m + \left(n + \frac{m}{4}\right)O_2 = nCO_2 + \frac{m}{2}H_2O. \qquad \text{(VII.1)}$$

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The right-hand side of this equation corresponds to the composition of an equilibrium mixture of combustion products at low temperatures. The molar concentrations for this case will be designated by m^{++}.

The ratio of the number of moles of combustion products to the number of moles of the initial substances is:

$$\frac{\Sigma m^{++}}{\Sigma m_i} = \frac{n + \frac{m}{2}}{1 + n + \frac{m}{4}}. \qquad \text{(VII.2)}$$

If $\alpha > 1$, the products of combustion must contain excess oxygen:

$$C_nH_m + \alpha\left(n + \frac{m}{4}\right)O_2 = nCO_2 + \frac{m}{2}H_2O + (\alpha - 1)\left(n + \frac{m}{4}\right)O_2 \quad (\alpha > 1). \qquad \text{(VII.3)}$$

The ratio of the number of moles of combustion products to the number of moles of the initial substances is:

$$\frac{\Sigma m^{++}}{\Sigma m_i} = \frac{\frac{m}{4} + \alpha\left(n + \frac{m}{4}\right)}{1 + \alpha\left(n + \frac{m}{4}\right)}. \qquad \text{(VII.4)}$$

At low temperatures the equilibrium of water vapor

$$CO + H_2O \rightleftarrows CO_2 + H_2 + 9{,}647\ \frac{\text{Kcal}}{\text{mole}} \qquad \text{(VII.5)}$$

is shifted in the direction of CO_2 and H_2 formation (the heat of combustion of a product of incomplete carbon oxidation CO is greater than that of H_2); therefore, at $\alpha < 1$, the composition of the mixture of combustion products at equilibrium at a low temperature (below 500° K) will be determined by equations:

$$C_nH_m + \alpha\left(n + \frac{m}{4}\right)O_2 = nCO_2 + \left[\alpha \cdot \frac{m}{2} - 2(1 - \alpha)n\right]H_2O + (1 - \alpha)\left(2n + \frac{m}{2}\right)H_2 \qquad \text{(VII.6)}$$

at

$$\frac{2n}{2n + \frac{m}{2}} \leqslant \alpha \leqslant 1$$

or

$$C_nH_m + \alpha\left(n + \frac{m}{4}\right)O_2 = \left[(2\alpha - 1)n + \alpha\frac{m}{2}\right]CO_2 + \left[2(1 - \alpha)n - \alpha\frac{m}{2}\right]CO + \frac{m}{2}H_2 \qquad \text{(VII.7)}$$

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at

$$\frac{n}{2n+\frac{m}{2}} \leqslant \alpha \leqslant \frac{2n}{2n+\frac{m}{2}}.$$

The ratio of the number of moles of combustion products to the number of moles of the initial substances in both cases amounts to:

$$\frac{\Sigma m_{i+}}{\Sigma m_i} = \frac{n+\frac{m}{2}}{1+\alpha\left(n+\frac{m}{4}\right)}, \tag{VII.8}$$

i.e., it grows as α decreases *.

The fact that the products of incomplete hydrocarbon combustion, as a rule, contain a considerable proportion of CO is to be attributed to the following cause. The equilibrium of water vapor, which at high temperatures shifts considerably in the direction of CO and H_2O formation, is "inhibited" during cooling of combustion products, so that the composition of the gases analyzed at low temperature does not correspond to the state of true equilibrium.

The composition of combustion products may be computed on the basis of formula (V.52) while determining the relationships between the molar concentrations of the combustion products according to combustion equations (VII.1), (VII.3), (VII.6), and (VII.7).

Another method may also be indicated which does not call for a preliminary construction of combustion equations. On the basis of formulas (VII.7), computations are made of $a = \frac{(m)_H}{(m)_C}$ and $b = \frac{(m)_O}{(m)_C}$; $(m)_C$ is calculated from formula (V.52) which in this case has the form of:

$$[m]_C = \frac{G}{\mu_C + a\mu_H + b\mu_O}. \tag{VII.9}$$

Further:

$$[m]_H = a\,[m]_C; \qquad [m]_O = b\,[m]_C.$$

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* In proceeding from equation (VII.8) it is possible to draw certain preliminary conclusions regarding the position of the maximum on the curves, reflecting the dependence of combustion temperature and the maximum explosion pressure upon the composition of the initial mixture in a sealed vessel.

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The composition of the initial mixture can be determined from formulas:

$$m_{iC_nH_m} = \frac{1}{n}[m]_C; \qquad m_{iO_2} = \frac{1}{2}[m]_O. \tag{VII.10}$$

Inasmuch as the mixture of combustion products for all α's is composed only of three substances, between which no reactions whatever are taking place, it suffices to have three balance equations for each of the three elements to calculate the composition of such a mixture. For $\alpha > 1$:

$$\left.\begin{aligned} m_{CO_2}^{++} &= [m]_C, \\ m_{H_2O}^{++} &= \frac{[m]_H}{2}, \\ 2m_{CO_2}^{++} + m_{H_2O}^{++} + 2m_{O_2}^{++} &= [m]_O, \end{aligned}\right\} \tag{VII.11}$$

whence

$$m_{O_2}^{+} = \frac{[m]_O - 2m_{CO_2}^{+} - m_{H_2O}^{++}}{2}. \tag{VII.12}$$

For $\frac{2n}{2n + \frac{m}{2}} \leqslant \alpha \leqslant 1$:

$$\left.\begin{aligned} m_{CO_2}^{++} &= [m]_C, \\ 2m_{CO_2}^{++} + m_{H_2O}^{++} &= [m]_O, \\ 2m_{H_2O}^{+} + 2m_{H_2}^{++} &= [m]_H. \end{aligned}\right\} \tag{VII.13}$$

Having determined $m_{CO_2}^{++}$ from the equation of balance for oxygen, we obtain:

$$m_{H_2O}^{--} = [m]_O - 2m_{CO_2}^{++}, \tag{VII.14}$$

and further, from balance equation for hydrogen:

$$m_{H_2} = \frac{[m]_H - 2m_{H_2O}^{++}}{2}. \tag{VII.15}$$

Finally, for $\frac{n}{2n + \frac{m}{2}} \leqslant \alpha \leqslant \frac{2n}{2n + \frac{m}{2}}$, we have

$$\left\{\begin{aligned} m_{H_2}^{++} &= \frac{1}{2}[m]_H, \\ m_{CO_2} + m_{CO}^{++} &= [m]_C, \\ 2m_{CO_2} + m_{CO}^{++} &= [m]_O. \end{aligned}\right. \tag{VII.16}$$

Subtracting the third equation from the second, we obtain

$$m_{CO_2}^{++} = [m]_O - [m]_C, \qquad (VII.17)$$

and further:

$$m_{CO} = [m]_C - m_{CO_2}^{++}. \qquad (VII.18)$$

Let it be mentioned here that this entire calculation is meaningful only when applied to further discussions and computations; we shall therefore disregard the formation of solid carbon after Boudoir's formula

$$2CO \rightleftarrows CO_2 + C + 39{,}356 \text{ Kcal} \qquad (VII.19)$$

as a result of a process which progresses slowly at low temperatures -- as this is common for most processes with new-phase formation -- and fails totally to conform with equilibrium conditions at high temperatures (above 1,000 - 1,200° K)*.

(2) Calculation of the State of Combustion Products Corresponding to High Pressures

In taking advantage of the fact that the equilibrium state of the system does not depend on the method by which this state was achieved, let us assume that, from the beginning, the initial stage has reached equilibrium at the starting temperature, say, of 25° C, so that its composition is determined by equations (VII.1), (VII.3), (VII.6), or (VII.7). Thereafter, the mixture was heated to some definite temperature T. At the same time, only such reactions were developing in it which do not lead to an increase of the number of moles. In a system formed by carbon, hydrogen, and oxygen, such a reaction is the reaction of water vapor**. It will be readily seen from equation (VII.5) that this reaction can occur only if there is a shortage of oxygen, i.e., when $\alpha < 1$. If $\alpha \geq 1$, the composition, which corresponds to high pressures at any temperature, coincides with the composition corresponding to

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* See footnote on page 35.

** If nitrogen is present, then, apart from the water-vapor reaction, we should also take into account reaction $N_2 + O_2 \rightleftarrows 2NO$ which, with rising temperatures, shifts in the direction of NO formation.

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equilibrium at low temperatures (equation VII.3). When $\alpha < 1$, the mixture -- in view of the progress of reaction (VII.5) -- is composed of four components: CO_2, CO, H_2O, and H_2. Its composition is determined by three balance equations and the equilibrium constant

$$K_6 = \frac{p_{CO_2} \cdot p_{H_2}}{p_{CO} \cdot p_{H_2O}} = \frac{\overline{m}_{CO_2} \cdot \overline{m}_{H_2}}{\overline{m}_{CO} \cdot \overline{m}_{H_2O}}, \qquad \left(\text{Since } p_k = \frac{m_k}{\sum m} P\right),$$

where $\overline{m}$ - molar concentrations of combustion products in a system whose composition corresponds to high pressures. We have a system of four equations:

$$\left.\begin{aligned} \overline{m}_{CO_2} + \overline{m}_{CO} &= [m]_C, \\ 2\overline{m}_{H_2O} + 2\overline{m}_{H_2} &= [m]_H, \\ 2\overline{m}_{CO_2} + \overline{m}_{CO} + \overline{m}_{H_2O} &= [m]_O, \\ \frac{\overline{m}_{CO_2} \cdot \overline{m}_{H_2}}{\overline{m}_{CO} \cdot \overline{m}_{H_2O}} &= K_6. \end{aligned}\right\} \tag{VII.20}$$

We introduce the designations:

$$1 - K_6 = \beta, \tag{VII.21}$$

$$[m]_O - 2[m]_C = \gamma, \tag{VII.22}$$

$$\frac{1}{2}[m]_H - \gamma = \delta, \tag{VII.23}$$

$$\frac{1}{2}[m]_H + [m]_C - \beta\gamma = \eta, \tag{VII.24}$$

$$\delta[m]_C = \xi. \tag{VII.25}$$

Then

$$\overline{m}_{CO} = \frac{\eta \pm \sqrt{\eta^2 - 4\beta\xi}}{2\beta}, \tag{VII.26}$$

$$\overline{m}_{CO_2} = [m]_C - \overline{m}_{CO}, \tag{VII.27}$$

$$\overline{m}_{H_2O} = \gamma + \overline{m}_{CO}, \tag{VII.28}$$

$$\overline{m}_{H_2} = \delta - \overline{m}_{CO}. \tag{VII.29}$$

If both roots of equation (VII.26) are positive, then the selection of the correct root value is effected after substitution in equations (VII.27) to (VII.29).

The values of $\overline{m}_{CO}$, $\overline{m}_{CO_2}$, $\overline{m}_{H_2O}$, and $\overline{m}_{H_2}$ may also be determined on the basis of the following considerations. From equation (VII.5) it follows that, if one proceeds from the composition corresponding to the low temperatures, the loss in CO_2, as a result of the reaction of water vapor, will be equal to the loss in H_2, the growth of CO, and the growth of H_2O. Consequently, when $\frac{2n}{2n+\frac{m}{2}} \leqslant \alpha \leqslant 1$:

$$K_6 = \frac{(m_{CO_2}^{++} - \overline{m}_{CO})(m_{H_2}^{++} - \overline{m}_{CO})}{\overline{m}_{CO}(m_{H_2O}^{++} + \overline{m}_{CO})}. \qquad \text{(VII.30)}$$

In making simple transformations we produce:

$$(1 - K_6)\overline{m}_{CO}^2 - (m_{CO_2}^{++} + m_{H_2}^{++} + K_6 m_{H_2O}^{++})\overline{m}_{CO} + m_{CO_2}^{++} m_{H_2}^{++} = 0.$$

After comparison of the coefficients of the last equation with expressions (VII.21) to (VII.25) and (VII.13) to (VII.15), we arrive at the conclusion that

$$m_{CO_2}^{++} + m_{H_2}^{++} + K_6 m_{H_2O}^{++} = \eta, \qquad \text{(VII.31)}$$

$$m_{CO_2}^{++} m_{H_2}^{++} = \xi, \qquad \text{(VII.32)}$$

moreover, in the above scheme,

$$\gamma = m_{H_2O}^{++}, \quad \delta = m_{H_2}^{++}.$$

Finally we return to the very same scheme of computation. Besides, it is obvious that this scheme includes the preliminary calculation of the composition corresponding to the low temperatures.

When

$$\frac{n}{2n+\frac{m}{2}} \leqslant \alpha \leqslant \frac{2n}{2n+\frac{m}{2}}:$$

$$\frac{(m_{CO_2}^{++} - \overline{m}_{H_2O})(m_{H_2}^{++} - \overline{m}_{H_2O})}{(m_{CO}^{++} + \overline{m}_{H_2O})\,\overline{m}_{H_2O}} = K_6. \qquad \text{(VII.33)}$$

In solving this equation for $\overline{m}_{H_2O}$, we obtain:

$$\overline{m}_{H_2O} = \frac{\lambda \mp \sqrt{\lambda^2 - 4\beta\xi}}{2\beta}, \qquad \text{(VII.34)*}$$

where

$$\lambda = m_{CO_2}^{++} + m_{H_2}^{++} - K_6 m_{CO}^{++}.$$

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* See remarks in the text pertaining to equation (VII.26).

An identical result would have been produced, had the system of equations (VII.20) been solved for $\overline{m}_{H_2O}$. Furthermore,

$$\overline{m}_{CO_2} = m^{++}_{CO_2} - \overline{m}_{H_2O}, \tag{VII.35}$$

$$\overline{m}_{H_2} = m^{++}_{H_2} - \overline{m}_{H_2O}, \tag{VII.36}$$

$$\overline{m}_{CO} = m^{++}_{CO} + m_{H_2O}. \tag{VII.37}$$

Let it be noted that in the previously recorded scheme (Equations (VII.21) to (VII.29)) at

$$\frac{n}{2n+\frac{m}{2}} \leqslant \alpha \leqslant \frac{2n}{2n+\frac{m}{2}}:$$

$$\gamma = -m^{++}_{CO}, \quad \delta = m^{++}_{H_2} + m^{++}_{CO}.$$

It is evident that $\sum \overline{m} = \sum m$ and

$$\frac{\Sigma \overline{m}}{\Sigma m_i} = \frac{\Sigma m^{++}}{\Sigma m_i}. \tag{VII.38}$$

The enthalpy of the mixture, whose composition corresponds to equilibrium at high pressure, may be determined for the given temperature T on the basis of formula:

$$\overline{H}_{T\,\mathrm{prod}} = \sum_j \overline{m}_j H^{\circ}_{T}. \tag{VII.39}$$

Section 2. Calculation of the State of Combustion Products In Case of Powerful Dissociation

In Section 1 we analyzed the first stage of computations of the state of combustion products by the approximation method. Here we shall consider the second and the third stages.

The Second Stage. Let it be assumed that a mixture, composed of undissociated combustion products and having a starting pressure P_0, is brought into equilibrium state by means of dissociation of its components at constant volume and constant temperature T. As we showed in Chapter V, the composition of a mixture formed by m elements and n components is determined by m balance equations and n-m independent equilibrium constants. For a system consisting of three elements -- C, H, and O --

the material-balance equations look like this:

$$\left.\begin{aligned} m'_{CO_2}+m'_{CO}&=[m]_o,\\ 2m'_{H_2O}+2m'_{H_2}+m'_{OH}+m'_{H}&=[m]_H,\\ m'_{H_2O}+2m'_{CO_2}+2m'_{O_2}+m'_{OH}+m'_{O}+m'_{CO}&=[m]_O \end{aligned}\right\} \qquad \text{(VII.40)}$$

(all quantities determined during the second stage of computations will be primed).

In order to pass from molar concentrations of the components on to their partial pressures, it is necessary to multiply both parts of equations (VII.40) by $\frac{P'}{\sum m'}$, where P' -- pressure of equilibrium mixture, $\sum m'$ -- total number of moles in it. But since dissociation occurs at constant temperature and constant volume -- that volume which was occupied by the undissociated combustion products at pressure P_0 --

$$\frac{P'}{\Sigma m'}=\frac{P_0}{\Sigma m}.$$

Consequently,

$$\left.\begin{aligned} p'_{CO_2}+p'_{CO}&=[m]_C\frac{P_0}{\Sigma m}\\ 2p'_{H_2O}+2p'_{H_2}+p'_{OH}+p'_{H}&=[m]_H\frac{P_0}{\Sigma m},\\ p'_{H_2O}+2p'_{CO_2}+2p'_{O_2}+p'_{OH}+p'_{O}+p'_{CO}&=[m]_O\frac{P_0}{\Sigma m}. \end{aligned}\right\} \qquad \text{(VII.41)}$$

When we introduce designations:

$$[m]_C\frac{P_0}{\Sigma m}=\{p\}'_C; \quad [m]_H\frac{P_0}{\Sigma m}=\{p\}'_H; \quad [m]_O\frac{P_0}{\Sigma m}=\{p\}'_O, \qquad \text{(VII.42)}$$

we obtain balance equations of the same type as equations (V.12) to (V.14). Hence, the composition of an equilibrium mixture may be calculated following the scheme recorded for the case of combustion at constant volume (Chapter V, Section 1). This actually constitutes the simplification introduced by Zel'dovich and Polyarny into the calculation of combustion processes at constant pressure.

From the preceding discussion, including the considerations contained in Section 1, Chapter V, it is clear that $\{p\}'_C$, $\{p\}'_H$, and $\{p\}'_O$, are those partial pressures which the atomic components should have had, had the mixture of undissociated combustion products, taken at starting pressure P_0, been dissociated at constant volume and constant temperature to the level of atoms. Therefore, as before, we shall treat

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$\{p\}'_C$, $\{p\}'_H$, and $\{p\}'_0$ as conditional partial pressures of atomic components. However, it should be noted, that in contrast with the quantities similar to them, which we have used during calculations of the composition of combustion products at constant volume, and which can be determined by equations (V.10), the quantities that can be determined by equations (VII.42) will be the same for all temperatures for which computation is made, since we postulate that at all temperatures the mixture of undissociated products has the pressure P_0.

The quantity $\sum \overline{m} = \sum m^{++}$ is calculated either on the basis of composition determined in the 1st computation stage, or according to formulas (VII.2), (VII.4), (VII.8) and the known value of $\sum m_i$.

It is advantageous to derive more general formulas for the calculation of $\{p\}'_C$, $\{p\}'_H$, and $\{p\}'_0$.

When $\alpha \geqslant 1$, while using equation (VII.3), we obtain

$$m^{++}_{CO_2} = [m]_C, \tag{VII.43}$$

$$m^{++}_{H_2O} = \frac{m}{2n}[m]_C, \tag{VII.44}$$

$$m^{++}_{O_2} = \frac{(\alpha-1)\left(n+\frac{m}{4}\right)}{n}[m]_C. \tag{VII.45}$$

In summing up, we find

$$\sum m^{++} = \sum \overline{m} = \frac{\frac{m}{4}+\alpha\left(n+\frac{m}{4}\right)}{n}[m]_C \tag{VII.46}$$

(compare with (VII.4))

Further, from formulas (VI.7), we get

$$[m]_H = \frac{m}{n}[m]_C, \tag{VII.47}$$

$$[m]_0 = \frac{2\alpha\left(n+\frac{m}{4}\right)}{n}[m]_C. \tag{VII.48}$$

Substituting equations (VII.46), (VII.47), (VII.48) in formulas (VII.42) we obtain:

$$\{p\}'_C = \frac{n}{\frac{m}{4}+\alpha\left(n+\frac{m}{4}\right)}P_0, \tag{VII.49}$$

$$\{p\}'_H = \frac{m}{\frac{m}{4} + \alpha\left(n + \frac{m}{4}\right)} P_0, \qquad \text{(VII.50)}$$

$$\{p\}'_O = \frac{2\alpha\left(n + \frac{m}{4}\right)}{\frac{m}{4} + \alpha\left(n + \frac{m}{4}\right)} P_0. \qquad \text{(VII.51)}$$

For $\alpha \leqslant 1$ we get in the same manner

$$\sum m'' = \sum \overline{m} = \frac{n + \frac{m}{2}}{n} [m]_C \qquad \text{(VII.52)}$$

(compare with (VII.8)).

Substituting equations (VII.52), (VII.47) and (VII.48) into formulas (VII.42) we have:

$$\{p\}'_C = \frac{n}{n + \frac{m}{2}} P_0, \qquad \text{(VII.53)}$$

$$\{p\}'_H = \frac{m}{n + \frac{m}{2}} P_0, \qquad \text{(VII.54)}$$

$$\{p\}'_O = \frac{2\alpha\left(n + \frac{m}{4}\right)}{n + \frac{m}{2}} P_0. \qquad \text{(VII.55)}$$

Thus, if at $\alpha > 1$ all three quantities -- $\{p\}'_C$, $\{p\}'_H$, and $\{p\}'_O$ -- depend on α, then at $\alpha \leqslant 1$ only $\{p\}'_O$ depends on α and it changes in direct proportion to α. This should be borne in mind when calculation is made for a number of different initial mixture compositions in the face of oxygen shortage*.

The composition, determined from equations (VII.41) and the corresponding five equilibrium constants, corresponds to pressure $P' > P_0$. On the basis of the known

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* Although the calculations reviewed so far in this chapter are simple enough, we nevertheless record a large number of ready formulas which will facilitate the checking of the accuracy of the calculated results at this initial stage of computations. This is important since on these results depends the correctness of further calculations. Besides, these formulas permit us to discern certain regularities, which not only facilitate calculations but also enable us to predict certain results of the complete computation of the state of combustion products.

partial pressures p' it is not difficult to calculate the enthalpy of the mixture.

$$H'_{T\,\text{prod}} = \sum_k m'_k H^\circ_{Tk}. \tag{VII.56}$$

At the same time

$$p'_k = m'_k \cdot \frac{P'}{\Sigma m'} = m'_k \frac{P_0}{\Sigma \bar{m}}.$$

Whence

$$m'_k = \frac{\Sigma \bar{m}}{P_0} p'_k.$$

Consequently,

$$H'_{T\,\text{prod}} = \frac{\Sigma \bar{m}}{P_0} \sum_k p'_k H^\circ_{Tk}. \tag{VII.57}$$

<u>The Third Stage.</u> Let the mixture, whose composition and enthalpy were calculated in the course of the second stage, be permitted to expand reversibly and isothermically to such an extent as to assure a reduction in pressure to P_0. Dissociation will grow thereby. But we shall not determine the change of composition. Instead, we shall right away determine the change of enthalpy and volume of the mixture with diminishing pressure from P' to P_0. From the type of the equations of equilibrium dissociation reactions, Zel'dovich and Polyarny were able to conclude that the effects connected with dissociation -- for example, the increase of enthalpy and the growth of volume -- are proportional to a negative fractional power of pressure. In conformity therewith we have:

$$H'_{\text{prod}} - \bar{H}_{\text{prod}} = AP'^{-n_H}, \tag{VII.58}$$

where n_H = a certain proper fraction.

We shall take a logarithm of (VII.58):

$$\lg (H'_{\text{prod}} - \bar{H}_{\text{prod}}) = \lg A - n_H \lg P'.$$

Let us now assume that, with the drop of pressure from P' to P_0, the composition of the mixture initially did not change. We shall denote by V' that volume which the composition mixture, calculated during the second stage, would have had at pressure P_0, and by $\bar{V}$ the volume of this mixture at pressure P', which is equal to the volume of the undissociated products at pressure P_0. In conformity with the law of ideal gases we have: $\frac{V'}{\bar{V}} = \frac{P'}{P_0}$;

$$\frac{V'-\bar{V}}{\bar{V}}=\frac{P'-P_0}{P_0}=\frac{\Sigma m'-\Sigma\bar{m}}{\Sigma\bar{m}}=\zeta', \qquad \text{(VII.59)}$$

where ζ' — a quantity which characterizes the effect of dissociation on the volume if the pressure is constant, or on pressure if the volume is constant.

In a way similar to (VII.58), we write

$$\zeta'=BP'^{-n_\zeta}. \qquad \text{(VII.60)}$$

Taking the logarithm, we obtain

$$\lg\zeta'=\lg B-n_\zeta\lg P'. \qquad \text{(VII.61)}$$

In setting a number of values for initial pressure P_0, we shall calculate for each of them the mixture composition, pressure P', enthalpy H'_{prod}, difference $H'_{prod} - \bar{H}_{prod}$, and the quantity ζ. We construct the curves of lg $(H'_{prod} - \bar{H}_{prod})$ and lg ζ' versus lg P' (see Figure 14)*. It appears that these curves are very close to straight lines, which fact evidences the constancy of n_H and n_ζ over a wide range of pressures. This permits us to write the following:

$$n_H\approx-\frac{\Delta\lg(H'_{prod}-\bar{H}_{prod})}{\Delta\lg P'}; \qquad \text{(VII.62)}$$

$$n_\zeta\approx-\frac{\Delta\lg\zeta'}{\Delta\lg P'}. \qquad \text{(VII.63)}$$

Exponents n_H and n_ζ may now be calculated in the following manner. After we have picked three random values for initial pressure P_0 -- of which one coincides with the given value, while of the remaining two, one is greater (say, double), and the other is smaller (say, by half) than the given value -- we calculate the composition, pressure P', enthalpy H'_{prod}, difference $H'_{prod} - \bar{H}_{prod}$, and the quantity ζ', which correspond to these three values of initial pressure, as well as lg P', lg $(H'_{prod} - \bar{H}_{prod})$, and lg ζ'. Then, on the basis of formulas (VII.62) and (VII.63) we determine the average values of n_H and n_ζ for the interval between the highest and lowest values of P'.

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* The curves in Figure 14 are plotted on the basis of the data in Example 5 (see below).

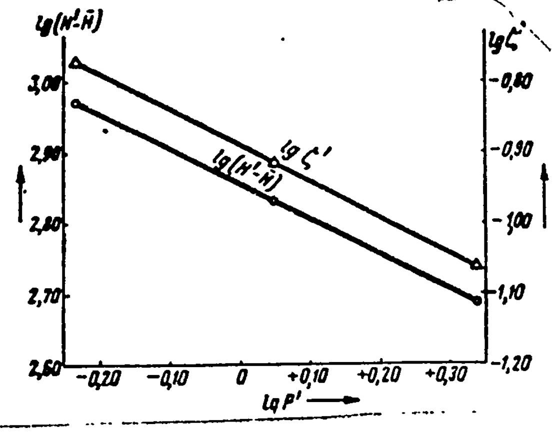

Figure 14. Curve of lg (H'-H̄) and lg ζ', versus lg P'.

To determine $\overline{H}_{prod}$ of the equilibrium mixture of combustion products at pressure P_0, we shall proceed as follows. In conformity with the assumptions made earlier and in view of the constancy of n_H over a wide range of pressures, we have:

$$H_{prod} - \overline{H}_{prod} = AP_0^{-n_H},$$
$$H'_{prod} - \overline{H}_{prod} = AP'^{-n_H}.$$

We shall divide one of these equations by the other:

$$\frac{H_{prod} - \overline{H}_{prod}}{H'_{prod} - \overline{H}_{prod}} = \left(\frac{P_0}{P'}\right)^{-n_H}.$$

Hence,

$$H_{prod} = \overline{H}_{prod} + (H'_{prod} - \overline{H}_{prod}) \left(\frac{P'}{P_0}\right)^{n_H}. \qquad \text{(VII.64)}$$

Having determined $\overline{H}_{prod}$ in the first stage of calculations and H'_{prod} in the second stage, and having found the value of n_H, we can now, on the basis of formula (VII.64), determine the enthalpy H_{prod} of the mixture of combustion products at pressure P_0.

The values of $\overline{H}_{prod}$, H'_{prod}, and H_{prod} should be calculated for no less than three temperatures, so as to assure that H_{T_i} prod, calculated as formerly according to formula (VI.17), will be located between the extreme values of H_{prod}. Thereafter, the combustion temperature T_e may be found by interpolation from the condition:

$$H_{T_e prod} = H_{T_i init}$$

It must be mentioned here that the exponent n_H (like n_ζ) may be determined only once, since its values, calculated for different temperatures over a range from 200-400°, differ little one from another.

The expansion degree may be determined in the following manner. By a method, perfectly analogous to that of the derivation of formula (VII.64), we produce

$$\zeta = \zeta'\left(\frac{P'}{P_0}\right)^{n_\zeta}. \qquad \text{(VII.65)}$$

Calculating ζ' from formula

$$\zeta' = \frac{P'}{P_0} - 1 \qquad \text{(VII.66)}$$

and ζ from formula (VII.65) for those temperatures for which H_{prod} is to be calculated, and knowing combustion temperature T_e, we find on the basis of one of the interpolation formulas (V.68) to (V.71), the value of ζ_e, i.e., that relative increment of volume, equal to the relative growth of the number of moles, which is caused by dissociation that brings the system into equilibrium state at given pressure P_0 and temperature of combustion T_e:

$$\zeta_e = \frac{V - \bar{V}}{\bar{V}} = \frac{\Sigma m_e - \Sigma \bar{m}}{\Sigma \bar{m}} = \frac{\Sigma m_e}{\Sigma \bar{m}} - 1.$$

Hence,

$$\sum m_e = (1 + \zeta_e) \sum \bar{m}. \qquad \text{(VII.67)}$$

The degree of expansion may now be calculated with the help of formula (VI.22).

Example 5. Solve the problem formulated in Example 3 (page 63) by the Zel'dovich-Polyarny approximation method.

On the basis of formulas (VII.9) we find

$$[m]_C = 14{,}8717; \quad [m]_H = 59{,}4866; \quad [m]_O = 47{,}5893 \ \frac{\text{g-atom}}{\text{kg}}$$

On the basis of formula (VII.10)

$$m_{i\,CH_4} = 14{,}8717; \quad m_{i\,O_2} = 23{,}7947 \ \frac{\text{mole}}{\text{kg}}$$

and from formula (VI.17)

$$H_{T_i\,init} = 2{,}943.1 \ \frac{\text{Kcal}}{\text{kg}}$$

First stage. From formulas (VII.13), (VII.14), and (VII.15) we find:

$$m^{++}_{CO_2} = 14{,}8717; \quad m^{++}_{H_2O} = 17{,}8459; \quad m^{++}_{H_2} = 11{,}8974 \ \frac{\text{mole}}{\text{kg}}$$

By summation we get

$$\sum m^{++} = \sum \bar{m} = 44{,}6150 \ \frac{\text{mole}}{\text{kg}}$$

Further calculations will be made for the temperature of 3,200° K. With the help of formulas (VII.31), (VII.32), (VII.26) to (VII.29), we find the mixture composition

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of combustion products valid for high pressure.

$$\eta = 29,2229; \quad \xi = 176,9346.$$

Further

$$\begin{aligned} \overline{m}_{CO} &= 7,8937, \\ \overline{m}_{CO_2} &= m_{CO_2}^{++} - \overline{m}_{CO} = 6,9780, \\ \overline{m}_{H_2O} &= m_{H_2O}^{++} + \overline{m}_{CO} = 25,7396, \\ \overline{m}_{H_2} &= m_{H_2}^{++} - \overline{m}_{CO} = 4,0037. \end{aligned}$$

According to formula (VII.39):

$$\overline{H}_{prod} = 2,262.3 \ \frac{Kcal}{kg}$$

Second stage. From formulas (VII.42) we calculate:

$$\{p\}'_C = 0,33333; \quad \{p\}'_H = 1,33333; \quad \{p\}'_O = 1,06667 \ \text{atm.}$$

By the method of selection of the value of p'_{H_2}, according to the scheme in Section 1, Chapter V (equations (V.21) to (V.28)), we calculate the partial pressures of combustion products in the assumption that dissociation takes place at constant volume, i.e., that volume which the undissociated combustion products would have occupied at pressure P_0.

On the basis of formula (VII.57) we find the enthalpy $H'_{T prod}$ of the mixture of the calculated composition at 3,200° K:

$$H'_{3200 prod} = 3468,7 \ \frac{Kcal}{Kg}$$

Third stage. In the assumption that $n_H = \frac{1}{2}$, we calculate, on the basis of formula (VII.64):

$$H_{3200 prod} = 2262,3 + (3468,7 - 2262,3)\sqrt{1,2188} = 3594,1 \ \frac{Kcal}{Kg}$$

On comparing this value of H_{prod} with the value of $H_{T_i prod}$, we arrive at the conclusion that the combustion temperature is below 3,200° K.

In repeating the calculation for 3,000° K on the same assumption that $n_H = \frac{1}{2}$, we find:

$$H_{3000 prod} = 2871,7 \ \frac{Kcal}{Kg}$$

After comparison of $H_{3,200 prod}$ and $H_{3,000 prod}$ with $H_{T_i \ init}$, we conclude that the temperature of combustion lies between 3,000° and 3,200° K, though closer to 3,000° K.

We shall now define the value of exponent n_H with greater precision, and determine n_ζ. For this purpose we calculate the composition, P', H'_{prod} and ζ' at 3,000° K for two more values of initial pressure P_0: 0.5 atm and 2 atm.

The calculation results for all the three values of P_0 are incorporated in Table 8.

Table 8

P_0	0.5 atm	1.0 atm	2.0 atm
P'	0,5845	1,1217	2,1729
ζ'	0,1689	0,1217	0,0865
H'	3086,8	2831,5	2636,8
$H' - \bar{H} = H' - 2262{,}3$	935,6	680,3	485,6

Further calculation is made according to formulas (VII.62) and (VII.63) for two intervals: (1) between P_0 = 0.5 atm and P_0 = 1 atm, (2) between P_0 = 1 atm and P_0 = 2 atm -- and the average result is taken thereof. The process of computation is clear from Table 9.

Table 9

P_0	$\lg P'$	$\Delta \lg P'$	$\lg(H'-\bar{H})$	$\Delta \lg(H'-\bar{H})$	$\lg \zeta'$	$\Delta \lg \zeta'$	n_H	n_ζ
0,5	−0,23325	0,28312	2,97107	−0,13836	−0,77232	−0,14246	0,489	0,503
1,0	+0,04987	0,28717	2,83271	−0,14646	−0,91478	−0,14835	0,510	0,517
2,0	+0,33704		2,68625		−1,06313			

Finally we obtain:

$$n_H = 0{,}500; \quad n_\zeta = 0{,}510.$$

It should be noted that exponent n_H, calculated for 3,200° K, amounts to 0.459. This value refers to enthalpy $H_{3,200 prod} = 3,583.4$, which differs only negligibly from $H_{3,200 prod}$ corresponding to $n_H = \frac{1}{2}$. Therefore, for the whole temperature range under consideration (2,800-3,200° K), n_H may be assumed equal to its value for the temperature which most closely approaches combustion temperature, i.e., a value equal to $\frac{1}{2}$. Since this value of n_H does not differ from the one we adopted earlier, we do not recalculate enthalpy H_{prod} for 3,000 and 3,200° K. Exponent n_ζ may also be assumed to be equal to $\frac{1}{2}$ without a substantial error.

We now calculate $\overline{H}_{prod}$, H'_{prod}, H_{prod} for 2,800° K. The computation result, together with the results of calculations for two other temperatures, is to be found in Table 10.

Table 10

Calculation Stage	Temperature	2800°K	3000°K	3200°K
1-й	$\overline{m}_{CO}$	7,6980	7,8031	7,8937
	$\overline{m}_{CO_2}$	7,1737	7,0686	6,9780
	$\overline{m}_{H_2O}$	25,5439	25,6490	25,7396
	$\overline{m}_{H_2}$	4,1994	4,0943	4,0037
	$\overline{H}_{prod}$	2040,3	2151,2	2262,3
2-й	P'	1,0567	1,1217	1,2187
	H'_{prod}	2359,0	2831,5	3468,7
3-й	H_{prod}	2367,9	2871,7	3594,1
	ζ	0,0582	0,1289	0,2415

By interpolation from condition $H_{T_e prod} = H_{T_i init}$ we find

$$T_e = 3,022.8^\circ \text{ K}$$

Let us now compute the degree of expansion. For this purpose we shall determine ζ' according to formula (VII.66) and ζ according to formula (VII.65) for all three temperatures. By means of the Gaussian interpolation formula (V.71) we find:

$$\zeta_e = 0{,}1396;\ \frac{\Sigma m_e}{\Sigma \overline{m}} = 1{,}1396.$$

Further:

$$\frac{\Sigma \overline{m}}{\Sigma m_i} = \frac{3{,}0}{2{,}6} = 1{,}1538;$$

$$\frac{\Sigma m_e}{\Sigma m_i} = 1{,}1396 \cdot 1{,}1538 = 1{,}3149.$$

Finally, according to formula (VI.22),

$$E = 13{,}330$$

Let us compare the results of this problem's solution by the direct and the approximation methods. For this purpose we shall incorporate them in Table 11.

Table 11

Characteristic	Direct Method	Approximate Method
T_e	3023,7° K	3022,8° K
E	13,335	13,330
ζ_e	0,1397	0,1396

From this comparison it appears that both methods produce practically coinciding results.

Chapter VIII

ON THE METHODS OF COMPOSITION CALCULATION FOR MIXTURES OF COMBUSTION PRODUCTS

In our earlier computations of the composition of a mixture of combustion products, we used the method of the selection of values for the partial pressure of one of the components. This method is relatively simple but it cannot always be applied. This chapter will deal with other methods of computation.

Section 1. Method of Successive Approximations in Case of Weak Dissociation

If the contents of certain components in a mixture are small compared to the contents of other substances -- a case characteristic for weak dissociation -- then the mixture composition is usually determined in the following manner.

Let the mixture formed by m elements consist of n components. By methods previously outlined, we compose n equations for the determination of their partial pressures. Further, in the first approximation we set the values of those ℓ partial pressures equal to zero, which under given conditions are small in comparison to the partial pressures of other components. To determine the remaining $n - \ell$ partial pressures, we use the balance equations which are always linear. In those cases when $n - \ell > m$, we use balance equations composed of those partial pressures which are not equal to zero. In the second approximation, the determined values of $n-\ell$ partial pressures are introduced into the unutilized ℓ equations and determine the values of the ℓ partial pressures which in the first approximation were assumed to be equal to zero. These values are then introduced into the $n-\ell$ equations, which were used in the first approximation, and the new values of the remaining $n-\ell$ partial pressures are thus defined. In the third and subsequent approximations, we proceed in a similar way, continuing the calculations until we attain, with set precision, a coincidence of the values of partial pressures in two successive approximations.

In the first approximation, one should not equate to zero the partial pressures of those components whose concentration in the mixture is considerable. This would lead to a divergent sequence of values of the partial pressures to be determined. In those cases when the number of partial pressures, which may not be equated to zero in the first approximation, considerably exceeds the number of balance equations, the method of successive approximations usually fails to lead to an easily solvable system of equations and may be used under definite conditions only in conjunction with other methods.

Example 6. A mixture is exploded in a spherical vessel with central ignition. The composition of this mixture is characterized by the following values of its components' partial pressures: $p_{i_{H_2}} = 2.693$ atm; $p_{i}O_2 = 0.285$ atm; $p_i^* H_2O = 0.022$ atm; $p_i^* = 3{,}000$ atm. Initial temperature $T_i = 291^\circ$ K. Determine the theoretical value of the maximum explosion pressure.

According to formulas (V.74) and (V.75), we find $(p)_H = 18.6598 \cdot 10^{-3}T$; $\{p\}_0 = 2{,}03436 \cdot 10^{-3}T$. To determine the six unknown partial pressures -- p_{H_2O}, p_{H_2}, p_{O_2}, p_{OH}, p_O, and p_H -- we set up a system composed of two balance equations (V.77) and (V.78) and four equilibrium equations (V.16) to (V.19). Since a considerable excess of hydrogen was taken, we shall first postulate that the mixture of combustion products is composed only of water vapor and hydrogen. From the balance equations we obtain in this case:

$$p'_{H_2O} = \{p\}_0, \quad p'_{H_2} = \frac{\{p\}_H}{2} - p'_{H_2O}.$$

Substituting the determined values of p'_{H_2O} and p'_{H_2} into equations (V.16) to (V.19), we find the second approximation for partial pressures of the remaining components, p''_H, p''_{OH}, p''_O, and p''_{O_2}. Introducing these into the balance equation, we find p''_{H_2O}, and p''_{H_2} *. The third approximation, determined in a similar manner for 2,400° K yields results which practically coincide with those obtained in the second approximation (see Table 12). For partial pressures at 2,200 and 2,000°K, it is all the

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* Indexes ', ", (n-1), and (n) refer to the first, second, (n-1)th, and n-th approximations, respectively.

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[redacted]

more sufficient to calculate the second approximation, and this makes the operation both very simple and rapid.

Table 12

T = 2,400° K	First Approximation	Second Approximation	Third Approximation
$p_{H}^{(n)} = K_8 \sqrt{p_{H_2}^{(n-1)}}$	0	0,0720	0,0719
$p_{OH}^{(n)} = K_3 \left(p_{H_2O}^{(n-1)} / \sqrt{p_{H_2}^{(n-1)}}\right)$	0	0,0075	0,0075
$p_{O}^{(n)} = K_9 \left(p_{H_2O}^{(n-1)} / p_{H_2}^{(n-1)}\right)$	0	0	0
$p_{O_2}^{(n)} = K_7 \left(p_{H_2O}^{(n-1)} / p_{H_2}^{(n-1)}\right)^3$	0	0	0
$p_{H_2O}^{(n)} = \{p\}_O - p_{OH}^{(n)} - p_{O}^{(n)} - 2p_{O_2}^{(n)}$	4,8825	4,8750	4,8750
$p_{H_2}^{(n)} = \frac{1}{2}\left(\{p\}_H - p_{H}^{(n)} - p_{OH}^{(n)} - 2p_{H_2O}^{(n)}\right)$	17,5093	17,4770	17,4771

Making further calculations according to the scheme from Chapter V, we obtain:

$$U_{T_i} \text{ init} = 273.415 \ \frac{\text{lit-atm}}{\text{lit}}$$

and by graphic interpolation on the basis of data from Table 13, we find

$$T_e = 2,236^\circ \text{ K}; \quad P_e = 20.88 \text{ atm.}$$

Table 13

Seq. No.	Components	2,000° K	2,200° K	2,400° K
		Partial Pressures		
1	H_2	14,5879	16,0389	17,4771
2	H	0,0068	0,0246	0,0719
3	H_2O	4,0683	4,4736	4,8749
4	OH	0,0004	0,0020	0,0075
	P (Atm)	18,6634	20,5391	22,4314
	$U_T\text{prod} \ (\frac{\text{lit-atm}}{\text{lit}})$	265,237	272,168	279,580

[redacted]

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Example 7. Calculate the composition of combustion products of a methane-oxygen mixture at constant volume, if $\alpha = 6$, $P_i = 1$ atm, $T_i = 298.16^\circ$ K, in the assumption that $T_e = 2{,}400^\circ$ K.

According to the combustion reaction of methane we have

$$\frac{m_{iO_2}}{m_{iCH_4}} = \frac{p_{iO_2}}{p_{iCH_4}} = 2\alpha = 12.$$

At the same time $p_{iO_2} + p_{iCH_4} = 1$ atm, hence,

$$p_{iCH_4} = \frac{1}{13}\ ama, \quad p_{iO_2} = \frac{12}{13}\ atm$$

By formulas (V.10) we obtain:

$$\{p\}_C = 0{,}61918, \quad \{p\}_H = 2{,}47672, \quad \{p\}_O = 14{,}86032\ atm$$

As before, we shall assume that in the state of equilibrium the mixture of combustion products of methane-oxygen composition consists of eight components. We shall make our calculation with precision up to the fifth decimal until coincidence of partial pressure values in two successive approximations is achieved up to the fourth decimal. *

In the first approximation we assume the values of p'_{H_2}, p'_H, p'_{OH}, p'_O, and p'_{CO} to be equal to zero. To determine the remaining three unknowns, we will use balance equations (V.12) to (V.14). The result is:

$$p'_{CO_2} = \{p\}_C = 0{,}61918;$$

$$p'_{H_2O} = \frac{1}{2}\{p\}_H = 1{,}23836;$$

$$p'_{O_2} = \frac{1}{2}(\{p\}_O - 2p'_{CO_2} - p'_{H_2O}) = 6{,}19180$$

In the second approximation -- with the aid of five independent equilibrium constants and the values of p'_{CO_2}, p'_{H_2O}, p'_{O_2} determined in the first approximation -- we find:

$$p''_O = K_{12}\sqrt{p'_{O_2}} = 0{,}02275; \qquad \text{(VIII.1)}$$

$$p''_{H_2} = K_2\frac{p'_{H_2O}}{\sqrt{p'_{O_2}}} = 0{,}00194; \qquad \text{(VIII.2)}$$

$$p''_H = K_{11}\frac{\sqrt{p'_{H_2O}}}{\sqrt[4]{p'_{O_2}}} = 0{,}00076; \qquad \text{(VIII.3)}$$

---

* In calculations for practical purposes, such precision, as a rule, appears to be superflous.

$$p''_{OH} = K_{10}\sqrt{p'_{H_2O}}\sqrt[4]{p'_{O_2}} = 0{,}18186; \tag{VIII.4}$$

$$p''_{CO} = K_1\frac{p'_{CO_2}}{\sqrt{p'_{O_2}}} = 0{,}00560. \tag{VIII.5}$$

Further we have:

$$p''_{CO_2} = \{p\}_C - p''_{CO} = 0{,}61358; \tag{VIII.6}$$

$$p''_{H_2O} = \frac{1}{2}(\{p\}_H - p''_{OH} - p''_H - 2p''_{H_2}) = 1{,}14511; \tag{VIII.7}$$

$$p''_{O_2} = \frac{1}{2}(\{p\}_O - p''_{H_2O} - p''_O - p''_{OH} - 2p''_{CO_2} - p''_{CO}) = 6{,}13892. \tag{VIII.8}$$

These values of p''_{CO_2}, p''_{H_2O}, and p''_{O_2} we shall now use to determine the partial pressures of O, H_2, H, OH, and CO in the third approximation, and so on (see Table 14).

Table 14

	First Approximation	Second Approximation	Third Approximation	Fourth Approximation	Fifth Approximation
$p_O^{(n)} = K_{12}\sqrt{p_{O_2}^{(n-1)}}$	0	0,02275	0,02265	0,02265	0,02265
$p_{H_2}^{(n)} = K_2\left(p_{H_2O}^{(n-1)}/\sqrt{p_{O_2}^{(n-1)}}\right)$	0	0,00194	0,00180	0,00180	0,00180
$p_H^{(n)} = K_{11}\left(\sqrt{p_{H_2O}^{(n-1)}}/\sqrt[4]{p_{O_2}^{(n-1)}}\right)$	0	0,00076	0,00073	0,00073	0,00073
$p_{OH}^{(n)} = K_{10}\sqrt{p_{H_2O}^{(n-1)}}\sqrt[4]{p_{O_2}^{(n-1)}}$	0	0,18186	0,17450	0,17481	0,17480
$p_{CO}^{(n)} = K_1\left(p_{CO_2}^{(n-1)}/\sqrt{p_{O_2}^{(n-1)}}\right)$	0	0,00560	0,00557	0,00557	0,00557
$p_{CO_2}^{(n)} = \{p\}_C - p_{CO}^{(n)}$	0,61918	0,61358	0,61361	0,61361	0,61361
$p_{H_2O}^{(n)} = \frac{1}{2}\left(\{p\}'_H - p_{OH}^{(n)} - p_H^{(n)} - 2p_{H_2}^{(n)}\right)$	1,23836	1,14511	1,14895	1,14879	1,14879
$p_{O_2}^{(n)} = \frac{1}{2}\left(\{p\}_O - p_{H_2O}^{(n)} - p_O^{(n)} - p_{OH}^{(n)} - 2p_{CO_2}^{(n)} - p_{CO}^{(n)}\right)$	6,19180	6,13892	6,14072	6,14064	6,14064

In this manner, if efforts are made to assure that the divergence between two successive approximations should not exceed unity in the fourth decimal, then in Example 6 already the second approximation and here only the fourth approximation will yield a satisfactory result. This is to be attributed to the fact that excess H_2 suppresses H_2O dissociation in both directions, whereas an excess of O_2 suppresses only in one direction.

Section 2. On the Method of the Selection of Values for Partial Pressures of Combustion Products

Chapters V-VII contain examples of the application of the method pertaining to the selection of values for one of the unknown partial pressures. Though the arbitrary fixing of value for partial pressure of one component appears to make it impossible to eliminate the need for dealing with an equation of an order higher than the second, this goal may very often be achieved by fixing partial pressure values for two components. This method is complicated, yet in dealing with multi-component systems in the face of strong dissociation, it still proves to be the least cumbersome.

For example, let us consider the computation scheme pertaining to this method for partial pressures of combustion products of hydrocarbon in oxygen if the pressure is constant. We have eight components and three elements. We form a system of three balance equations (VI.4) to (VI.6) and five independent equilibrium equations:

$$\frac{p_{CO}\sqrt{p_{O_2}}}{p_{CO_2}} = K_1; \quad \frac{p_{H_2}\sqrt{p_{O_2}}}{p_{H_2O}} = K_2;$$

$$\frac{p_{OH}\sqrt{p_{H_2}}}{p_{H_2O}} = K_3; \quad \frac{p_H}{\sqrt{p_{H_2}}} = K_8; \quad \frac{p_O}{\sqrt{p_{O_2}}} = K_{12}.$$

We fix the values of p_{H_2} and p_{O_2} arbitrarily. In this case the partial pressure values of the rest of the components may be calculated following the scheme:

$$p_{H_2O} = \frac{p_{H_2}\sqrt{p_{O_2}}}{K_2}; \quad p_H = K_8\sqrt{p_{H_2}};$$

$$p_{OH} = \frac{K_3}{\sqrt{p_{H_2}}}p_{H_2O}; \quad p_{CO_2} = \frac{2p_{H_2O} + p_{OH} + 2p_{H_2} + p_H}{a\left(1 + \frac{K_1}{\sqrt{p_{O_2}}}\right)};$$

[redacted]

$$p_O = K_{12}\sqrt{p_{O_2}}; \quad p_{CO} = \frac{K_1}{\sqrt{p_{O_2}}} \cdot p_{CO_2}.$$

It is convenient to vary the values of p_{H_2} and p_{O_2} alternately while using the following equations for purposes of checking:

$$p_{H_2O} + 2p_{O_2} + p_{OH} + p_O - (b-2)\,p_{CO_2} - (b-1)\,p_{CO} = 0; \qquad (VI.6)$$

$$p_{CO_2} + p_{CO} + p_{H_2O} + p_{O_2} + p_O + p_{H_2} + p_H + p_{OH} = P_0. \qquad (VI.4)$$

Comparing this scheme to the calculation scheme for the same system of equations as recorded in Section 1, Chapter VI, we notice that the mathematical operations are being strongly reduced with each approximation. However, the number of approximations increases sharply. It is expedient to pre-evaluate roughly, by one method or another, the order of magnitude of those partial pressures which are to be varied.

Section 3. Method of Mixture Composition Computation on the Basis of Partial-Pressure Values of Its Components*

If the approximate partial-pressure values of components are known, the following procedure may be envisaged for their precise determination. Using the method described above, we shall construct a system of equations for the determination of partial pressures. We shall then introduce therein the more precisely defined values of the unknown partial pressures in the form of a sum of their approximate values and corresponding corrections, $p_k = p'_k + \Delta p_k$. If the squares and higher degrees of corrections as well as their products are disregarded, the equations may be reduced to linear ones in relation to corrections Δp_k. This system of linear equations may be solved in the usual manner**.

Using this procedure, we may, for example, construct a computation scheme for the composition of a mixture of combustion products at constant pressure in the

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*The principle of this method is outlined by A. P. Vanichev in his monograph (2).

**The method of equilibrium calculation described by Huff, Gordon, and Morrell (42) is also based on the reduction of the problem to the solution of a system of linear equations in relation to the corrections for the approximate values of unknown quantities (partial pressures and temperature).

following way. With the help of the method described in the preceding chapter, we find a composition whose mixture would be in equilibrium if this could be achieved by dissociation, at constant volume, of undissociated combustion products with initial pressure equal to the set constant pressure at which combustion is taking place. In this manner, we shall obtain the approximate values of the true partial pressures of combustion products at constant pressure. On the average they will, evidently, be somewhat overrated, while the composition, on the whole, will correspond to a somewhat underrated degree of dissociation. Corrections for these approximate values may be found by the method outlined above.

We shall apply this method to determine the composition of combustion products for mixtures of hydrocarbons with oxygen at constant pressure.

Let us construct a system of eight equations:

$$\frac{p_{CO}\sqrt{p_{O_2}}}{p_{CO_2}} = K_1; \qquad \text{(VIII.9)}$$

$$\frac{p_{H_2}\sqrt{p_{O_2}}}{p_{H_2O}} = K_2; \qquad \text{(VIII.10)}$$

$$\frac{p_{OH}\sqrt{p_{H_2}}}{p_{H_2O}} = K_3; \qquad \text{(VIII.11)}$$

$$\frac{p_H}{\sqrt{p_{H_2}}} = K_8; \qquad \text{(VIII.12)}$$

$$\frac{p_O}{\sqrt{p_{O_2}}} = K_{12}; \qquad \text{(VIII.13)}$$

$$2p_{H_2O} + 2p_{H_2} + p_{OH} + p_H - ap_{CO_2} - ap_{CO} = 0; \qquad \text{(VIII.14)}$$

$$p_{H_2O} + 2p_{O_2} + p_{OH} + p_O - (b-2)\,p_{CO_2} - (b-1)\,p_{CO} = 0; \qquad \text{(VIII.15)}$$

$$p_{CO_2} + p_{CO} + p_{H_2O} + p_{O_2} + p_O + p_{H_2} + p_H + p_{OH} = P_0. \qquad \text{(VIII.16)}$$

The following designations will be introduced as corrections for the approximate values of partial pressures:

$$\Delta p_{CO_2} = -z, \quad \Delta p_{O_2} = -x, \quad \Delta p_{H_2O} = -v, \quad \Delta p_O = -t,$$
$$\Delta p_{CO} = -y, \quad \Delta p_{H_2} = -w, \quad \Delta p_{OH} = -u, \quad \Delta p_H = -s.$$

Substituting in equations (VIII.12) and (VIII.13) the expressions:

$$p_H = p'_H - s, \quad p_{H_2} = p'_{H_2} - w, \quad p_O = p'_O - t, \quad p_{O_2} = p'_{O_2} - x,$$

and after extracting the square root from the differences p'_{H_2} - w and p'_{O_2} - x, on the basis of binominal series, we obtain

$$p'_H - s = K_8 \sqrt{p'_{H_2}} - K_8 \frac{w}{2\sqrt{p'_{H_2}}},$$

$$p'_O - t = K_{13} \sqrt{p'_{O_2}} - K_{13} \frac{x}{2\sqrt{p'_{O_2}}},$$

and since

$$p'_H = K_8 \sqrt{p'_{H_2}},$$

$$p'_O = K_{13} \sqrt{p'_{O_2}},$$

then

$$s = K_8 \frac{w}{2\sqrt{p'_{H_2}}}, \tag{VIII.17}$$

$$t = K_{13} \frac{x}{2\sqrt{p'_{O_2}}}. \tag{VIII.18}$$

In thus expressing s by w and t by x, we can change over from a system of eight to a system of six equations.

After substitution expressions in equation (VIII.9)

$$p_{CO_2} = p'_{CO_2} - z,$$

$$p_{CO} = p'_{CO} - y,$$

$$p_{O_2} = p'_{O_2} - x,$$

and upon extracting the square root from the difference p'_{O_2} - x on the basis of binominal series, we obtain:

$$\frac{(p'_{CO} - y)\left(\sqrt{p'_{O_2}} - \frac{x}{2\sqrt{p'_{O_2}}}\right)}{p'_{CO_2} - z} = K_1;$$

$$p'_{CO}\sqrt{p'_{O_2}} - y\sqrt{p'_{O_2}} - \frac{p'_{CO}}{2\sqrt{p'_{O_2}}} x + \frac{xy}{2\sqrt{p'_{O_2}}} = K_1 p'_{CO_2} - K_1 z.$$

Disregarding the term containing the product of corrections xy we finally get:

$$p'_{CO} \cdot x + 2p'_{O_2} \cdot y - 2K_1 \sqrt{p'_{O_2}} \cdot z = 2p'_{CO} \cdot p'_{O_2} - 2K_1 p'_{CO_2} \sqrt{p'_{O_2}}. \tag{VIII.19}$$

Equations (VIII.10) and (VIII.11) may be transformed in exactly the same way:

$$p'_{H_2} \cdot x + 2p'_{O_2} \cdot w - 2K_2 \sqrt{p'_{O_2}} \cdot v = 2p'_{H_2} \cdot p'_{O_2} - 2K_2 p'_{H_2O} \sqrt{p'_{O_2}}. \tag{VIII.20}$$

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$$p'_{OH}\cdot w+2p'_{H_2}\cdot u-2K_3\sqrt{p'_{H_2}}\cdot v=2p'_{OH}\cdot p'_{H_2}-2K_3p'_{H_2O}\sqrt{p'_{H_2}}. \qquad \text{(VIII.21)}$$

The balance equations may be transformed into the following expressions:

$$\left(2+\frac{K_8}{2\sqrt{p'_{H_2}}}\right)w+2v+u-az-ay=$$

$$=2p'_{H_2}+p'_H+2p'_{H_2O}+p'_{OH}-ap'_{CO_2}-ap'_{CO}; \qquad \text{(VIII.22)}$$

$$\left(2+\frac{K_{13}}{2\sqrt{p'_{O_2}}}\right)x+v+u-(b-2)z-(b-1)y=$$

$$=2p'_{O_2}+p'_O+p'_{H_2O}+p'_{OH}-(b-2)p'_{CO_2}-(b-1)p'_{CO}; \qquad \text{(VIII.23)}$$

$$\left(1+\frac{K_8}{2\sqrt{p'_{H_2}}}\right)w+\left(1+\frac{K_{13}}{2\sqrt{p'_{O_2}}}\right)x+z+y+v+u=$$

$$=p'_{H_2}+p'_H+p'_{O_2}+p'_O+p'_{CO_2}+p'_{CO}+p'_{H_2O}+p'_{OH}-P_0. \qquad \text{(VIII.24)}$$

Thus we produce a system of six linear equations. Such a system may be solved in a general form by means of determinants, but in practice it is more convenient to work it out by the method of elimination, after substitution of the values of equilibrium constants and the approximate values of partial pressures.

Example 8. Determine the composition and enthalpy of a mixture of combustion products for a methane-oxygen mixture at constant pressure P_0 = 1 atm, α = 0.8, and T = 3,400° K.

On the basis of generalized formulas (VII.53) to (VII.55), we calculate*

$$\{p\}'_C=0,33333, \quad \{p\}'_H=1,33333, \quad \{p\}'_O=1,06667.$$

By method of selection of the p'_{H_2} values following the scheme in Section 1, Chapter V (equations (V.21) to (V.28)), we determine the partial pressures of combustion products in the assumption of dissociation at constant volume, i.e., the volume which would be occupied by undissociated combustion products at 1 atm pressure. This yields:

$$\begin{aligned} p'_{H_2}&=0,1856, & p'_O&=0,0949,\\ p'_H&=0,2047, & p'_{O_2}&=0,0562,\\ p'_{H_2O}&=0,2850, & p'_{CO}&=0,2779,\\ p'_{OH}&=0,1873, & p'_{CO_2}&=0,0555. \end{aligned}$$

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* The generalized formulas (VII.53) to (VII.55) help us avoid completely the first calculation stage of the Zel'dovich-Polyarny method.

Substituting these values together with the values of equilibrium constants in equations (VIII.19) to (VIII.24), we produce a system which may be conveniently written in the form of a table of coefficients:

	z	y	x	w	v	u		
(1)	−0,562	+0,112	+0,277	0	0	0	=	0,000114
(2)	0	0	+0,185	+0,112	−0,073	0	=	−0,000085
(3)	0	0	0	+0,187	−0,244	+0,370	=	−0,001090
(4)	−1,2	−2,2	+2,846	0	+1	+1	=	0,002600
(5)	−4	−4	0	+2,552	+2	+1	=	0,003000
(6)	+1	+1	+1,846	+1,552	+1	+1	=	0,347000

After dividing equation (1) by the coefficient for z, we have:

(1')$z - 0.199y - 0.493x = - 0.000203$

We multiply (1') by -1.2 and subtract it from equation (4), then we multiply (1') by -4 and subtract from (5). Finally, we subtract (1') from (6). In this manner we get rid of z in all equations, except the first one. As a result of this, we obtain a system of five equations with five unknown quantities

	y	x	w	v	u		
(2')	0	+0,185	+0,112	−0,073	0	=	−0,000085
(3')	0	0	+0,187	−0,244	+0,370	=	−0,001090
(4')	−2,439	+2,254	0	+1	+1	=	0,002356
(5')	−4,796	−1,972	+2,552	+2	+1	=	0,002188
(6')	+1,199	+2,339	+1,552	+1	+1	=	0,347203

Thus, successively eliminating the unknowns one by one, we arrive at an equation with a single unknown*:

$$7.560u = 0.329373,$$

whence

$$u = 0.043568.$$

Now, successively proceeding from equation (1'), from the end to the beginning, we find the remaining unknown quantities:

$$v = 0.108227, \qquad x = 0.012533,$$
$$w = 0.049186, \qquad y = 0.074782,$$
$$z = 0.021040.$$

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* The operation may be greatly simplified through use of a calculating machine (22).

Section 4. Ranges of Applicability of Different Computation Methods

Certain typical methods for approximate calculation of the composition of combustion products, permitting us to solve a large number of diverse problems, were discussed above. The procedure by which these problems may be treated are of course not restricted to those recorded in this book. Their number, as a matter of fact, may be quite large*.

The most common is the method by which a system of equations may be reduced to a single equation with one unknown quantity through successive elimination of all the remaining unknown quantities. A system of linear equations, such as balance equations, is thereby reduced to an equation of the first degree. More complex systems, consisting of several equilibrium equations, are usually brought to a high-degree equation which may be solved by methods of approximation as described in special manuals (see, for instance, Numerical Analysis by W. E. Milne). If such an equation has several real positive roots, we select the one which, upon substitution into the equation for the determination of the remaining unknown quantities, produces positive real values for same. There can be only one such root in view of the uniqueness of the state of chemical equilibrium (15).

However, not only the solution, but also the construction of such high-degree equations constitutes a highly laborious operation. Consequently, this method of mixture composition determination, as a rule, is impracticable regardless of its universal applicability.

In making calculations, one should select the kind of method which assures the required accuracy and at the same time proves to be the simplest. Since the determination of the mixture composition of combustion products is the most cumbersome

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* See, for example, (2, 3, 6, 16, 21, 36, 42, 49). At the present time, high-speed computers are more and more often being used for extensive computations.

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The s and t values are found from equations (VIII.17) and (VIII.18):

$$s = 0{,}027151, \quad t = 0{,}010603.$$

These corrections are subtracted from the corresponding approximate values of partial pressures. The calculation results are recorded in Table 15, where they are compared with the results of the more accurate calculation method of p_{O_2} value selection.

Table 15

	Results of Composition calculation by approximate partial-pressure values	Results of Computation by method of p_{O_2} value selection
p_{H_2}	0,1364	0,1371
p_H	0,1775	0,1758
p_{H_2O}	0,1768	0,1830
p_{OH}	0,1437	0,1400
p_O	0,0843	0,0825
p_{O_2}	0,0437	0,0425
p_{CO}	0,2031	0,2037
p_{CO_2}	0,0345	0,0353
P	1,0000	0,9999

The determined partial-pressure values are used for the calculation of enthalpy by formula (VI.18). Here is the result:

$$H_{3,400\text{prod}} = 4{,}544.0 \ \frac{\text{Kcal}}{\text{mole}} .$$

The direct method produces the value of $4{,}521 \ \frac{\text{Kcal}}{\text{mole}}$. Let it be said here that by way of an example we have selected a relatively unfavorable case, since the approximate values exceed the accurate values by 35% on the average. Nevertheless, the final result is totally satisfactory. As a matter of fact, here we have still another method of approximate computation of the state of combustion products at constant pressure*.

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* Repeated application of the method outlined herein, makes it possible to produce the values of partial pressure with any desired precision.

[redacted]

operation in computations of combustion processes, it is obvious that the smaller is the number of mixture components to be calculated, the simpler is the computation. It is therefore thought useful to delineate tentatively the temperature boundaries for the calculation of various reactions, mostly those of dissociation which augment the number of mixture components. The progress of this or that reaction does not depend only on temperature, but also upon pressure and the initial composition of the mixture. Yet, temperature constitutes the principal factor. If the initial composition of a mixture of hydrocarbons with oxygen or air is approaching stoichiometric composition, then, for pressures on the order of 1-25 atm, one may assume that dissociation below 1,600-1,800° K is insignificantly small and only the reaction of water vapor (at $\alpha < 1$) should be calculated. At temperatures lower than 2,600-2,800° K dissociation of H_2, O_2, N_2, and the formation of NO, when $\alpha \approx 1$, develop only to a negligible degree (incidentally, N_2 dissociation may be disregarded even at higher temperatures). The effect of the excess of one or another component of the initial mixture upon dissociation of combustion products is determined by the Le Chatelier rule.

When dissociation is weak, it is advisable to use the method of successive approximations, as outlined in Section 1 of this chapter; if dissociation is strong, the method of selection of partial-pressure values of one of the components, or other methods (Chapter VIII, Section 2, 3), should be used. For orientation purposes it is useful to record the curves of the dependence of the composition of combustion gases upon temperature. In figures 11 and 12 (pages 26 and 27) curves are represented which show the dependence of the composition of pure gaseous CO_2 and H_2O upon temperature at 1 atm pressure (36). The same curves are represented in Figure 15 for the products of octane combustion with air at α = 0.7, 1.0, 1.3 and 1 atm pressure (16). In Figure 16, similar curves are reproduced for combustion products of coal gas at α = 1 and for different nitrogen contents (36)

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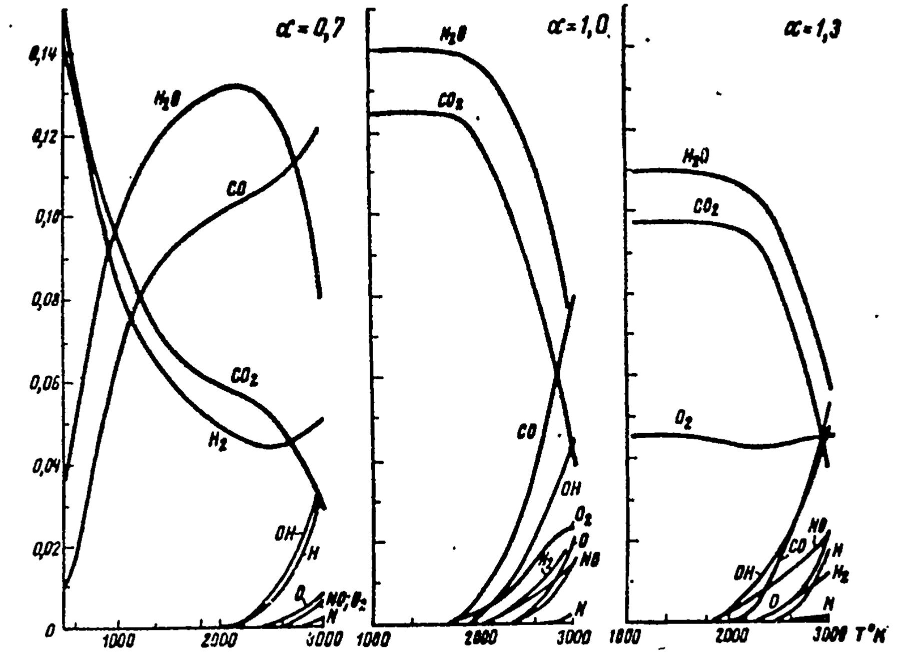

Figure 15. Equilibrium composition of the products of octane combustion at P_0 = 1 atm (variation of N_2 concentration with temperature is not shown). (Zel'dovich and Polyarny). Partial pressures in atm are plotted on the Y-axis.

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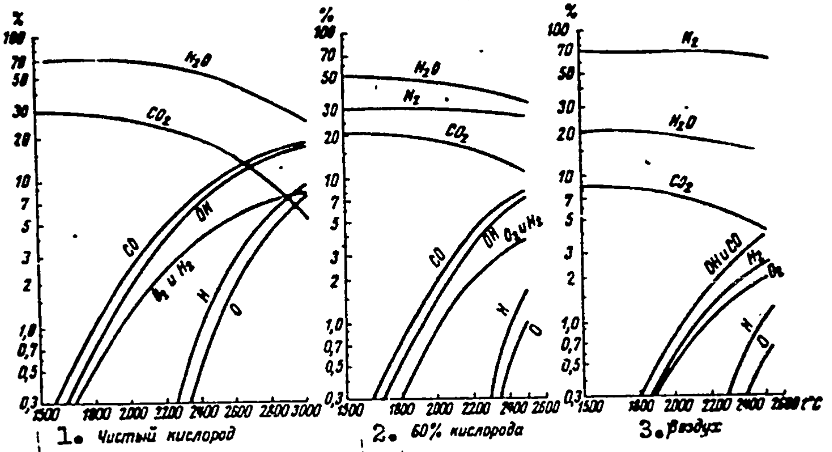

1. Чистый кислород
2. 60% кислорода
3. Воздух

Figure 16. Equilibrium composition of the products of coal gas combustion in ambient atmosphere, in air enriched up to 60% by oxygen, and in pure oxygen ($\alpha = 1$) (Fehling)

(1) Pure oxygen; (2) 60% oxygen; (3) air.

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Chapter IX

THERMODYNAMIC RESEARCH BY THE METHOD OF EXPLOSION

Section 1. General Principles

The comparison of the experimental data on maximum explosion pressure with the results of theoretical computations enables us to draw a conclusion on the accuracy of the data taken as a basis for the calculation; it also permits us to determine individual unknown quantities. The explosion method used to be applied most frequently in the past and is still used in the present (see, for instance, (59)) to determine the specific heats and the heats of dissociation of the products of combustion, although the progress of statistical physics and experimental research in the field of molecular structures has somewhat changed the character of this method's application. At the same time this has given deeper insight into the nature of the phenomena occuring during explosion in a sealed vessel and it has permitted us to specify the conditions necessary for the application of the method of explosion; as a result of this, a number of errors committed by reasearchers in the past can now be successfully avoided.

It is a matter of primary importance to make sure that the postulates on which the computation is based (see Chapter (IV) should sufficiently accurately correspond to the actual progress of the process. The degree of this correspondence may be established by comparing the experimental and theoretical values of the maximum pressure of explosion in conditions in which it is a priori possible to disregard the effect of the unknown quantities (heat capacities, heats of dissociation) upon the magnitude of the explosion pressure; the degree of correspondence may also be established by means of analysis of indicator diagrams.

The composition of the initial mixture is determined by the problems facing the researcher. At the same time due consideration should be given to the limits of ignitability and the rate of burning, which should neither be too high, nor too low. When the explosions are highly intensive, pressure often cannot be determined from the indicator diagram due to the ensuing irregular diaphragm vibrations. In order to reduce the intensity of the explosion, the initial mixture is being diluted by one of the principal substances (participating in the reaction) or by inert gases, if it is desired to maintain the ratio between the basic mixture components unchanged. Since this reduces the upper limit of the temperature range over which the thermodynamic properties of the combustion products may be determined, it is desirable that other methods for the prevention of irregular fluctuations of gas be devised. Moreover, these new methods should not diminish the precision in the determination of the maximum explosion pressure due to increased heat losses, for example. Certain steps have already been taken in this direction. In particular, positive results were produced through replacement of oxygen as oxidizer by N_2O, the decrease of initial pressure (63), and the reduction of the distance between the ignition point and the walls of the explosion vessel.

In slow explosions, we can notice convection which leads to considerable heat losses. Attempts were made to calculate these heat losses (30,37); however, no sufficiently reliable method for their determination is available so far. Moreover, it has been demonstrated by experimental data that, in cases of low-velocity explosions, the postulates -- which form the basis for maximum explosion pressure calculations and the pertinent corrections for temperature gradient (see Section 2 of this chapter) -- no longer correspond to the actual development of the process, which in this case turns out to be irregular (37, 50). Thermodynamic investigations by method of explosion should therefore be conducted in such conditions when the explosion rate is sufficiently high to permit us to ignore the convection of combustion products. An increase in combustion velocity may be achieved by adding small quantities of substances which contribute to the formation of radicals assuring the rapid progress of the chain reaction. Thus, for example, explosions of mixtures of carbon monoxide with oxygen are accelerated by the addition of small quantities

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of hydrogen (37,63).

Apart from convection, other sources of heat losses referred to in Chapter III should also be taken into account. A rigorous centering of the spark-gap is imperative. The explosion vessel should not be too small, lest it become difficult to avoid a considerable eccentricity of the spark-gap (47). The surface of ignition electrodes must be as small as possible (63). In certain mixtures -- for instance, in mixtures of hydrogen with oxygen containing excess hydrogen -- heat losses may be reduced to nil through addition of a small proportion of water vapors. A rise in starting pressure of the initial mixture also contributes to a reduction of heat losses.

A serious complication is constituted by the transcendence of the experimental values of maximum explosion pressure over those obtained theoretically under the postulates referred to above. For example, in the case of oxyacetylene mixture with an excess of O_2, this phenomenon attains a value of 5% (21). In view of the fact that this phenomenon is little known and, at any rate, cannot be quantitatively accounted for or regulated in any possible way, one should avoid making experiments under conditions in which this phenomenon may occur, for example, in case of O_2 excess in oxyhydrogen, methane-oxygen, and oxyacetylene mixtures.

In the calculation of maximum explosion pressure in closed volume, recorded in Chapter V, it was assumed that there is an even distribution of temperature in combustion products at the moment when the flame reaches the walls of the vessel. This simplifying premise is fundamentally wrong, but in most cases it does not lead to considerable errors. When these errors assume a substantial significance, a correction for the temperature gradient in combustion products should be introduced into the value of maximum explosion pressure. The methods of computation of this correction will be discussed in the next section.

The initial mixture composition and other conditions of the experiment are selected in conformity with the research objectives. If the aim is to determine a certain quantity, the experimental conditions must be such as to assure that the proportion of the unknown quantity in the total heat contents of the mixture be sufficiently large. For example, if the value of the thermal effect is to be found, then efforts should be made to make the experiment in such a manner as to contribute to the maximum development of the corresponding process. For the heat-capacity determination of one or another reaction product, it is necessary that its concentration at the moment of realization of the maximum explosion pressure be large, while the degree of its dissociation and the degree of reaction development between this and the other components of the mixture be small enough. These requirements will be defined below in a more concrete form during the discussion of various examples of thermodynamic research by the method of explosion.

Section 2. Calculation of the Maximum Explosion-Pressure Correction for Irregularity of Temperature Distribution in Combustion Products

According to Lewis-Elbe's data, the presence of a temperature gradient reduces the pressure in the system by 0.1-1.0% in comparison to that which would have been registered in it had temperature distribution been uniform (47, 48). In the tests conducted by Fenning and Whiffin, this quantity happened to reach 1.3%. This also is approximately the order of the greatest deviation of the measured maximum explosion-pressure values from the average measurement figures. Nevertheless, in a number of cases, particularly during heat-capacity determinations, the introduction of a correction for the temperature gradient seems to be advisable. The following considerations speak in favor of this recommendation. First of all, the error in an average figure is smaller than the error in an individual measurement figure. However, when the results of tests -- say, the experimental values of heat capacity of this or that combustion product -- are represented in the form of functions of temperature, then these results are subjected to further averaging by the method of least squares, for instance. At the same time, in consequence of the change of the quantitative composition of the initial mixture and the corresponding change of combustion temperature, the magnitude of the correction for temperature gradient changes considerably (37, 48) and this may substantially affect the shape of the experimental curve. If this correction is not calculated, then -- according to Fenning and Whiffen -- absurd results may ensue in a number of cases. The specific heats of inert gases might grow strongly with temperature, the thermal capacity of carbon monoxide might prove to be almost constant, and so on. The following fact also speaks in favor of the conclusion that calculation of the correction for the temperature gradient is unquestionably helpful. The variation of this correction with the variation of the combustion temperature constitutes a considerable percentage of the corresponding growth or drop of the specific heat which occurs mostly at the expense of the vibrational component. Thus the introduction of this correction may prove to be very important for a more precise definition of the data which form the basis for the calculation of thermodynamic functions by statistical methods.

We shall compute the quantity $P_e/P_{e\,grad}$, i.e., the relationship of maximum explosion pressure -- which corresponds to uniform temperature distribution -- to the pressure, which corresponds to its true distribution at the moment when the flame contacts the walls of the bomb. Let us mentally split the gas enclosed within the spherical vessel into a series of small concentric spherical layers, with the center at the ignition point. In calculating the ratio $P_e/P_{e\,grad}$ it is assumed: (1) that convection, as well as heat exchange, between the neighboring layers is insignificantly small; (2) that the growth of pressure in the bomb is proportional to the mixture mass burned; (3) that the compression of the unit spherical layers up to their combustion proceeds adiabatically; (4) that they burn practically at constant pressure; (5) that subsequent compression of the spherical layers to maximum explosion pressure develops adiabatically; and (6) that by the moment the flame reaches the walls of the bomb, complete chemical equilibrium and equilibrium energy distribution according to the degrees of freedom are achieved in all the layers.

If α is the proportion of burned gas in relation to the initial mixture as a whole and P_α is the pressure formed in the bomb by that time, then, according to postulate (2):

$$P_\alpha = P_i + \alpha (P_{e\,grad} - P_i). \qquad \text{(IX.1)}$$

Although the approximative character of this relationship is obvious, a detailed analysis (18,21) shows that its accuracy is totally acceptable. As to the other assumptions, their validity for cases of not overly slow burning is confirmed by the fact that calculations made on the basis of these postulates produce a temperature-drop value of the same order of magnitude as those of the experimentally determined temperature gradients.

On the basis of these assumptions, one may determine the state of the combustion products in a number of elementary layers; now the ratio P_e/P_egrad is calculated according to the thus determined temperature distribution, concentrations (total number of moles), and specific intrinsic energy.

The computation of the state of combustion products in the elementary spherical layer $d\alpha$ at the boundary of the sphere, within which a proportion α of the gas mixture is contained, is composed of three stages: (1) calculation of temperature T_u, up to which the mixture is heated in consequence of adiabatic compression prior to combustion, (2) calculation of temperature T_b, reached by the mixture as a result of burning at constant pressure P_α, (3) calculation of equilibrium temperature T_e, corresponding to pressure $P_e$grad.

<u>First stage.</u> From the known thermodynamic equation

$$TP^{\frac{1-\gamma}{\gamma}} = \text{const} \qquad \text{(IX.2)}$$

it follows that

$$\lg T_u = \lg T_i + \frac{\gamma_u - 1}{\gamma_u} \lg \frac{P_\alpha}{P_i}, \qquad \text{(IX.3)}$$

where P_α is determined from equation (IX.1), and γ_u is determined by the following formula:

$$\gamma_u = \frac{H_u - H_i}{U_u - U_i} = \frac{\Sigma m_{ij} H_{T_u j} - \Sigma m_{ij} H_{T_i j}}{\Sigma m_{ij} U_{T_u j} - \Sigma m_{ij} U_{T_i j}} \qquad \text{(IX.4)}$$

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(here, to simplify calculations, we use the average specific heats*). Hence,

$$\frac{\gamma_u - 1}{\gamma_u} = \frac{R(T_u - T_i)\Sigma m_i}{\Sigma m_{ij} H_{T_u j} - \Sigma m_{ij} H_{T_i j}}. \qquad \text{(IX.4')}$$

Equation (IX.3) may be worked out by trial-and-error method, which does not present any difficulty, since the right-hand part of the equation depends relatively little on T_u.

Second stage. The state of the combustion products of a mixture enclosed in layer $d\alpha$ at constant pressure may be determined by the previously described direct or approximate methods of calculation for P = const. However, a considerably simpler and more accurate procedure is the following one (13), which is based on the Zel'dovich-Polyarny method of approximation outlined in Chapter VII. Let us suppose that the first to burn at constant pressure is the layer $d\alpha$, whereby pressure P' is being attained. Thereafter, reversible and isothermic compression or expansion to pressure $P\alpha$ is assumed to occur. In accordance with this assumption, one should first determine the state of all the combustion products of layer $d\alpha$ for constant volume. The initial state of the layer immediately before the commencement of burning is the state which corresponds to T_u calculated on the basis of equation (IX.3). We have

$$p_{uj} = p_{ij}\frac{T_u}{T_i}; \qquad \text{(IX.5)}$$

The material balance equations for the ℓ-th element at initial temperatures T_i and T_u, respectively, are:

$$\{p\}_{lT_i} = \left(\sum_j l_j p_{ij}\right)\frac{T}{T_i}, \qquad \text{(IX.6)}$$

$$\{p\}_{lT_u} = \left(\sum_j l_j p_{uj}\right)\frac{T}{T_u}, \qquad \text{(IX.7)}$$

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* To attain a greater degree of accuracy in the first stage of the $P_e/P_{e\,grad}$ computation, this stage could be broken up into a series of substages in each of which one could analyze the effect of the small increase of pressure as compared with that of the preceding substage.

where ℓ_j is the number of atoms of the ℓ-th element in the j-th component of the initial mixture. Substituting the value of P_{uj} from equation (IX.5) in equation (IX.7) and comparing the latter with (IX.6), we find

$$(p)_{lT_u} = (p)_{lT_i}. \tag{IX.8}$$

This determines the following order of calculation. On the basis of the scheme recorded in Chapter V, we calculate the composition of the mixture of combustion products and its pressure P' for a series of temperatures T, located both above and below T_e which was determined in the assumption that temperature distribution is uniform. In addition to this for these T values we calculate enthalpy H' on the basis of formula (VI.18), $\sum m'$ according to formula*.

$$\Sigma m' = \frac{GP}{\sum_k p_k \mu_k} \tag{IX.9}$$

(compare with VI.21), $\overline{H}$ from equation (VII.39), and ζ' by formula

$$\zeta' = \frac{\Sigma m'}{\Sigma \overline{m}} - 1 \tag{IX.10}$$

(compare with VII.59).

For one of the temperatures, approximately in the middle of the interval in question, we determine the same quantities for three values of P_i, for example, for the given value, for half that value, and for one-quarter that value. The average values of n_H and n_ζ can be found from formulas (VII.62) and (VII.63).

Further, on the basis of a formula similar to (VII.64), we calculate for each $d\alpha$ layer the enthalpy of combustion products at constant pressure, H_b, for three temperatures in such a manner as to assure that enthalpy H_u of the layer in the initial state with respect to burning, which is to be found from expression

$$H_u = \sum_j m_{ij} H_{T_u j}, \tag{IX.11}$$

should appear between the two extreme values of H_b. Thereupon, by interpolation

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* Here we have assigned the ' (prime) mark to quantities which have a conditional significance for this calculation.

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from condition

$$H_b = H_u \tag{IX.12}$$

we can find the values of combustion temperature T_b of the layer. After having calculated the magnitude of ζ_b for the same three temperatures on the basis of a formula similar to (VII.65), we determine, by means of interpolation the value of ζ_b corresponding to the known value of T_b. Knowing ζ_b, from an equation similar to (VII.67) we find $\sum m_b$; then $U_b = H_b - (\sum m_b) R T_b$.

Thus, the above simplified method of T_b and $\sum m_b$ calculation calls for no computation of the mixture composition of combustion products for each of the considered $d\alpha$ layers, which must be no less than five in number. In accordance with the statements made in Section 1, Chapter III, it should be emphasized here that, in calculating the ratio $P_e/P_{e\,grad}$, one should take the dissociation of combustion products into account to the fullest extent possible.

Third stage. During adiabatic compression of the mixture of combustion products in layer $d\alpha$, the temperature of the mixture rises to the value of T_e which is determinable by formula

$$\lg T_e = \lg T_b + \frac{\gamma_b - 1}{\gamma_b} \lg \frac{P_{e\,grad}}{P_e}, \tag{IX.13}$$

This formula is analogous to formula (IX.3). But the third stage differs from the first in that here account must be taken of the degree of dissociation of combustion products. For this purpose, in calculating T_b and $\sum m_b$ for the layer contiguous to the wall of the bomb, i.e., for $\alpha = 1$, the quantities H_b, U_b and $\sum m_b$ must be computed for four to five temperature values. The highest of them must not be lower than T_e for the elementary volume located in the center of the vessel, i.e., for $\alpha = 0$. At the same time it is desirable for H_u to be in the lower section of the H_b versus T curve. It is evident that adiabatic compression of layer $d\alpha$ to the pressure of $P_{e\,grad}$ will bring it to a state characterized by definite points on curves $U_b(T)$ and $\sum m_b(T)$ calculated for $\alpha = 1$.

We have:

$$\gamma_b = \frac{C_p}{C_v} = 1 + \frac{R}{C_v}, \tag{IX.14}$$

whereby C_v is determined from the following formula*:

$$C_v = \frac{1}{\frac{1}{2}(\Sigma m_e + \Sigma m_b)} \cdot \frac{U_e - U_b}{T_e - T_b}. \tag{IX.15}$$

From the last two equations we obtain

$$\gamma_b = 1 + \frac{R(\Sigma m_e + \Sigma m_b)(T_e - T_b)}{2(U_e - U_b)}. \tag{IX.16}$$

Equation (IX.13) may be solved by the method of selection. In practice, the following procedure is convenient. We calculate the left- and the right-hand parts of this equation for several values of T_e and, using the same scale, we construct the curves of their dependence upon lg T_e (Figure 17). The point of intersection of these curves will give the value of the unknown equilibrium temperature T_e of layer $d\alpha$. On the basis of the known T_e value, we determine the values of Σm_e and U_e by means of interpolation.

The described computation must be made at least for five values of α: 0, 0.2, 0.4, 0.6, and 1.0. In this manner we obtain the distribution of temperature T_e, of the number of moles Σm_e, and of intrinsic energy U_e in the products of combustion at the moment when the flame reaches the walls of the bomb.

Let it be remembered that α represents the proportion of the total gas mass enclosed within the sphere at the boundary of which the $d\alpha$ layer in question is located. Evidently, the volume dV_α of such a layer is related to the specific volume v_α of the mixture of combustion products in this layer by equation:

$$dV_\alpha = v_\alpha \cdot M \cdot d\alpha, \tag{IX.17}$$

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* Here the method to achieve greater accuracy is the same as in the case of the first computation stage (see footnote on page 111).

where M is the total gas mass in the vessel and

$$v_\alpha = \frac{(\Sigma m_{e\alpha})\, RT_{e\alpha}}{P_{e\,\mathrm{grad}}}. \qquad \text{(IX.18)}$$

The volume of the vessel is

$$V = \int_0^1 dV = M \int_0^1 v_\alpha \, d\alpha. \qquad \text{(IX.19)}$$

Upon equalization of temperature, the specific volume of the mixture of combustion products within the vessel as a whole will be the same and equal to $v = \frac{V}{M}$. Consequently,

$$v = \int_0^1 v_\alpha \, d\alpha. \qquad \text{(IX.20)}$$

At the same time

$$v = \frac{RT_e \Sigma m_e}{P_e}, \qquad \text{(IX.21)}$$

where quantities T_e, $\sum m_e$, and P_e are related to the state of thermal equilibrium between the layers, i.e., to the state of even temperature distribution. From equations (IX.18), (IX.20), and (IX.21), it follows that

$$\frac{P_e}{P_{e\,\mathrm{grad}}} = \frac{T_e \Sigma m_e}{\int_0^1 T_{e\alpha} \Sigma m_{e\alpha} \, d\alpha}. \qquad \text{(IX.22)}$$

Here index α indicates that the corresponding quantity is a function of α.

For specific inner energy of the mixture of combustion products, after the leveling of temperature without heat losses, we have an equation similar to (IX.20):

$$U_e = \int_0^1 U_{e\alpha} \, d\alpha. \qquad \text{(IX.23)}$$

Having thus determined the value of U_e, we find T_e on the basis of curve $U_e(T)$, calculated according to the scheme from Chapter V in the assumption of uniform temperature distribution; by way of interpolation, we define the corresponding value of $\sum m_e$. After calculating integral $\int_0^1 T_{e\alpha} \Sigma m_{e\alpha} \, d\alpha$, we determine the magnitude of P_e/P_{egrad} by formula (IX.22).

Knowing the P_e/P_{egrad} ratio, we may adjust the experimental value of maximum explosion pressure and compare the theoretical value of P_e with this adjusted experimental quantity.

Let it be noted here that, owing to the inaccuracies admitted in calculation, the value of T_e -- calculated in terms of even temperature distribution and according to curve P(T) produced by the method described in Chapter V -- will, as a rule, differ somewhat from the value of T_e computed on the basis of U_e defined from equation (IX.23) and on the basis of curve U(T). This difference between the two values of T_e is small, however, and justifies the belief (21, 37) that the calculation inaccuracies which are responsible therefore do not substantially affect the ratio P_e/P_{egrad}.

We shall now consider the temperature distribution -- at the moment when the flame reaches the walls of the bomb -- depending on the distance from the center (13).

The density of the mixture of combustion products in layer dα is determined by expression

$$\delta_\alpha = \frac{1000 \cdot P_{egrad}}{(\Sigma m_{c\alpha}) R T_{e\alpha}}. \qquad \text{(IX.24)}$$

In a manner similar to (IX.20), we derive a formula for the density of the mixture of combustion products after temperature equalization:

$$\delta = \int_0^1 \delta_\alpha \, d\alpha. \qquad \text{(IX.25)}$$

For the mass of gas enclosed within the sphere with radius r_α, which contains the α proportion of the total quantity of gas, we can write the following:

$$\bar{\delta}_\alpha \cdot \frac{4}{3} \pi r_\alpha^3 = \alpha G \qquad \text{(IX.26)}$$

or,

$$\bar{\delta}_\alpha \cdot \frac{4}{3} \pi r_\alpha^3 = \alpha \delta \cdot \frac{4}{3} \pi r^3, \qquad \text{(IX.27)}$$

where r is the bomb radius, $\bar{\delta}_\alpha$ is the average density of the mixture of combustion products in the sphere with radius r_α :

$$\bar{\delta}_\alpha = \frac{1}{\alpha}\int_0^\alpha \delta_\alpha \, d\alpha. \qquad (IX.28)$$

It follows from equation (IX.27) that

$$\frac{r_{\alpha e}}{r} = \left(\alpha \frac{\delta}{\bar{\delta}_\alpha}\right)^{\frac{1}{3}}. \qquad (IX.29)$$

The ratio $\frac{\delta}{\bar{\delta}_\alpha}$ is determined from equations (IX.24), (IX.25), and (IX.28):

$$\frac{\delta}{\bar{\delta}_\alpha} = \frac{\int_0^1 \frac{d\alpha}{T_{e\alpha}\Sigma m_{e\alpha}}}{\frac{1}{\alpha}\int_0^\alpha \frac{d\alpha}{T_{e\alpha}\Sigma m_{e\alpha}}}. \qquad (IX.30)$$

Example 9. A mixture is burning in a bomb with central ignition. Its composition and the other initial conditions coincide with those of Example 2 (page 55.) The experimentally observed maximum explosion pressure $P_{egrad} = 7.458$ atm. Calculate maximum explosion pressure P_e, corresponding to even temperature distribution.

First stage. Substituting the numerical values of P_{egrad} and P_i in equation (IX.1) and that of T_i in equation (IX.3), we obtain:

$$P_\alpha = 0{,}8926 + \alpha \cdot 6{,}5654; \qquad (a)$$

$$\lg T_u = 2{,}48116 + \frac{\gamma_u - 1}{\gamma_u} \lg \frac{P_\alpha}{P_i}. \qquad (b)$$

Using the data from Table IV (Appendix V) and formula (IX.4'), we calculate the value of $\frac{\gamma_u - 1}{\gamma_u}$ for 400, 600, and 800° K.

Table 16

T_u	$\lg T_u$	$\frac{\gamma_u - 1}{\gamma_u}$
400	2,60206	0,34286
600	2,77815	0,34027
800	2,90309	0,33780

Equation (b) for each α is solved by method of selection. For example, for $\alpha = 0.2$ at 400° K, the right-hand part of equation (b) is equal to 2.61587; at 600° K it amounts to 2.61485. Consequently, $T_u = 413°$ K. After determining the enthalpy values of the initial mixture components for T_u by means of interpolation on the basis of Table IV (Appendix IV) from formula (IX.11), we find the values of H_u. The results of the first calculation stage are listed in Table 17.

Table 17

α	P_α (atm)	T_u (°K)	H_u $\frac{Kcal}{kg}$
0	0,8926	302,8	1891,09
0,2	2,20568	413	1973,61
0,4	3,51876	484	2027,19
0,6	4,83184	539	2066,87
1,0	7,458	623	2132,85

Second stage. In order to determine the temperature range over which the calculations should be effected, we shall first find the so-called "conditional temperature of explosion," $T_{e\,grad}$, i.e., the temperature at which the sum of partial pressures calculated according to the scheme in Chapter V is equal to $P_{e\,grad}$. After the composition and pressure of the mixture of combustion products was determined for constant volume at temperatures of 2,600, 2,800, and 3,000° K (see Example 2), we find by interpolation from condition $\sum_k Pk = 7.458$ that $T_{e\,grad} = 2{,}795°$ K.

We shall now extend the analyzed temperature interval through additional computation of the composition of combustion products following the same pattern of computation for 2,200, 2,400, and 3,200° K. For each of the six temperature values, we also calculate P', enthalpy H' by formula (VI.18), and $\sum m'$ from equation (IX.9). For 2,600, 2,800, and 3,000° K, in addition to this, we also determine the values of intrinsic energy U' (see Example 2) which we shall require for further operations. In utilizing formulas of the (VII.11) and (VII.12) type, we find: $\bar{m}_{H_2O} = 33.1210$, $m_{O_2} = 2.7431$, $\sum \bar{m} = 114.6833 \frac{\text{mole}}{\text{kg}}$. From (VII.39) we further compute $\bar{H}$, while determining $H'-H$ and ζ' by formula (IX.10). The results of these calculations will be found in Table 18.

Table 18

T°K	2200	2400	2600	2800	3000	3200
H'	1678,22	1889,14	2137,69	2451,03	2844,73	3338,45
$\bar{H}$	1641,36	1807,38	1974,97	2143,74	2313,38	2483,72
$H'-\bar{H}$	36,86	81,76	162,72	307,29	531,35	854,73
ζ'	0,00230	0,00525	0,01079	0,02092	0,03622	0,05955
P'	5,76683	6,30984	6,87271	7,47365	8,13258	8,86371
U'			1539,13	1799,96	2136,70	

Exactly the same calculation should now be made for 2,600° K for $P_i = 0.4463$ atm and $P_i = 0.22315$ atm (Table 19). The values of n_H and n_ζ are to be found from formulas (VII.62) and (VII.63).

Table 19

P_i (atm)	P'	$H'-\bar{H}$	ζ'	n_H	n_ζ
0,4463	3,44811	209,52	0,01366	0,366	0,342
0,22315	1,73169	273,08	0,01801	0,376	0,372

The average values are:

$$n_H = 0.37, \qquad n_\zeta = 0.36.$$

Further, on the basis of the data from Table 18 and the formulas of (VII.64) and (VII.65) type, we compute H_b and ζ_b for each of the five values of α for no less than three temperature values, and for $\alpha = 1.0 - H_b$, ζ_b, and U_b for four temperature

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values: 2,600, 2,800, 3,000, and 3,200^0 K (Table 21). By interpolation on the basis of the data of Table 17, proceeding from condition (IX.12), we determine T_b; then we find ζ_b, $\sum m_b$, and U_b, following the procedure described above. The results of the second stage of computation are recorded in Table 20.

Table 20

α	T_i°K	Σm_b	U_b
0	2341,6	115,628	1353,37
0,2	2433,9	115,696	1414,37
0,4	2490,8	115,754	1454,59
0,6	2537,0	115,783	1485,50
1,0	2600,0	115,885	1534,47

Table 21

T_e	lg T_e	U_e	Σm_e
2600	3,41497	1534,48	115,885
2800	3,44716	1800,20	117,084
3000	3,47712	2152,94	118,965
3200	3,50515	2619,85	121,949

Third stage. Let us now consider, for example, the calculation of T_e for $\alpha = 0.2$. In setting definite values for T_e, we find the values of $(\gamma_b - 1)/\gamma_b$ on the basis of the data contained in Tables 20 and 21 and formula (IX.16). Thereafter we calculate the right- and left-hand parts of equation (IX.13) (see Table 22) and plot a graph of their dependence upon lg T_e (Figure 17). The intersection point of the lines produces the value of $T_e = 2{,}950.5^\circ$ K. Since the relationship of the left-hand part of equation (IX.13) versus lg T_e is expressed by a straight line, and that of the right-hand part by a curve, which by its shape approaches a straight line, such graphic interpolation must be accurate enough.

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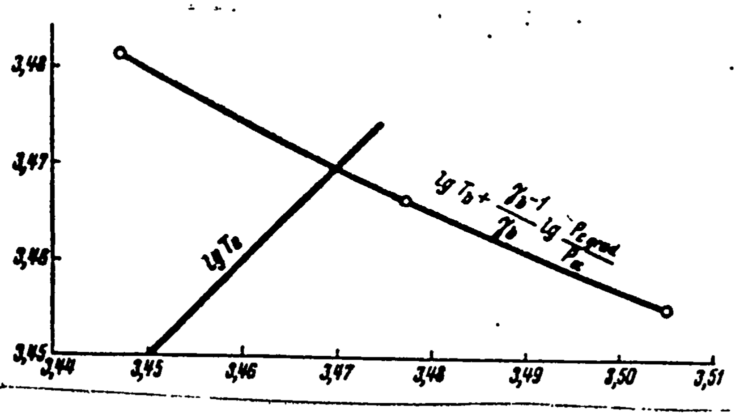

Figure 17. Interpolation graph for values of temperature T_e of the spherical layer.

Further, by interpolation on the basis of the data from Table 21, we compute: $U_e = 2{,}055.94\ \frac{\text{Kcal}}{\text{kg}}$ and $\sum m_e = 118.406\ \frac{\text{mole}}{\text{kg}}$. The results of the third computation stage are incorporated in Table 23.

Table 22

T_e	$\lg T_e$	$\lg T_b + \frac{\gamma_b - 1}{\gamma_b} \cdot \lg \frac{P_{e\,grad}}{P_a}$
2800	3,44716	3,48147
3000	3,47712	3,46648
3200	3,50515	3,45530

Table 23

x	T_r, °K	U_e	Σm_e	$T_e \Sigma m_e$	r_m/r
0	3164,1	2526,64	121,321	$3{,}83872 \cdot 10^6$	0
0,2	2950,5	2055,94	118,406	$3{,}49357 \cdot 10^5$	0,60527
0,4	2823,3	1836,21	117,259	$3{,}31047 \cdot 10^5$	0,75363
0,6	2739,7	1712,10	116,674	$3{,}19652 \cdot 10^5$	0,85502
1,0	2600,0	1534,47	115,885	$3{,}01301 \cdot 10^6$	1

Final stage. In calculating $\int_0^1 U_{rx}\,dx$ on the basis of Table 23, we find $U_e = 1{,}841.0\ \frac{\text{Kcal}}{\text{kg}}$. Using the data in Table 13, we determine T_e and the corresponding

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values of H_e and Σm_e. Then we compute $\int_0^1 T_{e\alpha}\Sigma m_{e\alpha}\,d\alpha = 3.29826\cdot 10^5$ and, finally, by formula (IX.22) we obtain

$$\frac{P_e}{P_{e\,grad}} = 1.00526$$

The results of $r_{e\alpha}$ calculation on the basis of formulas (IX.30) and (IX.29) are to be found in Table 23. Figure 18 shows the curve of temperature T_e distribution as a function of the distance from the bomb center.

The results of calculations according to the method outlined are compared in Tables 24 and 25 with the results obtained by the direct method, i.e., by computation of the composition of combustion products for each of the investigated unit layers separately (compare with Example 4)*.

Table 24

	T_b^o K		T_e^o K	
	Simplified Method	Direct Method	Simplified Method	Direct Method
0	2341,6	2343,4	3164,1	3162,6
0,2	2433,9	2435,3	2950,5	2949,9
0,4	2490,8	2491,3	2823,3	2823,9
0,6	2537,0	2538,2	2739,7	2739,7
1,0	2600,0	2599,8	2600,0	2599,8

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* In order to avoid any possible divergence between the results of these two calculations, which may result from intermediate round-offs, the computations recorded herein are made with greater precision than normally required.

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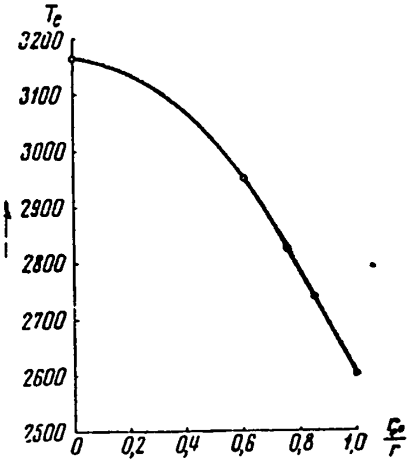

Figure 18. Distribution of temperature T_e as a function of the distance from the center of bomb (Gurvich and Shaulov).

The accuracy of $P_e/P_{e\,grad}$ magnitude calculation may be improved through increase of the number of analyzed unit layers. If we use the simplified computation method outlined hereinbefore, this operation calls for relatively minor additional calculations.

Table 25

Method of calculation	$\frac{P_e}{P_e \text{ grad}}$	Experimental value of maximum explosion pressure.		Experimental Value of temperature of explosion
		Observed P_e grad	Converted P_e	
Simplified	1.00526	7,458	7,497	2807,7
Direct	1,00540	"	7,498	2807,4

Section 3. Determination of Mean Heat Capacity (Enthalpy Increment) by the Method of Explosion

In the first approximation we may consider the heat capacity of gas as consisting of four independent components -- progressive, rotational, oscillatory and electronic (see Appendix 1). Moreover, the first two are independent of the temperature. According to the classical theory the specific heat C_v of a gas resulting from progressive and rotary degrees of freedom comprises about $\frac{5}{2}$ R for diatomic gas and 3 R for monatomic gas; C_p is equal to $\frac{7}{2}$R and 4R, respectively. The variation of thermal capacity with temperature is caused primarily by the oscillatory component, as well as by the electronic component and by interaction of oscillatory and rotary movements of the molecule*. The errors in determination of the frequencies of normal oscillations, as well as of the position of electron levels, or the indeterminacy of these data may lead to substantial errors in thermal capacity values calculated by statistical methods for high temperatures. The explosion method constitutes the only method for their direct experimental determination. Cases are known when this method helped to reveal errors in statistical calculations and in the data pertaining to the structure of molecules on which these calculations are based.

Had it been possible to disregard the dissociation of combustion products and the exchange reactions between them -- reactions of the type of water vapor reaction -- as well as the uneven distribution of temperature in the combustion products, the computation of thermal capacity on the basis of the observed maximum explosion pressures would have been a relatively simple operation.

According to the law of ideal gases,

$$T_e = T_i \frac{\Sigma m_i}{\Sigma m_e} \cdot \frac{P_e}{P_i}. \qquad (IX.31)$$

This equation permits us to determine combustion temperature T_e on the basis of the experimental value of maximum explosion pressure P_e. Moreover, ratio $\Sigma m_i / \Sigma m_e$ may be determined (if dissociation is to be neglected) on the basis of simple stoichiometric considerations.

For the f-th product of combustion, the change of intrinsic energy during temperature rise from T_i to T_e may be found from equation (IV.1):

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*For thermal capacity break-down into components and for data on the relation of thermal capacity to enthalpy, see Appendix I.

$$(U^\circ_{T_e} - U^\circ_{T_i})_f = \frac{1}{m_f}\left\{(-\Delta U^\circ_{T_i})_{\text{comb.}} - \sum_{k=1}^{n|f} m_k (U^\circ_{T_e} - U^\circ_{T_i})_k\right\}, \qquad \text{(IX.32)}$$

where n is the number of substances constituting the mixture of combustion products; the symbol $|f$ above the symbol of sum indicates that summation is to be effected for all values of k, with the exception of k = f.

Hereupon, it is easy to determine

$$C_{vf}^{T_e+T_i}; \quad (H^\circ_{T_e} - H^\circ_{T_i})_f = (U^\circ_{T_e} - U^\circ_{T_i})_f + R(T_e - T_i); \quad C_{pf}^{T_e+T_i};$$

and, knowing the values of heat contents at T_i, to find $(H^0_{T_e} - H^0_0)_f$. This quantity may be compared directly with the data of statistical calculation.

However, disregard of dissociation of combustion products at high temperature may result in substantial errors. The necessity of dissociation computation considerably complicates calculations. To determine the composition of the mixture of combustion products in this case, we must know the values of n-m independent equilibrium constants (see Section 1, Chapter V). The data for equilibrium constant calculation for high temperatures may be obtained by methods of statistical thermodynamics (see Appendix 1); the same causes which lead to errors in computations of thermal capacity (heat contents) values will thereby also be responsible for errors in K_p. However, the latter exert a far lesser degree of influence on calculation results. By selecting special test conditions -- such as conditions which will assure maximum suppression of the corresponding processes -- these errors may be reduced to a negligibly small quantity. For example, in order to determine hydrogen thermal capacity, oxyhydrogen mixtures were exploded (37, 63) which contained a considerable excess of H_2 responsible for the dissociation of water. At the same time, this contributed to a sufficiently high H_2 concentration in combustion products and enabled the curve of explosion pressure to be satisfactorily registered on film. The relatively high initial pressure observed in these experiments also facilitated the suppression of dissociation. Meanwhile, this and the addition of small quantities of water vapor to the initial mixture assured a reduction in heat losses to a

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practically negligible quantity.

Most of the data obtained by the method of explosion pertain to temperatures within the 2,000-3,000° K range. At higher temperatures, dissociation proves to be too high and it is difficult to produce a satisfactory diagram of pressure variation.

Supposing it is required to determine the thermal capacity (increment of heat contents) of the f-th component of a mixture of combustion products. Subtracting from both parts of equation (V.58) the quantity

$$\frac{1}{RT} p_f (H^{\circ}_{T_e} - H^{\circ}_0)_f$$

we obtain

$$U_{T\,prod} - \frac{1}{RT} p_f (H^{\circ}_{T_e} - H^{\circ}_0)_f = \frac{1}{RT}\left(\sum_{k=1|f}^{n} p_k H^{\circ}_{Tk} + p_f H^{\circ}_{0f}\right) - P. \qquad (IX.33)$$

We introduce the designation:

$$U''_{T\,prod} = \frac{1}{RT}\left(\sum_{k=1|f}^{n} p_k H^{\circ}_{Tk} + p_f H^{\circ}_{0f}\right) - P. \qquad (IX.34)$$

From equation (IX.33) for T_e -- bearing in mind that $U_{T_e prod} = U_{T_i init}$ -- we have

$$(H^{\circ}_{T_e} - H^{\circ}_0)_f = \frac{RT_e (U_{T_i init} - U''_{T_e prod})}{p_{ef}} \qquad (IX.35)$$

or

$$\bar{C}_{pf}^{T_e \div 0} = \frac{R (U_{T_i init} - U''_{T_e prod})}{p_{ef}}. \qquad (IX.36)$$

The following sequence of thermal capacity calculation ensues from the above on the basis of the known maximum explosion pressure P_e (relative to even temperature distribution in combustion products, i.e., calculated correspondingly in accordance with the scheme outlined in the preceding section, whenever this is required). We calculate the composition and the pressure of the mixture of combustion products, as outlined in Chapter V, for no less than three temperature values, and on the basis of P_e and curve P(T) we determine combustion temperature T_e. For each of these temperatures we determine $U''_{T prod}$ by formula (IX.34) and by means of interpolation we find the values of $U''_{T_e prod}$ and p_{ef} corresponding to T_e. After

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having computed the value of $U_{T_i \text{init}}$ from formula (V.58), we determine the increment in heat contents of the f-th component by formula (IX.35) or its thermal capacity at constant pressure by formula (IX.36).

Example 10. In the progress of experiment, in conditions, for which calculations were made in Example 6 (page 90) of the theoretical value of maximum explosion pressure, its observed value (related to uniform temperature distribution) turned out to be equal to 20.80 atm. Determine the thermal capacity of H_2 at combustion temperature T_e while assuming the enthalpies of the other components and all equilibrium constants to be known and equal to the values recorded in the tables of Appendix IV.

Having calculated, by means of the method of successive approximations, the composition and pressure of combustion products at 2,000, 2,200, 2,400° K (see Example 6), we find $T_e = 2{,}228^\circ$ K by graphic interpolation from condition $\sum_k pk = 20.80$ atm. To this temperature corresponds $p_{eH_2} = 16.2375$ atm, which can also be determined graphically. By formula (IX.34) we find: $U''_{2{,}000\text{prod}} = 211.3512$, $U''_{2{,}200\text{prod}} = 212.2477$; $U''_{2{,}400\text{prod}} = 213.5792 \ \frac{\text{lit-atm}}{\text{lit}}$, whence, by interpolation, we find $U''_{T_e\text{prod}} = 212.408 \ \frac{\text{lit-atm}}{\text{lit}}$.

Substituting all these values, including that of $U_{T_i \text{init}}$, (see Example 6) in equation (IX.35), we find

$$(H^\circ_{2228} - H^\circ_0)_{H_2} = 16{,}625 \ \frac{\text{Kcal}}{\text{mole}} .$$

Should we, while disregarding combustion products dissociation, use equations (IX.31) and (IX.32), the result would be: $T_e = 2{,}229.4^\circ$ K, and

$$(H^\circ_{2229.4} - H^\circ_0)\,H_2 = 16{,}723 \ \frac{\text{Kcal}}{\text{mole}} .$$

In those cases when thermal capacities are unknown for more than one component, they sometimes may be determined as a result of explosions, whose number is equal to the number of the unknown quantities, where the temperature T_e is the same, but where the composition of the initial mixture is different. Coincidence of combustion temperatures for different initial mixture compositions may be achieved by means of STAT

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placement of diluents, and through variation of the initial pressure and temperature. This method was used already by Pier (53) on Nernst's recommendation. In exploding oxyhydrogen mixtures diluted by argon, he determined, simulataneously with water vapor thermal capacity, the thermal capacity of argon in order to prove the practicability of the explosion method. This and analogous experiments enabled Pier and other investigators (37, 61) to draw the conclusion that this method of thermal capacity determination is free from methodic errors.

Let us assume that thermal capacities of s components of a mixture of combustion products are unknown, while those of r mixture components are known. As in the derivation of equation (IX.35), we produce s equations which look like this:

$$\sum_{l=1}^{s} p_{el}(H^{\circ}_{T_e} - H^{\circ}_0)_l = RT_e(U_{T_i}\text{init.} - U''_{T_e}\text{prod}), \qquad (IX.37)$$

where the magnitude of U''_{T_e} prod, corresponding to combustion temperature T_e, which is the same for all tests, may be found by interpolation on the basis of curve U''_T prod (T). Here U''_Tprod is determined by formula in a manner similar to (IX.34)

$$U''_T\text{prod} = \frac{1}{RT}\left(\sum_{k=1}^{r} p_k H^{\circ}_{Tk} + \sum_{l=1}^{s} p_l H^{\circ}_{0l}\right) - P. \qquad (IX.38)$$

The sequence of operations is the same as in the case of one unknown thermal capacity, with the sole difference that the final stage of calculations here is constituted by the solution of the system of s equations of (IX.37) type.

<u>Example 11</u>. We are required to determine the thermal capacities of H_2 and H_2O. For this purpose we made two tests in a bomb, with steam heating, under the following initial conditions: Test (1) -- $p_iH_2 = 2.176$, $p_iO_2 = 0.346$, $p^*_iH_2O = 0.938$, $p_i = 3.460$ atm, $T_i = 373.5°$ K. Test (2) -- $p_iH_2 = 3.132$, $p_iO_2 = 0.298$*, $P_i = 3.430$ atm, $T_i = 373.5°$ K. The observed maximum explosion pressure P_e (relative to uniform temperature distribution) in Test (1) is 17.98 atm; in Test (2) it is 18.05 atm.

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* The small amount of water vapor is disregarded in this case since it has no significance in the illustration of the computation method.

Using the method of successive approximations, we determine by graphic interpolation from condition $\sum_k p_k = P_e$:

$$T_e^{(1)} = 2,155^\circ \text{ K}, \qquad T_e^{(2)} = 2,151^\circ \text{ K}$$

(figures in parentheses denote the test number). The coincidence of combustion temperatures is satisfactory. Hence, the given two tests may produce two equations required for the solution of the problem at hand.

After determining the values of p_{eH_2}, p_{eH_2O}, and $U''_{T_e\,\text{prod}}$, corresponding to T_e, and substituting them in formula (IX.37), we produce a system of two equations:

$$\begin{aligned} 8,552\,(H^\circ_{2153} - H^\circ_0)_{H_2} + 9,405\,(H^\circ_{2153} - H^\circ_0)_{H_2O} &= 342,1254, \\ 14,595\,(H^\circ_{2153} - H^\circ_0)_{H_2} + 3,430\,(H^\circ_{2153} - H^\circ_0)_{H_2O} &= 307,4114, \end{aligned}$$

Solving these equations, we find $(H^\circ_{2153} - H^\circ_0)_{H_2} \div 15.914$, and $(H^\circ_{2153} - H^\circ_0)_{H_2O} = 21.908$ $\frac{\text{Kcal}}{\text{mole}}$, respectively

$$\bar{C}_{v_{H_2}}^{2153+0} = 5,405;\ \bar{C}_{v_{H_2O}}^{2153+0} = 8,188\ \frac{\text{cal}}{\text{mole} \cdot \text{degree}}$$

By changing the quantity of diluent and the other initial conditions, we may determine the values of the thermal capacity (heat contents) increment for a number of temperatures over a more or less wide range; using the method of least squares, we can derive an equation of the dependence of these quantities upon temperature within this interval.

Table 26

T°K	$(H^\circ - H^\circ_0)_{H_2}$ test
2184	16,285
2228	16,625
2500	18,750
2576	19,580
2616	19,885

Example 12. The values of the heat contents increment recorded in Table 26 are determined for a number of temperatures over the 2,184-2,616° K range.

Assuming that the quantity $(H^\circ - H_0^\circ)_{H_2}$ as function of temperature over this interval may be expressed by equation

$$H^\circ - H_0^\circ = a_0 + a_1 T + a_2 T^2,$$

and finding the values of a_0, a_1, a_2 by the method of least squares (22), we obtain

$$(H_T^\circ - H_0^\circ)_{H_2} = -1{,}8490 + 8{,}2882 \cdot 10^{-3} \cdot T + 1{,}7 \cdot 10^{-9} \cdot T^2$$

(where $2184 \leqslant T \leqslant 2616$).

In those cases when there is a systematic divergence between the experimental and theoretical values of the heat-contents (thermal-capacity) increment, it sometimes becomes possible -- by way of a detailed analysis of the conditions and results of the test, calculation postulates, and the shapes of the experimental and theoretical curves of the unknown quantity versus temperature -- to detect the reason for this divergence and to correct these or the other initial data or, at least, to formulate the conditions for such adjustment.

The experiments carried out by Lewis and Elbe on determination of the average thermal capacity of oxygen in ozone-oxygen explosions may be cited as an example of this(46). In these tests the proportion of the quantity of oxygen to that of ozone varied from 0.85 to 3.5; initial pressure varied from 300 to 760 mm Hg; combustion temperature ranged from 1,400 to 2,500° K. It was revealed that the experimental values of O_2 thermal capacity were higher than those determined theoretically. Moreover this difference increased with temperature. By careful analysis it was possible to establish that the observed divergence came as a result of the failure to consider 1Δ of the electron level whose existence was theoretically duly predicted, although its position remained unknown. Experimental data produced by the method of explosion permitted us roughly to evaluate the energy of this level. Later on, Johnston and Davis were able to define it more precisely and to make a corresponding recalculation of the thermodynamic functions.

In analyzing experimental data, it is well to compare the temperature-dependent components of the observed and calculated thermal-capacity values. In this man STAT it becomes easier to determine the cause of the divergence between them, since its relative value turns out to be greater.

Section 4. Determination of the Heats of Dissociation by the Method of Explosion

Tests to determine the heat of dissociation are conducted in conditions such as to assure the development of the corresponding process in a degree required for the amount of heat absorbed thereby so as to constitute a sufficiently large proportion of the heat of combustion. This is being achieved by routine methods by causing a shift of equilibrium in the desired direction.

By way of an example we shall consider here the case of the determination of the energy of water-vapor dissociation with hydroxyl formation (21) which develops according to equation:

$$H_2O \rightleftarrows OH + \frac{1}{2}H_2. \qquad \text{(IX.39)}$$

Water vapor dissociates also in another direction:

$$H_2O \rightleftarrows H_2 + \frac{1}{2}O_2. \qquad \text{(IX.40)}$$

Apparently, the excess of oxygen shifts equilibrium (IX.39) to the right, toward greater dissociation, while it displaces equilibrium (IX.40) to the left, toward lesser dissociation. Tests carried out with considerable oxygen excess and strong dilution of the initial mixture -- which reduces combustion temperature to such an extent that dissociation (IX.38) becomes negligible -- produced higher values of maximum explosion pressure, as compared to those obtained by theoretical calculations. This is attributed (21, 63) to the previously mentioned phenomenon of excitation inhibition of the oscillatory levels. In view of this fact, the excess of O_2 must be minor to cause oxygen concentrations in combustion products to be small. At the same time the initial mixture should be diluted by inert gases only to the extent required to prevent the formation of shock waves. On the basis of the availab STAT experimental data (63), we are justified in assuming that, in these conditions, the postulates, on which calculations are founded, correspond to the true progress of the process with sufficient accuracy.

The thermal effect of dissociation ΔH^o_0 diss may be determined by the method of selection on the basis of the equality condition of the theoretical and experimental values of maximum explosion pressure.

If we fix, for example, a few (not less than three) values of ΔH^o_0 diss for this purpose, we can calculate the corresponding values of hydroxyl enthalpy H^o_{TOH} and equilibrium constants K_p. The latter may be calculated from the formula (App. I.77) in Appendix I. For those cases in which the calculator does not know the values of Φ^{*o} for all substances which take part in this reaction, the magnitude of $\Delta\Phi^{*o}$ may be produced by back computation on the basis of the known quantities K_p and ΔH^o_0 by formula

$$\Delta\Phi^{*\circ} = 4{,}5756 \lg K_p + \frac{\Delta H^\circ_0}{T}. \qquad \text{(IX.41)}$$

In determining maximum explosion pressure P_e for each of the arbitrarily fixed values of ΔH^o_0 diss within the assumed interval of the probable values of this quantity, and in tracing a curve of the theoretical values of P_e as a function of ΔH^o_0 diss , we find the unknown quantity by interpolation on the basis of the observed maximum explosion pressure. As to the correction for temperature gradient, strictly speaking, a calculation of this quantity should be made for each given value of ΔH^o_0 diss. Then the unknown value of ΔH^o_0 diss will be determined by the X-axis of the point of intersection of the curves of the theoretical and adjusted experimental maximum explosion pressures versus ΔH^o_0 diss. In the majority of cases, however, such accuracy is uncalled for, and it suffices to calculate the correction for temperature gradient for any one of the ΔH^o_0 diss values within the selected range.

The accuracy of this heat-of-dissociation calculation is not too high. Yet, the method of explosion may be very useful in the cases when spectral and other experimental data do not provide an opportunity for unambiguous determination of this in Bierrum's experiments, Pier in his

quantity, and produce for it a number of approximately equally probable but strongly differing values for instance.

Example 13. In order to determine the heat of water-vapor dissociation with formation of hydroxyl (reaction (IX.39)), an oxyhydrogen mixture diluted by helium is exploded in a bomb. Its composition and the other initial conditions are the same as in the example in point (2)(page 70). The experimentally observed maximum explosion pressure $P_{e\,grad} = 7.458$ atm.

Assuming that the unknown value of thermal effect ΔH^o_0 diss of reaction (IX.38) is to be found in the interval between 61.000 and 65.000 Kcal, let us calculate the theoretical maximum explosion pressure P_e for three values of $\Delta H^o_{0\,diss}$ within the said interval, i.e., 61.000, 63.000, and 65.000 Kcal.

First we shall compute K_3 and H^o_{OH} for these ΔH^o_0 diss values at 2,600, 2,800, and 3,000° K (Tables 27 and 28). Then we shall find the three corresponding values of P_e as this was done in Example 2. The results of these computations are recorded in Table 29.

Table 27

T (°K)	$\Delta H^{\circ}_{03} = 61{,}000$	$\Delta H^{\circ}_{03} = 63{,}000$	$\Delta H^{\circ}_{03} = 65{,}000$
	Values of K_3		
2600	0,02680	0,01820	0,01235
2800	0,06548	0,04571	0,03191
3000	0,1403	0,1003	0,07166

Table 28

T (°K)	$\Delta H^{\circ}_{03} = 61{,}000$	$\Delta H^{\circ}_{03} = 63{,}000$	$\Delta H^{\circ}_{03} = 65{,}000$
	Values of H^o_{OH}		
2600	52,498	54,498	56,498
2800	54,240	56,240	58,240
3000	56,009	58,009	60,009

Table 29

ΔH°_{03}	T_e (°K)	P_e (atm)
61,000 63,000 65,000	2781,0 2808,9 2833,5	7,439 7,502 7,562

We shall calculate the temperature gradient correction for ΔH^{o}_{03} = 63.000 Kcal. The result is $P_e/P_{e\,grad}$ = 1.00526 and P_e = 7.497 atm, (see Example 9). Finally, by graphic interpolation (we can see from Figure 19 that the P_e versus ΔH^{o}_{03} plot represents an almost straight line) on the basis of Table 29 data, we find the value of ΔH^{o}_{03} which corresponds to P_e = 7.497 atm. It is equal to 62.830 Kcal. (Had the temperature gradient not been taken into account, the result would have been ΔH^{o}_{03} = 61.580 Kcal, i.e., 1.250 Kcal less.)

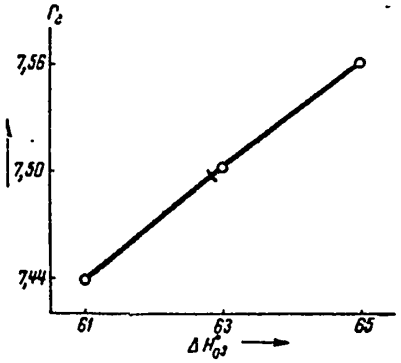

Figure 19. Interpolation graph for determination of the heat of dissociation on the basis of maximum explosion pressure.

For six such tests, Lewis and Elbe found $\Delta H^{o}_{03} = 63 \pm 1$ Kcal.

CONCLUSIONS

In the preceding pages, we have reviewed only the most common problems solved by the method of explosion. It goes without saying that this does not restrict the uses of this method. It has often been used recently for complex checks on the accuracy of the data selected for thermodynamic calculations of combustion processes at high temperatures in their totality. The comparison of the theoretical and experimental values of maximum explosion pressure, along with the analysis of test conditions and the principal computation premises, affords us a deeper insight into the essence of the phenomena occuring during combustion.

The existence of deviations from the postulates forming the basis of calculations -- of anomalies which often cannot be taken into account and, moreover, are not always known -- constituted the most serious objection against the application of the explosion method for thermodynamic research. However, a careful study of the experimental data permits us to select the kind of experimental conditions under which the anomalies become insignificantly small or can be accounted for. We can cite a whole series of examples for the successful use of the explosion method. One of them -- the determination of oxygen thermal capacity which helped to clarify the question pertaining to the energy levels of the O_2 molecule -- is recorded above (Chapter IX, Section 3). By the method of explosion, Wohl (61) was able to determine the values of the heats of chloride and hydrogen dissociation into atoms, which are in satisfactory agreement with the values determined later on by spectroscopic analysis.

The errors in the data produced by some investigators who applied this method are to be attributed most frequently (47) either to failure to comply with the prerequisites of the tests (Chapter II, Section 2), or to the presence of considerable anomalies, which were not duly taken into account, or, finally, to incomplete consideration of dissociation and other high-temperature chemical processes. Thus, for

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instance, heat losses were taking place (62) in Bierrum's experiments, Pier in his initial tests failed to consider dissociation (53), and so on. All this evidences the fact that the use of the method of explosion calls for profound, all-round, and thorough analysis of the test throughout its entire development. For a number of cases the following research stages may be outlined: (1) qualitative analysis of the explosions of mixtures with different fuel-oxidizer ratios to determine the region in which experimental data may be successfully processed, and to establish qualitatively (for example, by type of indicator diagram) the presence of one or another anomaly; (2) quantitative investigation (test and calculation) for the purpose of precise determination of the effects of various factors on the magnitude of the maximum explosion pressure, as well as with the view to collecting data for calculation of unknown quantities ; (3) analysis of the results produced, for instance, to expose the reasons leading to a divergence between the experimental and theoretical data, or for the determination of any given quantity. All these stages may be closely interwoven with each other in the process of investigation.

This book is offered to the reader with the intent of providing only a general idea of the method of explosion. Depending on the problems, research by means of this method may assume varying characteristics. The application range of the explosion method will also depend on the imagination and ingenuity of the researcher.

The data obtained by the method of explosion or confirmed by it may be used for the computation of combustion processes in industry. One should take into account the conditions in which a given process develops and their deviation from the conditions of combustion in a spherical vessel with central ignition. The mastery of these calculation methods is useful both from the point of view of theory and for purposes of practical application, since combustion processes at the present time are being ever more extensively used in modern technology.

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Appendix I

ELEMENTARY INFORMATION ON STATISTICAL METHODS OF COMPUTATION OF THERMODYNAMIC QUANTITIES

For calculation of combustion processes, we use thermodynamic functions of gases calculated by methods of statistical physics on the basis of spectral data. It is not possible to deal with these methods in detail here. They are complicated and demand knowledge of the principles of the theory of molecular structure, molecular spectroscopy, and statistical physics. However, it might be useful for the reader to have a general idea on these subjects.

1. On the Principal Aspects of Statistical Physics

Statistical physics permits us to derive the observed properties of gases from the properties of the particles constituting these gases. If an attempt were to be made to solve this problem by methods of classical mechanics, one would have to know the coordinates and velocities of an exceedingly great number of particles.

But, in order to calculate theoretically the aggregate effect of the particles observed in experiment, it is only necessary to know the function showing which portion of the particles has the coordinates and pulses (or velocities) within a given small interval. The principal task of statistical physics is precisely to determine the kind of this function, known as the distribution function.

If the temperature and the potential are equal over the entire volume, it is possible to assume that distribution by coordinates is uniform -- this permits us to exclude it from the analysis -- while distribution according to pulses is isotropic, i.e., it is the same in all directions. In the absence of a field, this latter consideration allows us fully to characterize the state of the system by energy distribution.

Statistical physics deals with systems whose state does not change with time, i.e., the so-called equilibrium systems.

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The equilibrium state is a limit the system tends to arrive at under the given conditions. For statistical analysis, such a state is equivalent to the most probable. Thus, the problem consists in defining the most probable distribution.

Experiment suggests that the definition of "probability" in statistical physics must be the following: the probability W of a given distribution is equal to the number of different possibilities for its realization.

The answer to the question as to which possibilities should be considered different is not always the same. Classical statistics, which provides a different answer to this question than quantum statistics, yields the following expression for thermodynamic probability:

$$W = \frac{n!}{n_1!n_2!\ldots n_i!\ldots n_m!}, \qquad \text{(App.I.1)}$$

where $n_1, n_2, \ldots\ldots, n_i, \ldots\ldots, n_m$ is the number of molecules to be found in the states with energy $\varepsilon_1, \varepsilon_2, \ldots\ldots, \varepsilon_i \ldots\ldots \varepsilon_m$ respectively. n is the total number of molecules in the system, which is constant. The value of W is greatest when $n_1 = n_2 = \ldots = n_i = \ldots\ldots = n_m$, i.e., when the molecule distribution by levels is even. According to the law of the conservation of energy:

$$\sum \varepsilon_i n_i = U = \text{const.} \qquad \text{(App.I.2)}$$

Using equations (App.I.1) and (App.I.2) it is possible, from the condition of maximum W

$$\delta W = 0 \qquad \text{(App.I.3)}$$

to determine the most probable distribution characterizing the system in the state of thermal equilibrium:

$$n_i = Ae^{-\frac{\varepsilon_i}{kT}}. \qquad \text{(App.I.4)}$$

Hence,

$$n = \sum n_i = A\sum e^{-\frac{\varepsilon_i}{kT}}. \qquad \text{(App.I.5)}$$

From (App.I.4) and (App.I.5), we obtain

$$n_i = n \frac{e^{-\frac{\varepsilon_i}{kT}}}{\sum e^{-\frac{\varepsilon_i}{kT}}}. \qquad \text{(App.I.6)}$$

For a general case, when degenerated energy levels are to be registered

$$n_i = n \frac{g_i e^{-\frac{\varepsilon_i}{kT}}}{\sum g_i e^{-\frac{\varepsilon_i}{kT}}}, \qquad \text{(App.I.7)}$$

where g_i is the statistical weight (degeneracy) of the i-th level. This is the aspect of the law of distribution in classical statistics. For further derivations it is convenient to introduce a designation:

$$Q' = \sum g_i e^{-\frac{\varepsilon_i}{kT}}. \qquad \text{(App.I.8)}$$

The quantity Q' is called the sum of states.

2. Expression of Thermodynamic Quantities through the Sum of States

It is known that the transition of a system from unstable state to that of stability is accompanied by a growth of entropy S. At the same time this process -- if it is approached from the point of view of statistics -- is a process of transition from a less probable to a more likely state. A system in equilibrium is characterized by a maximum of entropy and at the same time by a maximum of thermodynamic probability. Thus, a definite relationship is to be observed between entropy and probability, which may be expressed by equality:

$$S = f(W).$$

From the fact that entropy is an additive and that probability is a multiplicative property, we may draw the conclusion that entropy is proportional to the logarithm of thermodynamic probability:

$$S = k \ln W + \text{const.}$$

It may be shown that k is a Boltzmann's constant equal to $\frac{R}{N}$. It was postulated by Planck that the second constant in this equation is equal to zero. Thus,

$$S = K \ln W \qquad \text{(App.I.9)}$$

The (App.I.9) relationship constitutes the cornerstone of statistical thermodynamics. It establishes a link between the observed properties of gases and the properties of their constituent particles, since -- as it may be seen from the above -- the thermodynamic probablilty for a gaseous system may be computed if the energy levels of molecules, which compose it, are known.

Expression (App.I.1), as well as the more general expression for thermodynamic probability used in classical statistics for calculations of the degeneration of levels,

$$W = n! \prod_i \frac{g_i^{n_i}}{n_i!}, \qquad \text{(App.I.10)}$$

is derived in the assumption that all particles are distinguishable -- as though each of them were provided by its individual number. Yet, actually they cannot be distinguished from each other in random motion. This fact calls for the introduction of a correction into the expression for W, by way of its division by n! A rigorous substantiation for such adjustment may be provided on the basis of quantum mechanics. Making this adjustment and using Stirling formula

$$\ln n! = n \ln n - n, \qquad \text{(App.I.11)}$$

we obtain from (App.I.1)

$$\ln W = n - \sum n_i \ln n_i. \qquad \text{(App.I.12)}$$

From equation (App.I.6) we find

$$\ln n_i = \ln n - \frac{\varepsilon_i}{kT} - \ln Q',$$

where $Q' = \sum e^{-\frac{\varepsilon_i}{kT}}$. After substitution of this expression in (App.I.12) while considering (App.I.2), we obtain

$$\ln W = n - n \ln n + \frac{U}{kT} + n \ln Q'.$$

[redacted]

Hence,

$$S = kn \ln \frac{Q'}{n} + \frac{U}{T} + kn.$$

For one mole of gas

$$S = R \ln \frac{Q'}{N} + \frac{H}{T}. \qquad \text{(App.I.13)}$$

Usually, for the zero energy level of molecules of a given type, their eigen zero-level is taken for statistical calculations, i.e., the energy of these molecules at absolute zero. We have:

$$\sum g_i e^{-\frac{\varepsilon_i}{kT}} = e^{-\frac{\varepsilon_0}{kT}} \sum g_i e^{-\frac{\varepsilon_i - \varepsilon_0}{kT}}.$$

Introducing the designation

$$Q = \sum g_i e^{-\frac{\varepsilon_i - \varepsilon_0}{kT}}, \qquad \text{(App.I.14)}$$

we produce:

$$Q' = e^{-\frac{U_0}{RT}} Q.$$

Substituting this expression in (App.I.13), we find

$$S = R \ln \frac{Q}{N} + \frac{H - U_0}{T}. \qquad \text{(App.I.15)}$$

From the elementary thermodynamics course, we know that

$$Z = H - TS, \qquad \text{(App.I.16)}$$

where Z is the thermodynamic potential. Hence,

$$-\frac{Z - U_0}{T} = S - \frac{H - U_0}{T}.$$

Comparing this equation with formula (App.I.15) and after indroducing the designation

$$\Phi^* = -\frac{Z - U_0}{T}, \qquad \text{(App.I.17)}$$

we produce

$$\Phi^* = R \ln \frac{Q}{N}. \qquad \text{(App.I.18)}$$

Furthermore, we have

$$\left(\frac{\partial Z}{\partial T}\right)_p = -S,$$

and since

$$Z = U_0 - RT\ln\frac{Q}{N}, \qquad \text{(App.I.19)}$$

as it transpires from equations (App.I.17) and (App.I.18), we get -- by differentiating (App.I.19) with respect to T -- from the last two expressions

$$S = R\ln\frac{Q}{N} + RT\left(\frac{\partial \ln Q}{\partial T}\right)_p. \qquad \text{(App.I.20)}$$

Finally, the average molar heat capacity at constant pressure over the range from 0° K to temperature T will be determined by formula

$$\overline{C}_p = \frac{H-U_0}{T} = \frac{H-H_0}{T} = S - \Phi^* = RT\left(\frac{\partial \ln Q}{\partial T}\right)_p. \qquad \text{(App.I.21)}$$

On the basis of formulas (App.I.18), (App.I.20), and (App.I.21), it is possible to calculate all the thermodynamic functions of gases, Φ^*, S, and $H - H_0$, required for the calculation of combustion processes, if we know quantity Q which can be determined by equation (App.I.14). Thus, the problem is reduced to the computation of the sum of states Q according to the known energy levels of the system.

Here we have recorded a simplified derivation of formulas (App.I.18), (App.I.20), and (App.I.21); we have presented what is essentially only an outline of the reasoning on which a more rigorous derivation is based. Yet, the restricted information contained herein provides a general idea of the methods of statistical thermodynamics useful to anyone who deals with the results of statistical calculations.

3. Calculation of the Sums of States -- Computation Formulas for Approximation of Harmonic Oscillator-Rigid Rotator

(a) Break-down of the Sums of States

In calculating the sums of states, the molecule energy ε may be conveniently broken down into two independent constituents, i.e., progressive constituent ε_t and intrinsic component ε_i :

$$\varepsilon = \varepsilon_t + \varepsilon_i.$$

From the expression for the sum of states it follows that

$$Q = Q_t Q_i.$$

Consequently, the expressions for Φ^* for the potential (App.I.18) and entropy (App.I.20) may also be broken down into two parts. Moreover, in view of the indiscernibility of the particles in random motion, and only in this case, the divisor N -- which appears with the introduction of the above-mentioned correction into the classical expression for W -- will enter precisely in the expressions for Φ^*_t and S_t which retain the form of (App.I.18), and (App.I.20), whereas for the inner constituents we obtain:

$$\Phi^*_i = R \ln Q_i, \qquad \text{(App.I.22)}$$

$$S_i = R \ln Q_i + RT \frac{d \ln Q_i}{dT}. \qquad \text{(App.I.23)*}$$

(b) Progressive Constituents of Thermodynamic Functions

Insofar as progressive motion stops at absolute zero, $\varepsilon_{0t} = 0$ and

$$Q_t = \sum e^{\frac{-\varepsilon_t}{kT}}.$$

Using the quantum-mechanics expression for ε_t, it is possible to show that

$$Q_t = \frac{(2\pi mkT)^{3/2}}{h^3} V,$$

where m is the weight of molecule (or atom), h is the Planck's constant, and V is the volume of the system. For one mole of gas

$$Q_t = \frac{(2\pi mkT)^{3/2}}{h^3} \cdot \frac{RT}{P}, \qquad \text{(App.I.24)}$$

where P is the pressure.

On the basis of formula (App.I.18), we obtain

$$\Phi^*_t = R\left\{\ln \frac{(2\pi mkT)^{3/2}}{h^3} \cdot \frac{kT}{P}\right\};$$

or

$$\Phi^*_t = R\left\{\frac{5}{2} \ln T + \frac{3}{2} \ln \mu - \ln P + \ln \left(\frac{2\pi k}{N}\right)^{3/2} \frac{k}{h^3}\right\}. \qquad \text{(App.I.25)}$$

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*Since Q_i is independent of pressure, there is no sense in taking a partial derivative.

where μ is the molecular weight of the substance.

Substituting the numerical values of the constants and expressing the pressure in atmospheres, we produce*

$$\Phi_t = \frac{5}{2} R \ln T + \frac{3}{2} R \ln \mu - R \ln P_{atm} - 7,2836 \frac{\text{cal}}{\text{mole}\cdot\text{degree}}, \quad \text{(App.I.26)}$$

where R must be expressed in $\frac{\text{cal}}{\text{mole}\cdot\text{degree}}$.

It is common for thermodynamic functions to be calculated for the standard state, i.e., the state of ideal gas when P = 1 atm.

Consequently, to calculate Φ_t^{*o}, we use formula:

$$\Phi_t^{*\circ} = \frac{5}{2} R \ln T + \frac{3}{2} R \ln \mu - 7,2836 \frac{\text{cal}}{\text{mole}\cdot\text{degree}} \quad \text{(App.I.27a)}$$

where the index ^{o} signifies the appurtenance to standard state. In passing over to common logarithms and after substitution of the numerical value of R, we finally produce:

$$\Phi_t^{*\circ} = 11,4390 \lg T + 6,8634 \lg \mu - 7,2836 \frac{\text{cal}}{\text{mole}\cdot\text{degree}} \quad \text{(App.I.27b)}$$

Further, in substituting (App.I.24) in (App.I.21) we find

$$(\bar{C}_p)_t = S_t^\circ - \Phi_t^{*\circ} = \frac{5}{2} R \quad \text{(App.I.28)}$$

which is in accord with the classical ideas. Hence,

$$S_t = \Phi^* + \frac{5}{2} R = \Phi^* + 4,9679. \quad \text{(App.I.29)}$$

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* Here and for further calculations it was assumed that (32):

$N = 6.02544\cdot 10^{23}$ mole^{-1};

$C = 2.997902\cdot 10^{10}$ cm·sec^{-1};

$h = 6.62377\cdot 10^{-27}$ erg·sec;

$k = 1.38026\cdot 10^{-16}$ erg·deg^{-1};

$R = 1.98716$ cal·mole^{-1}·deg^{-1};

$\frac{hc}{k} = 1.43867$ cm·deg;

$R \ln 10 = 4.5756$.

(c) Thermodynamic Functions of Monatomic Gas

The inner sum of states for monatomic gas may be broken down into two factors, i.e., the electron sum of states Q_e and the sum of states of nuclear spin Q_n:

$$Q_i = Q_e Q_n. \qquad \text{(App.I.30)}$$

Since neither the number of atoms in the system, nor the properties of their nuclei, vary during chemical changes, the total nuclear-spin constituent of thermodynamic functions of the reaction products is equal to the nuclear-spin constituent of thermodynamic functions of the initial substances. However, since it is not the absolute magnitude of these functions that usually presents interest, but their variations in the process of reaction, the nuclear-spin sum of states, as a rule, is not taken into account in computations.

The electron sum of states may be calculated by formula

$$Q_e = \sum_e g_e e^{-\frac{\varepsilon_e}{kT}}. \qquad \text{(App.I.31)}$$

For the lowest state, $\varepsilon_e = 0$. Hence, in developing formula (App.I.31), we produce

$$Q_e = g_0 + g_1 e^{-\frac{\varepsilon_1}{kT}} + g_2 e^{-\frac{\varepsilon_2}{kT}} + g_3 e^{-\frac{\varepsilon}{kT}} + \dots \qquad \text{(App.I.32)}$$

In view of the fact that to every value of the quantum number J, representing the total electron momentum of the quantity of atom motion, there correspond 2J+1 different possible orientations in the magnetic field, which constitute the states of atom almost indistinguishable from each other by energy, the statistical weight of each electron state is equal to 2J + 1. Consequently, Q_e may be written in the form of:

$$Q_e = \sum_e (2J_e + 1) e^{-\frac{\varepsilon_e}{kT}}. \qquad \text{(App.I.33)}$$

As a rule, one calculates only the principal electron level of the atom and one makes a summation for all its sublevels. In the first approximation, the difference in sublevel energies may be disregarded and the assumption can be made that the energy

[redacted]

of all sublevels is equal to zero. Then the electron sum of states will be equal to the statistical weight of the principal electron level:

$$Q_e = g_{e\,\mathrm{princ}} = \sum (2J+1). \qquad \text{(App.I.34)}$$

As it is well known, quantum number J is composed of orbital quantum number L and spin quantum number S, and takes all the positive values from L + S to L - S over one unit.

The number of these values, equal to the number of sublevels and termed as multiplicity of level, amounts to 2S + 1. It is possible to show that the statistical weight of the principal electron level is equal to the product of the number of possible spin orientations (multiplicity of term) multiplied by the number of possible orientations of orbital momentum

$$g_{e\,\mathrm{princ.}} = (2S+1)(2L+1). \qquad \text{(App.I.35)}$$

The values of S and L may be determined on the basis of term symbols recorded in reference tables (see, for instance, (7)). The letters S, P, and D correspond to the values of L, for example L = 0, 1, 2. Multiciplicity is designated by the figure located above to the left. For sublevel symbols, the values of J are recorded below to the right.

The excited levels are considered only in those cases when they are located low enough. One can adopt the following rough rule (10): if $\frac{hc\nu}{k} > 5T$, where ν is the energy of electron level in cm^{-1}, the constituent introduced by this level may be neglected in the sum of states.

The thermodynamic functions of monatomic gas are calculated by formulas:

$$\Phi^{*\circ} = \Phi_t^{*\circ} + R\ln Q_e; \qquad \text{(App.I.36)}$$

$$C_P = \frac{H_T^\circ - H_0^\circ}{T} = \frac{5}{2}R + RT\frac{d\ln Q_e}{dT}. \qquad \text{(App.I.37a)}$$

In cases when it is assumed that $Q_e = g_{e\mathrm{princ}}$,

$$\frac{d\ln Q_e}{dT} = 0.$$

Finally,

$$S^\circ = \Phi^{*\circ} + \bar{C}_p \qquad \text{(App.I.37b)}$$

<u>Example App.I.</u> Calculate the standard values of Φ^* - potential entropy S°, and the increment of enthalpy $H^\circ - H^\circ_0$ of atomic oxygen at 2,000° K.

From the term tables (7) for electron levels of oxygen atom, we have:

Term Symbol	Energy ν (cm^{-1})
$^3P_2$	0
$^3P_1$	158
$^3P_0$	227
$^1D_2$	15868
$^1S_0$	33793

We shall consider only three sublevels $^3P_2$, $^3P_1$, and $^3P_0$, belonging to the principal level ^3P. According to formula (App.I.32), we have:

$$Q_e = 5 + 3e^{-158hc/kT} + e^{-227hc/kT}. \qquad \text{(App.I.38)}$$

As a first approximation, we may consider the energy of all three sublevels to be identical and equal to zero. Since, as may be seen from the term symbol of ^3P,

$$2S + 1 = 3, \quad L = 1,$$

we obtain, on the basis of formula (App.I.35),

$$g_{e\,\mathrm{princ}} = 9.$$

Consequently,

$$R \ln Q_e = R \ln g_{e\,\mathrm{princ}} = 4.3662.$$

With the help of formulas (App.I.27b) and (App.I.36), we find

$$\Phi^{*\circ} = 11.4390 \lg T + 8.2644 - 7.2836 + 4.3662 = 11.4390 \lg T + 5.3470.$$

Thus, $\Phi^{*\circ}$ - potential is now expressed as a function only of temperature.

At 2,000° K:

$$\Phi^{*\circ} = 37{,}7605 + 5{,}3470 = 43{,}107 \frac{\text{cal}}{\text{mole}\cdot\text{degree}}.$$

Since we have assumed $Q_e = g_e$ princ and since consequently $\bar{C}_p = \frac{5}{2} R$,

$$\bar{C}_p = 4{,}9679 \frac{\text{cal}}{\text{mole}\cdot\text{degree}}$$

$$S^\circ = \Phi^{*\circ} + 4{,}9679 = 48{,}075 \frac{\text{cal}}{\text{mole}\cdot\text{degree}}$$

Finally

$$H^\circ - H_0^\circ = 2000 \cdot 4{,}9679 = 9936 \frac{\text{cal}}{\text{mol}} .$$

We will get more accurate results if we apply expression (App.I.38). In this case, at 2,000° K.

$$R \ln Q_e = 4{,}2590; \quad \Phi^{*\circ} = 43{,}000 \frac{\text{cal}}{\text{mole}\cdot\text{grad}}$$

Furthermore,

$$\frac{d \ln Q_e}{dT} = \frac{1}{Q_e} \frac{dQ_e}{dT} = 2{,}598 \cdot 10^{-5};$$

$$RT \frac{d \ln Q_e}{dT} = 0{,}1033.$$

Hence,

$$C_p = 4{,}9679 + 0{,}1033 = 5{,}0712 \frac{\text{cal}}{\text{mole}\cdot\text{grad}}$$

$$S^\circ = \Phi^{*\circ} + 5{,}0712 = 48{,}071 \frac{\text{cal}}{\text{mole}\cdot\text{grad}}$$

Finally,

$$H^\circ - H_0^\circ = 2000 \cdot 5{,}0712 = 10142 \frac{\text{cal}}{\text{mol}}$$

Thus, a more precise calculation introduces the greatest adjustment into the value of average heat capacity (and enthalpy).

(d) Break-down of the Inner Sum of States of Diatomic and Polyatomic Gases.

The internal energy constituent of a molecule, containing two or more atoms, is composed of the constituents of the rotary and oscillatory motions, as well as of electron and nuclear-spin constituents. In the first approximation -- that of harmonic oscillator - rigid rotator -- we may disregard the unharmonic nature of oscillations, the extension of bonds under the influence of centrifugal force, and the quantification of rotary energy, and we may consider all the four constituents of the internal sum of states as mutually independent. In this case:

$$Q_i = Q_{vib} Q_{rot} Q_e Q_n, \qquad \text{(App.I.39a)}$$

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where Q_{vib} is the vibrational constituent and Q_{rot} is the rotary constituent of the sum of states. The nuclear-spin constituent will not be taken into account for reasons referred to above.

From the form of the expressions for energy constituents of the molecule, as they result from the quantum theory, it ensues that at 0° K all molecular motion comes to a standstill, with the exception of vibrational motion. Therefore, in a breakdown of the internal sum of states, the zero energy will turn out to be entirely included in the expression for the oscillatory sum of states. In conformity therewith, and considering the fact that $g_{vib} = 1$, while Q_n is disregarded we obtain

$$Q_i = \sum e^{-\frac{\varepsilon_{vib} - \varepsilon_0}{kT}} \sum g_{rot}\, e^{-\frac{\varepsilon_{rot}}{kT}} \sum g_e e^{-\frac{\varepsilon_e}{kT}}. \qquad \text{(App.I.39b)}$$

(e) Thermodynamic Functions of Diatomic Gas

The electron sum of states $\overset{o}{Q}_e$ is determined by expression (App.I.32). In most cases, excitation equations may be neglected. In the first approximation, as in the case of monatomic gases, the energy of sublevels belonging to the principal electron level may be assumed to be the same and equal to zero. Then,

$$Q_e = g_{e\,princ.}$$

A powerful electricfield is active between the nuclei in a diatomic molecule. Therefore, the vector L, which represents the electron orbital momentum, effects a precession around the molecular axis, with its component along the direction of field M_L remaining constant. Moreover, for values of $L \neq 0$, the states, which differ only by the sign of M_L, have the same energy. Consequently, the electron states of diatomic molecules are classified according to $\Lambda = |M_L|$. It appears that the states with $\Lambda \neq 0$ are doubly degenerated (this leads to the splitting effect of the rotational lines in the spectrum, i.e., to the, so-called, "Λ- doubling"). The states characterized by the values of $\Lambda = 0, 1, 2, \ldots$ are designated respectively by letters $\Sigma, \Pi, \Delta, \ldots$ The number of states with almost equal energy pertaining to the

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[redacted]

same term -- multiplicity of term -- is equal, just as in the case of the atom, 2S + 1, where S is the resultant electron spin. For terms with $\Lambda \neq 0$, each multiplicity component is twice degenerated. Thus, for Σ- states the statistical weight is equal to multiplicity, and for all other states it is equal to doubled multiplicity.

The rotational sum of states is determined by equation:

$$Q_{rot} = \Sigma g_{rot} e^{-\frac{\varepsilon_{rot}}{kT}}. \qquad \text{(App.I.40)}$$

The quantum theory produces the following formula for the rotary energy of diatomic and linear polyatomic molecules (8):

$$\varepsilon_{rot} = B_v J(J+1) hc - D_v J^2 (J+1)^2 hc + \ldots, \qquad \text{(App.I.41)}$$

where B_v, D_v are the rotational constants and J is the rotational quantum number. While neglecting the second and the subsequent terms, and considering the rotational constant B as independent of the oscillatory quantum number V, we may produce a simplified formula:

$$\varepsilon_{rot} = BJ(J+1) hc. \qquad \text{(App.I.42)}$$

2J + 1 states with almost identical rotary energy correspond to each value of J. Consequently, $g_{rot} = 2J + 1$. Substituting (App.I.42) in (App.I.40) and introducing the designation $\frac{Bhc}{kT} = \rho$, we obtain

$$Q_{rot} = \sum_{J=0}^{\infty} (2J+1) e^{-J(J+1)\rho}. \qquad \text{(App.I.43)}$$

Since the rotary levels are situated close to each other, summation may be replaced in the first approximation by integration:

$$Q_{rot} = \int_0^{\infty} (2J+1) e^{-J(J+1)\rho} \, dJ = \frac{1}{\rho}.$$

Taking into account the molecule symmetry, we finally produce

$$Q_{rot} = \frac{kT}{Bhc\sigma}, \qquad \text{(App.I.44)}$$

where σ - is the symmetry number, characteristic for each point group and equal to the number of undiscernible positions of the molecule in the process of its simple rotation as a solid body. In the case of diatomic molecules, σ = 1 for molecules

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constructed by different atoms and $\sigma = 2$ for molecules composed of identical atoms.

Substituting of the numerical values of constants h, c, and k, we obtain by formula (App.I.22)*:

$$\Phi^*_{rot} = R\ln T - R\ln B - R\ln \sigma - 0{,}7228. \qquad \text{(App.I.45)}$$

From formula (App.I.23) we find

$$S_{rot} = \Phi^*_{rot} + R, \qquad \text{(App.I.46)}$$

whence, according to (App.I.21):

$$\bar{C}_{rot} = R, \qquad \text{(App.I.47)}$$

in agreement with the classical theory.

The vibrational sum of states is calculated on the basis of formula:

$$Q_{vib} = \sum e^{-\frac{\varepsilon_{vib}-\varepsilon_0}{kT}}. \qquad \text{(App.I.48)}$$

For the energy of nuclear vibration in a diatomic molecule, the quantum theory produces the formula:

$$\varepsilon_{vib} = hc\omega_e\left(v+\frac{1}{2}\right) - hc\omega_e x_e\left(v+\frac{1}{2}\right)^2 + \dots, \qquad \text{(App.I.49)}$$

where ω_e is the zero frequency, i.e., the vibration frequency for infinitely small amplitude values, and x_e is the unharmony constant.

If we disregard the unharmony of oscillations, i.e., assuming $x_e = 0$ we can come up with a simplified formula:

$$\varepsilon_{vib} = hc\omega_e\left(v+\frac{1}{2}\right). \qquad \text{(App.I.50)}$$

For v = 0

$$(\varepsilon_{vib})_0 = \varepsilon_0 = \frac{1}{2}hc\omega_e. \qquad \text{(App.I.51)}$$

This expression gives the magnitude of zero energy of the harmonic oscillator, which constitutes the lowest possible energy of the diatomic molecule considered as a

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* For calculations in approximation to a harmonic oscillator-rigid rotator, it is most convenient to use the rotary constant B_0, related to v = 0. which is connected with the equilibrium constants B_e and α_e by equation: $B_0 = B_e - \frac{\alpha_e}{2}$.

harmonic oscillator. Let it be noted that the value of zero energy is calculated here from the level at which the energy of a molecule at rest would be registered upon total suspension of vibrations.

Subtracting (App.I.51) from (App.I.50), we produce

$$\varepsilon_{vib} - \varepsilon_0 = hc\omega_e v. \qquad \text{(App.I.52)}$$

Substituting the value of $\varepsilon_{vib} - \varepsilon_0$ from (App.I.52) in formula (App.I.48), we find:

$$Q_{vib} = \sum e^{-\frac{hc\omega_e}{kT} v} = \sum^{-\frac{\theta}{T} v}, \qquad \text{(App.I.53)}$$

where $\theta = \frac{hc}{k}\omega_e$.

If we use the formula for the summation of an infinitely decreasing geometric progression, we get:

$$Q_{vib} = (1 - e^{-\frac{\theta}{T}})^{-1}. \qquad \text{(App.I.54)}$$

We now introduce the designation $\frac{\theta}{T} = x$. By way of transformation of (App.I.54), we produce

$$Q_{vib} = \frac{e^x}{e^x - 1}$$

and

$$\frac{\Phi^*_{vib}}{R} = \ln Q_{vib} = x - \ln(e^x - 1). \qquad \text{(App.I.55)}$$

Further, on the basis of formula (App.I.23), we determine

$$\frac{S_{vib}}{R} = \ln Q_{vib} + \frac{x}{e^x - 1}. \qquad \text{(App.I.56)}$$

In calculating Φ^*_{vib} and S_{vib}, we ordinarily use the tables (11, 19) of values of these quantities (or $\frac{\Phi^*_{vib}}{R}$ and $\frac{S_{vib}}{R}$) as functions of $x = \frac{\theta}{T}$ or of $\frac{\omega}{T}$.

Combined formulas (12). If we combine (App.I.45) with (App.I.27a) and (App.I.46) with (App.I.29), while considering the other constituents of the internal sum of states, we arrive at the following formulas for computation of thermodynamic functions of gas composed of diatomic or linear polyatomic molecules, as an approximation of harmonic oscillator- rigid rotator:

$$\Phi^{*\circ} = \frac{7}{2} R \ln T + \frac{3}{2} R \ln \mu - R \ln B_0 - R \ln \sigma + R \ln g_{e\,prin} - 8{,}0064 + \Phi^*_{vib}; \qquad \text{(App.I.57)}$$

$$S^\circ = (\Phi^{*\circ} - \Phi^*_{vib}) + \frac{7}{2} R + S_{vib}. \qquad \text{(App.I.58)}$$

Changing over to common logarithms and after substitution of the numerical value of R (in $\frac{\text{cal}}{\text{mole} \cdot \text{deg}}$), we have

$$\Phi^{*\circ} = 16{,}0146 \lg T + 6{,}8634 \lg \mu - 4{,}5756 \lg B_0 - 4{,}5756 \lg \sigma + 4{,}5756 \lg g_{e\,prin} - 8{,}0064 + \Phi^*_{vib}; \qquad \text{(App.I.59)}$$

$$S^\circ = (\Phi^{*\circ} - \Phi^*_{vib}) + 6{,}9551 + S_{vib}. \qquad \text{(App.I.60)}$$

Finally,

$$C_p = \frac{H^*_T - H^*_0}{T} = \frac{7}{2} R + (S_{vib} - \Phi^*_{vib}) = 6{,}9551 + \frac{(H^*_T - H^*_0)_{vib}}{T}. \qquad \text{(App.I.61)}$$

The rotational constant B is related to the moment of inertia I by expression

$$B = \frac{h}{8\pi^2 Ic}. \qquad \text{(App.I.62)}$$

Introducing this expression -- together with the numerical values of constants π, h, and c -- in formula (App.I.59), we obtain:

$$\Phi^{*\circ} = 16{,}0146 \lg T + 6{,}8634 \lg \mu + 4{,}5756 \lg I - 4{,}5756 \lg \sigma + 4{,}5756 \lg g_{e\,prin} + 168{,}3972 + \Phi^*_{vib}. \qquad \text{(App.I.63)}$$

Example App.2. Calculate the standard values of Φ*-potential, entropy, and enthalpy increment of gas OH at 2,000° K. The normal state of free hydroxyl is $^2\Pi$, frequency of vibrations $\omega_e = 3{,}727.95$ cm^{-1}, rotational constants $B_e = 18.862$, $\alpha_e = 0.693$, molecular weight $\mu = 17.008$.

We shall determine B_0 (see formula in the footnote on page 151): $B_0 = 18.515$. The electron sum of states, at the first approximation is equal to doubled multiplicity: $Q_e = 4$. Finally, the symmetry number $\sigma = 1$.

Introducing these values into equation (App.I.59), we obtain

$$\Phi^{*\circ} = 16{,}0146 \lg T - 2{,}6049 + \Phi^*_{vib}.$$

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On the basis of this formula, it is possible to calculate the value of Φ *- potential for any given temperature T. At 2,000° K 16.0146 lg T = 52.8647. From tables (11,19) we find:

$$\Phi^{*}_{vib} = 0,1426;$$

$$\frac{(H^{\circ}_T - H^{\circ}_0)_{vib}}{T} = 0,3947.$$

Consequently,

$$\Phi^{*\circ} = 52,8647 - 2,6049 + 0,1426 = 50,402 \frac{\text{cal}}{\text{mole}\cdot\text{grad}}$$

$$C_p = \frac{H^{\circ}_T - H^{\circ}_0}{T} = 6,9551 + 0,3947 = 7,350 \frac{\text{cal}}{\text{mole}\cdot\text{grad}}$$

$$S^{\circ} = 50,402 + 7,350 = 57,752 \frac{\text{cal}}{\text{mole}\cdot\text{grad}},$$

$$H^{\circ} - H^{\circ}_0 = 7,350 \cdot 2000 = 14\,700 \frac{\text{cal}}{\text{mole}}$$

These data are compared in Table App.I with the results of a more accurate calculation produced by Johnston and Dawson with due account being taken of unharmony, interaction of vibrations with rotation, and so on. From this comparison it may be seen that the most substantial error is introduced into the value of heat contents. As to the error in the value of Φ *-potential, it is negligible.

Table App.1

Thermodynamic functions	Approximation of harmonic oscillator-rigid rotator	Results of more accurate calculation by Johnston and Dawson	Error in the approximation of the harmonic oscillator-rigid rotator
Φ^{*}	50,402	50,432	- 0,06%
S°	57,752	57,915	0,28%
$H^{\circ} - H^{\circ}_0$	14 700	14 966	- 1,78%

(f) Thermodynamic Functions of Polyatomic Gas

For polyatomic molecules the rotary sum of states may be roughly represented by the expression:

$$Q_{rot} = \frac{1}{\sigma}\sqrt{\frac{\pi}{ABC}\left(\frac{\kappa T}{hC}\right)^3}, \qquad \text{(App.I.64)}$$

where A,B,C are the rotational constants determinable from the spectra.

The combined formulas for calculation of thermodynamic functions in this case have the aspect of

$$\Phi^{*\circ} = 4R\ln T + \frac{3}{2}R\ln\mu - \frac{1}{2}R\ln ABC - R\ln\sigma + R\ln g_{\text{prine}} - 7{,}2304 + \Phi^{*}_{vib}; \qquad \text{(App.I.65)}$$

$$S^{\circ} = (\Phi^{*\circ} - \Phi^{*}_{vib}) + 4R + S_{vib}. \qquad \text{(App.I.66)}$$

Changing over to common logarithms, and after substitution of the numerical value of R, we obtain

$$\Phi^{*\circ} = 18{,}3024\lg T + 6{,}8634\lg\mu - 2{,}2878\lg ABC - 4{,}5756\lg\sigma + 4{,}5756\lg g_{\text{prine}} - 7{,}2304 + \Phi^{*}_{vib}; \qquad \text{(App.I.67)}$$

$$S^{\circ} = (\Phi^{*\circ} - \Phi^{*}_{vib}) + 7{,}9486 + S_{vib}; \qquad \text{(App.I.68)}$$

$$C_p = \frac{H^{\circ}_T \quad H^{\circ}_0}{T} = 4R + (S_{vib} - \Phi^{*}_{vib}) = 7{,}9486 + \frac{(H^{\circ}_T - H^{\circ}_0)_{vib}}{T} \qquad \text{(App.I.69)}$$

If A, B, and C are replaced by the respective values of the principal moments of the molecule inertia -- I_A, I_B, I_C -- then the expression for Φ *- potential will look like this

$$\Phi^{*\circ} = 18{,}3024\lg T + 6{,}8634\lg\mu + 2{,}2878\lg I_A, I_B, I_C - 4{,}5756\lg\sigma + 4{,}5756\lg g_{\text{prine}} + 257{,}3751 + \Phi^{*}_{vib}. \qquad \text{(App.I.70)}$$

The expressions (App.I.57) and (App.I.58) are valid for linear polyatomic molecules.

The values of Φ^{*}_{vib} and S_{vib} may be determined by summation of the constituents for all oscillatory degrees of freedom:

$$\Phi^{*}_{vib} = \sum_{i=1}^{\lambda} \Phi^{*(i)}_{vib} \qquad \text{(App.I.71)}$$

$$S_{vib} = \sum_{i=1}^{\lambda} S^{(i)}_{vib}, \qquad \text{(App.I.72)}$$

where $\lambda = 3n - 5$ for linear molecules, and $\lambda = 3n - 6$ for nonlinear molecules. The values of $\Phi^{*(i)}_{vib}$ and $S^{(i)}_{vib}$ may be determined for each i-th frequency from formulas

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(App.I.55) and (App.I.56) or from the tables. In summation these values for degenerated frequencies are often multiplied by the degree of degeneration.

It should be noted that for first-approximation calculations it is more common, instead of zero frequencies ω_1, to utilize the basic frequencies ν_i which are produced directly from the spectrum and are related to the zero frequencies by equation (9):

$$\nu_i = \omega_i + 2x_{ii} + \frac{1}{2}\sum_{k \neq i} x_{ik} + \dots, \qquad \text{(App.I.73)}$$

where x_{ii} and x_{ik} are the unharmony constants.

Corresponding data are very often lacking for the calculation of zero frequencies. Incidentally, the use of ν_i produces a result closer to that of precise computation, than the one which is obtained when ω_i is used, since $\nu_i < \omega_i$, a fact which compensates for the failure to consider unharmony.

Example App.3. Calculate the standard values of Φ * - potential, entropy, and the enthalpy of water vapor at 2,000° K. Molecular weight $\mu = 18.016$; the rotational constants $A_0 = 27.79$, $B_0 = 14.508$, $C_0 = 9.289$; the basic vibration frequencies $\nu_1 = 3{,}651.7$, $\nu_2 = 1{,}595.0$, $\nu_3 = 3{,}755.8$. The statistical weight of the principal electron level $g_{e\,princ} = 1$. Symmetry number $\sigma = 2$.

Substituting the numerical values of μ, A_0, B_0, C_0, σ, and $g_{e\,princ}$ in formula (App.I.67), we obtain:

$$\Phi^{*\circ} = 18{,}3024 \lg T - 8{,}1652 + \Phi^{*}_{vib}.$$

Here $\Phi^{*\circ}$ is expressed as a function of temperature. For 2,000° K

$$18.3024 \lg T = 60.4168$$

On the basis of the tables (9), we determine:

$$(\Phi^{*}_{vib})_1 = 0{,}1509, \quad (\bar{C}_{p\,vib})_1 = 0{,}4101,$$
$$(\Phi^{*}_{vib})_2 = 0{,}7635, \quad (\bar{C}_{p\,vib})_2 = 1{,}0636,$$
$$(\Phi^{*}_{vib})_3 = 0{,}1396, \quad (\bar{C}_{p\,vib})_3 = 0{,}3893.$$

In summing up we find

$$\Phi^{*}_{vib} = 1{,}0540; \quad \bar{C}_{pvib} = 1{,}8630.$$

Consequently,

$$\Phi^{*\circ} = 60{,}4168 - 8{,}1652 + 1{,}0540 = 53{,}306 \frac{\text{cal}}{\text{mole}\cdot\text{grad}}$$

$$\bar{C}_p = 7{,}9486 + 1{,}8630 = 9{,}812 \frac{\text{cal}}{\text{mole}\cdot\text{grad}}$$

$$S^\circ = 53{,}306 + 9{,}812 = 63{,}118 \frac{\text{cal}}{\text{mole}\cdot\text{grad}}$$

$$H^\circ - H^{\circ}_0 = 9{,}812\cdot 2000 = 19624 \frac{\text{cal}}{\text{mole}}$$

In Table App.2 these data are compared with the results of more accurate calculations recorded in the article by Wagman, Kilpatrick, Taylor, et al. (58). As one can also see from this comparison, in this case, too, the most considerable relative error is the one introduced into the value of the enthalpy increment. The error in $\Phi^{*\circ}$, on the other hand, is comparatively small. Let it be noted here that, had we proceeded in the calculation of oscillatory constituents not from the basic, but from zero vibration frequencies, the errors, particularly those pertaining to S° and $H^\circ - H^\circ_0$, would have been considerably higher*.

Table App.2

Thermodynamic functions	First approximation	Results of accurate calculation	Error in the First approximation
$\Phi^{*\circ}$	53,306	53,380	0,14%
S°	63,118	63,260	0,23%
$H^\circ - H^\circ_0$	19,624	19,760	0,70%

The data, recorded in the tables of Appendix IV, which should be used in calculations of combustion processes, are produced by means of computations with due con-

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* However in comparing the results of precise calculations with those of approximate computations with the view to determining the relative importance of the diverse errors (due to failure to consider unharmony, due to centrifugal extension of bonds, etc.), it is precisely the zero frequencies that should be used for approximate calculation.

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sideration of unharmony, centrifugal extension of bonds, interaction of vibration with rotation, difference in energy between the components of the principal electron level, and so on. We shall not dwell on a discussion of such calculations (see (11)). The short outline of the approximation method of calculation of thermodynamic functions provided in this book clarifies in a sufficient measure the principle of statistical computations whose understanding is important to any person wishing to use the method of explosion, calculate the temperature of combustion, or figure any other characteristics of combustion processes.

4. Calcualtion of Equilibrium Constants

From the elementary course in thermodynamics it is known that

$$RT \ln K_p = -\Delta Z^0, \qquad \text{(App.I.74)}$$

where K_p is the equilibrium constant expressed through partial pressures of initial substances and reaction products and ΔZ^0 is the difference between the standard values of the thermodynamic potential of reaction products and initial substances. From (App.I.74) we derive:

$$R \ln K_p = -\frac{\Delta Z^\circ - \Delta H_0^\circ}{T} - \frac{\Delta H_0^\circ}{T}$$

or

$$R \ln K_p = \Delta \Phi^{*\circ} - \frac{\Delta H_0^\circ}{T}, \qquad \text{(App.I.75)}$$

where $\Delta\Phi^{*0}$ is the difference between the standard values of the Φ^* potential of the reaction products and initial substances and ΔH_0^0 is the heat-contents variation (thermal effect of reaction), extrapolated to absolute zero.

From formula (V.43) (page 43), we obtain

$$\Delta H_T^\circ = \Delta H_0^\circ + \Delta (H_T^\circ - H_0^\circ).$$

Whence,

$$\Delta H_0^\circ = \Delta H_T^\circ - \Delta (H_T^\circ - H_0^\circ). \qquad \text{(App.I.76)}$$

On the basis of this formula, it is possible to calculate the value of ΔH_0^0, if the reaction thermal effect ΔH_T^0 is known at constant pressure and any temperature T. Putting (App.I.75) into a form most convenient for calculation purposes, we produce

$$\lg K_p = 0{,}21855\left(\Delta\Phi^{*0} - \frac{\Delta H_0^\circ}{T}\right). \qquad \text{(App.I.77)}$$

Let it be noted, that the inaccuracies in thermal effect determination, as a rule, affect far more the magnitude of equilibrium constant, than the inaccuracies in Φ^* - potential calculation.

Example App.4. Calculate the equilibrium constant of the dissociation reaction of CO_2 ($CO_2 \rightleftarrows CO + \frac{1}{2} O_2$) for 2,000° K on the basis of the following data*:

$$\Phi^{*\circ}_{CO_2} = 61{,}850; \qquad \Phi^{*\circ}_{CO} = 54{,}078; \qquad \Phi^{*\circ}_{O_2} = 56{,}103;$$

$$\Delta H^\circ_{298.16} = 67\,636\ \frac{\text{cal}}{\text{mole}}; \qquad (H^\circ_{298.16} - H^\circ_0)_{CO_2} = 2238\ \frac{\text{cal}}{\text{mole}}$$

$$(H^\circ_{298.16} - H^\circ_0)_{CO} = 2073\ \frac{\text{cal}}{\text{mole}}; \qquad (H^\circ_{298.16} - H^\circ)_{O_2} = 2070\ \frac{\text{cal}}{\text{mole}}$$

We have:

$$\Delta(H^\circ_{298.16} - H^\circ_0) = 2073 + \frac{1}{2}\cdot 2070 - 2238 = 870\ \frac{\text{cal}}{\text{mole}}$$

On the basis of formula (App.I.76) we obtain:

$$\Delta H^\circ_0 = 67636 - 870 = 66766\ \frac{\text{cal}}{\text{mole}}$$

Further, we have

$$\Delta\Phi^{*0} = 54{,}078 + \frac{1}{2}\cdot 56{,}103 - 61{,}850 = 20{,}280;$$

$$\Delta\Phi^{*0} - \frac{\Delta H^\circ_0}{T} = 20{,}280 - \frac{66766}{2000} = -13{,}103.$$

According to formula (App.I.77)

$$\lg K_p = 0{,}21855 \cdot 13{,}103 = -2{,}8637.$$

Finally, $K_p = 0{,}001369.$

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* We are using here the modern data (20, 58) which differ slightly from those used for the compilation of the tables recorded in Appendix IV.

Appendix II

ENTROPY CALCULATION OF THE MIXTURE OF COMBUSTION PRODUCTS AT CONSTANT PRESSURE

For the computation of certain equilibrium processes, it is important to know the entropy of the mixture of combustion products at constant pressure.

1. Direct Calculation Method

As is well known, the entropy of a mixture of ideal gases is equal to the sum of the entropies of these gases, with the assumption that each of them occupies the total volume of the mixture and behaves as if there were no other gases. Consequently, the entropy of a mixture of combustion products is

$$S_{\text{prod}} = \sum_k m_k S_k, \qquad \text{(App.II.1)}$$

where m_k is the molar concentration of the k-th combustion product in that quantity of mixture for which S_{prod} is calculated; S_k is its entropy.

The first law of thermodynamics, in application to ideal gases, may be written in the form of (24):

$$dQ = -v\,dp + C_p\,dT. \qquad \text{(App.II.2)}$$

Hence,

$$\frac{dQ}{T} = dS = -\frac{v}{T}dp + \frac{C_p}{T}dT = -R\frac{dp}{p} + C_p\frac{dT}{T}.$$

Upon integration, we produce

$$S = -R\ln p + C_p \ln T + \text{const.} \qquad \text{(App.II.3)}$$

For a given temperature T and pressure p = 1 atm

$$S^{\circ}_T = C_p \ln T + \text{const}, \qquad \text{(App.II.4)}$$

where index° signifies, as previously, the appurtenance to standard state. Comparing (App.II.4) with (App.II.3), we find that for any pressure p and given temperature T

$$S_T = S^\circ_T - R\ln p. \qquad \text{(App.II.5a)}$$

Since the magnitude of the entropy of each of the gases which constitute an equilibrium mixture of combustion products, does not depend on the presence of other gases, then, for the k-th component of the mixture at given temperature T, it may be represented by the expression:

$$S_{Tk} = S^\circ_{Tk} - R\ln p_k. \qquad \text{(App.II.5b)}$$

Substituting (App.II.5b) in (App.II.1), we obtain:

$$S_{T\text{prod}} = \sum_k m_k (S^\circ_{Tk} - R\ln p_k). \qquad \text{(App.II.6)}$$

In all other respects the derivation of the formula for entropy calculation of a mixture of combustion products does not differ from the formula (V.54) derivation for the calculation of its internal energy.

We have

$$\sum m_k \mu_k = G.$$

From (App.II.6), it follows that

$$S_{T\text{prod}} = G\,\frac{\sum\limits_k m_k (S^\circ_{Tk} - R\ln p_k)}{\sum\limits_k m_k \mu_k}.$$

Substituting in this equation the expression of molar concentration through partial pressure -

$$m_k = p_k \frac{\sum m}{P},$$

we finally produce:

$$S_{T\text{prod}} = G\,\frac{\sum\limits_k p_k (S^\circ_{Tk} - R\ln p_k)}{\sum\limits_k p_k \mu_k}. \qquad \text{(App.II.7)}$$

If S^o_{Tk} is expressed in $\frac{\text{cal}}{\text{mole}\cdot\text{deg}}$, as in Table V of Appendix IV, then R must be also expressed in the same units, and μ k must be expressed in $\frac{\text{g}}{\text{mole}}$ and G in grams (for example, 1,000g); then $S_{T\text{prod}}$ will be expressed in $\frac{\text{cal}}{\text{deg}}$.

Example App.5. Calculate for 3,000° K the entropy of 1 kg of mixture of the products of methane combustion with oxygen if $\alpha = 0.8$, $T_1 = 298.16°$ K and the pressure, $P_0 = 1$ atm, is constant.

Following the pattern outlined in Chapter VI, we determine the composition of the mixture of combustion products (see Example 3, on page 63). Further, we have

$$\sum_k p_k(S^\circ_{3000\,k} - R\ln p_k) = \sum p_k(S^\circ_{3000\,k} - 4{,}5756\lg p_k) = 67{,}27335$$

The value of $\sum_k p_k\mu_k$, which in the given case is equal to the apparent molecular weight of the mixture, was calculated by us earlier and is recorded in Table 5, Chapter VI. On the basis of formula (App.II.7) we find

$$S_{3,000\,\mathrm{prod}} = 3{,}389.3\ \frac{\mathrm{cal}}{\mathrm{kg \cdot deg}}.$$

2. Approximate Method of Calculation (16)

In calculation of the state of combustion products at constant pressure by the Zel'dovich-Polyarny approximation method, it is not the actual mixture composition that is being computed thereby, but the composition which corresponds to a pressure somewhat higher than that given. We, therefore, cannot make use of formula (App.II.7) for entropy calculation.

As we mentioned in Chapter VII, for the calculation of the state of combustion products by the Zel'dovich-Polyarny method, that state of the system is adopted as the first approximation which is attained at high pressure P_B that inhibits dissociation. Let us calculate the entropy $\overline{S}$ of the mixture of combustion products under these conditions. We have

$$p_j = P_B \frac{\overline{m}_j}{\Sigma \overline{m}}.$$

Substituting this expression in formula (App.II.6) (instead of index k we use index j), we obtain:

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$$\begin{aligned} S &= \sum_j \bar{m}_j S_j^\circ - R\sum \bar{m}_j \ln\left(P_B \frac{\bar{m}_j}{\sum \bar{m}}\right) = \\ &= \sum_j \bar{m}_j S_j^\circ - R\cdot\sum \bar{m}_j \ln P_B - R\sum \bar{m}_j \ln \bar{m}_j + R\left(\sum_j \bar{m}_j\right)\cdot \ln \sum m; \\ \bar{S} &= \sum_j \bar{m}_j (S_j^\circ - R\ln \bar{m}_j) + R\left(\sum \bar{m}\right)\ln \sum \bar{m} - R\left(\sum \bar{m}\right)\ln P_B. \end{aligned} \qquad \text{(App.II.8)}$$

At the same time, applying formula (App.II.5a) to the whole mixture, we may write

$$\bar{S} = \bar{S}^\circ - R\left(\sum \bar{m}\right)\ln P_B. \qquad \text{(App.II.9)}$$

Comparing this latter equation with (App.II.8), we find:

$$\bar{S}^\circ = \sum_j \bar{m}_j (S_j^\circ - 4{,}5756 \lg \bar{m}_j) + 4{,}5756\left(\sum \bar{m}\right)\lg \sum \bar{m} \qquad \text{(App.II.10)}$$

(S_j^o are expressed in $\frac{\text{cal}}{\text{mole}\cdot\text{deg}}$).

Such would be the entropy of a mixture of combustion products at pressure P_o = 1 atm and a composition corresponding to high pressure. The latter may be calculated by the methods described in Section 1, Chapter VII.

Let us now compute the difference between the unknown true value of entropy S_{prod} of the mixture of combustion products at given constant pressure P_o and the extreme value of $\bar{S}$, corresponding to high pressure P_B. When temperature is constant, entropy is a function of pressure:

$$S = S(P).$$

Consequently,

$$S_{prod} - \bar{S} = \int_{P_B}^{P_0} dS. \qquad \text{(App.II.11)}$$

We shall make use of the first law of thermodynamics, which this time we shall write as follows:

$$dQ = dH - V\,dP.$$

Thereupon,

$$dS = \frac{dH - V\,dP}{T}.$$

After substitution of this expression in (App.II.11), we obtain

$$S_{prod} - \bar{S} = \frac{1}{T}\left\{\int_{P_B}^{P_0} dH - \int_{P_B}^{P_0} V\,dP\right\}. \qquad \text{(App.II.12)}$$

We have

$$\int_{P_B}^{P_0} dH = H_{prod} - \bar{H}. \qquad \text{(App.II.13)}$$

Further, in taking formula (VII.59) into account and considering the definition of the quantity $\bar{V}$, as given in Section 2, Chapter VII, we have

$$V = \bar{V}(1+\zeta) = \left(\sum \bar{m}\right)\frac{RT}{P}(1+\zeta).$$

Hence,

$$\int_{P_B}^{P_0} V\,dP = \left(\sum \bar{m}\right) RT \left\{\int_{P_B}^{P_0} \frac{dP}{P} + \int_{P_B}^{P_0} \frac{\zeta}{P}\,dP\right\}. \qquad \text{(App.II.14)}$$

Furthermore,

$$\int_{P_B}^{P_0} \frac{dP}{P} = \ln\frac{P_0}{P_B} \qquad \text{(App.II.15)}$$

$$\int_{P_B}^{P_0} \frac{\zeta}{P}\,dP = \int_{\infty}^{P_0} \frac{\zeta}{P}\,dP,$$

since P_B is very considerable and ultimately equal to ∞. Yet, since according to (VII.60)

$$\zeta = BP^{-n_\zeta},$$

we have:

$$\int_{\infty}^{P_0} \frac{\zeta}{P}\,dP = \int_{\infty}^{P_0} BP^{-n_\zeta - 1}\,dP = B\left.\frac{P^{-n_\zeta}}{-n_\zeta}\right|_{\infty}^{P_0} = -\frac{BP_0^{-n_\zeta}}{n_\zeta}.$$

Thereupon,

$$\int_{P_B}^{P_0} \frac{\zeta}{P}\, dP = -\frac{\zeta}{n_\zeta}. \qquad \text{(App.II.16)}$$

After substituting (App.II.15) and (App.II.16) in (App.II.14), and then (App.II.14) and (App.II.13) in (App.II.12), we produce

$$S_{prod} - \overline{S} = \frac{H_{prod} - \overline{H}}{T} + \\ + R\left(\sum \overline{m}\right)\frac{\zeta}{n_\zeta} - R\left(\sum \overline{m}\right)\ln P_0 + R\left(\sum \overline{m}\right)\ln P_B. \qquad \text{(App.II.17)}$$

Adding up equations (App.II.17) and (App.II.9), we finally obtain

$$S_{prod} = \overline{S}^{\circ} + \frac{H_{prod} - \overline{H}}{T} + R\left(\sum \overline{m}\right)\frac{\zeta}{n_\zeta} - R\left(\sum \overline{m}\right)\ln P_0. \qquad \text{(App.II.18)}$$

where $\overline{S}^{o}$ is determined by formula (App.II.10). Here R must be expressed in $\frac{\text{cal}}{\text{mole}\cdot\text{deg}}$, $H_{prod} - \overline{H}$ in $\frac{\text{cal}}{\text{mole}}$, so as to produce S_{prod} in $\frac{\text{cal}}{\text{mole}\cdot\text{deg}}$.

Example App.6. We shall solve the problem formulated in Example App.5 by the Zel'dovich-Polyarny approximation method, while using the results of calculations recorded previously in Example 5, Chapter VII (page 84).

We have:

$$4{,}5756\left(\sum \overline{m}\right)\lg\left(\sum \overline{m}\right) = 336{,}61\ \frac{\text{cal}}{\text{Kg}\cdot\text{deg}}$$

Consequently, according to (App.II.10)

$$\overline{S}_{\tau}^{\circ} = \sum_j \overline{m}_j\left(S_{\tau j}^{\circ} - 4{,}5756\lg \overline{m}_j\right) - 336{,}61.$$

On the basis of this formula, the values of $\overline{m}_j$ recorded in Table 10 of Example 5, and the standard values of entropy S_j^o of the components, we calculate:

$$\overline{S}_{3000}^{\circ} = 3128{,}16.$$

Further we have

$$\frac{(H_{prod} - \overline{H})_{3000}}{3000} = \frac{720520}{3000} = 240{,}17;$$

$$\frac{R\Sigma\overline{m}}{n_\zeta} = 177{,}211;$$

$$\frac{R\Sigma\overline{m}}{n_\zeta}\zeta_{3000} = 177{,}211 \cdot 0{,}1289 = 22{,}84.$$

[redacted]

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Since $P_o = 1$

$$R(\sum \overline{m}) \ln P_0 = 0.$$

Finally, from formula (App.II.18), we find

$$S_{3,000 prod} = 3,391.2 \ \frac{cal}{kg \cdot deg} \ .$$

Earlier, by direct method, we obtained the value of 3,389.3 $\frac{cal}{kg \cdot deg}$. Such agreement is quite satisfactory for the majority of practical purposes.

Appendix III

METHOD OF RAPID COMPUTATION OF SQUARE ROOTS ON THE BASIS OF THEIR APPROXIMATE VALUES WITH THE HELP OF THE CALCULATING MACHINE

In dealing with extensive systematic calculations requiring a considerable precision, such as, for instance, computations of partial pressures, calculating machines are often used. If the extraction of a square root with a precision of up to 5-7 significant digits constitutes a frequently repeated operation, then its performance by the method known from elementary arithmetic or with the aid of logarithmic tables turns into a tedious procedure. In these cases, the fastest, most convenient method which guarantees against accidental errors is the following.

Supposing a square root is to be extracted from a number q; let

$$\sqrt{q} = a + h. \tag{App.III.1}$$

where

$$|h| \ll a. \tag{App.III.2}$$

We have

$$q = a^2 + 2ah + h^2. \tag{App.III.3}$$

In view of condition (App.III.2), we may disregard the quantity h^2:

$$q \approx a(a + 2h). \tag{App.III.4}$$

If the approximate value of the square root (first approximation) is known, the following procedure may be followed in order to determine it more precisely.

We set up the number a by means of the machine digits; then we square it in such a manner that on the left-hand carriage-scale, to the right of a, there remain a few free squares, depending on the accuracy with which the square roots are to be

[redacted]

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extracted. Thereafter, the machine handle should be turned until there appears a figure $(q + \delta)$ on the right-hand scale, which should be as close as possible to q. The number which will appear thereby on the left-hand scale would be approximately equal to a + 2h. Let us assume that it is precisely equal to $a + 2\bar{h}$, i.e.,

$$q + \delta = a(a + 2\bar{h}), \qquad \text{(App.III.5)}$$

where, it is evident, $\bar{h} \approx h$. The quantity δ is the smaller, the greater is the number of figures contained in a and $a + 2\bar{h}$.

Subtracting a from $a + 2\bar{h}$, an operation which may easily be made mentally*, and adding to a one-half of the resulting difference from its sign, we produce $a + \bar{h}$, i.e., the second approximation of $\sqrt{q}$.

The whole operation lasts hardly any longer than an ordinary multiplication of two numbers on a calculating machine.

Let us evaluate the error of the second approximation.

From equations (App.III.3) and (App.III.5) it follows that

$$2a\bar{h} = 2ah + h^2 + \delta. \qquad \text{(App.III.6)}$$

whence

$$h = h + \frac{h^2}{2a} + \frac{\delta}{2a}. \qquad \text{(App.III.7)}$$

Thus, the determined $a + \bar{h}$ value of the square root differs from its precise $a + h$ value by quantity $\frac{h^2}{2a} + \frac{\delta}{2a}$. The latter is the smaller, the smaller are h and δ as compared with a. If $h^2 \gg \delta$, quantity $\frac{\delta}{2a}$ may be disregarded in comparison with $\frac{h^2}{2a}$. In this case the error of the second approximation is $\frac{2a}{h}$ times smaller than the error of the first approximation. For example, if h = 0.01a, the error of the second approximation is 200 times smaller than the error of the first approximation.

The approximate a value of the square root may be obtained with the help of

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* It is possible to produce the number $2\bar{h}$ right on the left-hand scale, if it is cancelled after the squaring of a.

square root tables* or a slide rule. Incidentally, it suffices to know the squares of numbers up to 20, in order to be able, without resorting to anything with the exception of a computer, to produce in two moves the value of the square root with the maximum precision characteristic for the machine in use.

Example. Extract the square root with a precision of up to seven significant digits of the number q = 35314.98. From the tables* we find a = 187.9. By means of the calculating machine we square a and continue to rotate the computer handle while selecting a number as close as possible to q. In this case this turns out to be 35314.97824. At the same time the number 187.9456 will appear on the left-hand scale of the machine. Hence, $2\bar{h} = 0.0456$ and $\bar{h} = 0.0228$. Consequently, $\sqrt{q} \approx a + \bar{h} =$ 187.9228.

Check: $187.9228^2 = 35314.97875984$.

By an extra turn of the handle in squaring 187.9228, it is possible to gain assurance that the determined square root value is correct up to one unit in the last figure.

The same result may be produced by means of two successive operations, if -- in the absence of square-root tables or a slide rule -- a = 190 is adopted as the first approximation. In this case $a(a+2\bar{h}) = 35314.996$ (i.e., $\delta = 0.016$); $a+2\bar{h} = 190 - 4.1316$; whence, $\bar{h} = -2.0658$ (thus $\bar{h}^2 \gg \delta$) and $a + \bar{h} = 187.9342$, while

$$\frac{h^2}{2a} \approx \frac{\bar{h}^2}{2a} \approx \frac{4}{380} \approx 0{,}01.$$

We can see from this that in the given case the second approximation produces the square root value with precision up to the first decimal place: 187.9. The third approximation will be obtained in assuming a = 187.9. It produces, as shown above, the value of 187.9228.

The error of the second approximation with precision up to the fourth digit after the period comprises 187.9342 - 187.9228 = 0.0114. At the same time the error of the first approximation of h = 187.9228 - 190 = -2.0772. Hence

$$\frac{h^2}{2a} + \frac{\delta}{2a} = \frac{4{,}31176}{380} + \frac{0{,}016}{380} = 0{,}01135 + 0{,}00004 = 0{,}0114.$$

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* See, for example, Spravochnik po Matematike (Handbook of Mathematics) by I. N. Bronstein and K. A. Semendyayev.

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Appendix IV

INITIAL DATA FOR THERMODYNAMIC COMPUTATIONS

Table 1

Certain Functions of Temperature (12)

T (°K)	$\frac{5}{2} R \ln T$	$\frac{7}{2} R \ln T$	$4R \ln T$
298,16	28,3052	39,6273	45,2884
300	28,3358	39,6701	45,3372
400	29,7650	41,6710	47,6239
500	30,8735	43,2229	49,3976
600	31,7793	44,4910	50,8468
800	33,2084	46,4918	53,1335
1000	34,3170	48,0438	54,9072
1200	35,2227	49,3118	56,3564
1400	35,9886	50,3840	57,5817
1500	36,3313	50,8638	58,1301
1600	36,6519	51,3127	58,6431
1800	37,2370	52,1318	59,5793
2000	37,7605	52,8647	60,4168
2200	38,2339	53,5275	61,1743
2400	38,6662	54,1327	61,8660
2600	39,0638	54,6891	62,5021
2800	39,4321	55,2049	63,0913
3000	39,7748	55,6847	63,6396
3200	40,0954	56,1336	64,1527
3400	40,3966	56,5552	64,6346
3600	40,6805	56,9527	65,0888
3800	40,9191	57,3287	65,5186
4000	41,2040	57,6856	65,9263
4200	41,4464	58,0249	66,3142
4400	41,6774	58,3484	66,6839
4600	41,8983	58,6576	67,0373
4800	42,1097	58,9536	67,3755
5000	42,3125	59,2375	67,7000

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Table II

Common Logarithms of Chemical Equilibrium Constants K_p (p_i in atm)

T(°K)	$\lg K_1 = \lg \frac{p_{CO}\sqrt{p_{O_2}}}{p_{CO_2}}$	$\lg K_2 = \lg \frac{p_{H_2}\sqrt{p_{O_2}}}{p_{H_2O}}$	$\lg K_3 = \lg \frac{p_{OH}\sqrt{p_{H_2}}}{p_{H_2O}}$	$\lg K_4 = \lg \frac{p_H^2}{p_{H_2}}$	$\lg K_5 = \lg \frac{p_O^2}{p_{O_2}}$	$\lg K_6 = \lg \frac{p_{CO_2} \cdot p_{H_2}}{p_{CO} \cdot p_{H_2O}}$	$\lg K_7 = \lg \frac{p_{H_2}^2 \cdot p_{O_2}}{p_{H_2O}^2}$	$\lg K_8 = \lg \frac{p_H}{\sqrt{p_{H_2}}}$	$\lg K_9 = \lg \frac{p_{H_2} \cdot p_O}{p_{H_2O}}$	$\lg K_{10} = \lg \frac{p_{OH}}{\sqrt{p_{H_2O}}\sqrt[4]{p_{O_2}}}$	$\lg K_{11} = \lg \frac{p_H\sqrt[4]{p_{O_2}}}{\sqrt{p_{H_2O}}}$	$\lg K_{12} = \lg \frac{p_O}{\sqrt{p_{O_2}}}$	$\lg K_{13} = \lg \frac{p_{NO}}{\sqrt{p_{N_2}}\sqrt{p_{O_2}}}$	$\lg K_{14} = \lg \frac{p_N}{\sqrt{p_{N_2}}}$	$\lg K_{15} = \lg \frac{p_{NO} \cdot p_{H_2}}{p_{H_2O}\sqrt{p_{N_2}}}$
300	—44,72	—39,77	—43,3	—70,23	—80,20	+4,947	—79,54	—35,115	—79,87	—23,415	—55,0	—40,1	—15,04	—59,05	—54,81
400	—32,43	—29,26	—31,7	—51,35	—58,60	+3,167	—58,52	—25,675	—58,56	—17,070	—40,305	—29,3	—11,13	—43,45	—40,39
600	—20,07	—18,64	—20,0	—32,41	—36,90	+1,433	—37,28	—16,205	—37,09	—10,68	—25,525	—18,45	— 7,194	—27,9	—25,834
800	—13,89	—13,28	—14,07	—22,88	—26,10	+0,610	—26,56	—11,44	—26,33	— 7,430	—18,08	—13,05	— 5,231	—20,1	—18,511
1000	—10,20	—10,05	—10,53	—17,13	—19,48	+0,147	—20,10	— 8,565	—19,79	— 5,505	—13,590	— 9,74	— 4,052	—15,45	—14,102
1200	— 7,755	— 7,90	— 8,17	—13,28	—15,10	—0,145	—15,80	— 6,64	—15,45	— 4,22	—10,59	— 7,55	— 3,267	—12,3	—11,167
1400	— 5,999	— 6,34	— 6,47	—10,51	—11,97	—0,341	—12,68	— 5,255	—12,325	— 3,30	— 8,425	— 5,985	— 2,706	—10,05	— 9,046
1600	— 4,715	— 5,20	— 5,20	— 8,429	— 9,610	—0,485	—10,40	— 4,214	—10,005	— 2,60	— 6,814	— 4,805	— 2,285	— 8,4	— 7,485
1800	— 3,690	— 4,27	— 4,19	— 6,803	— 7,772	-0,580	— 8,54	— 3,4015	— 8,156	— 2,055	— 5,5365	— 3,886	— 1,959	— 7,0	— 6,229
2000	— 2,862	— 3,52	— 3,40	— 5,496	— 6,298	-0,658	7,01	— 2,748	— 6,669	— 1,64	— 4,508	— 3,149	— 1,695	— 6,0	— 5,215
2200	— 2,193	— 2,91	— 2,74	— 4,424	— 5,091	—0,717	5,82	2,212	— 5,456	— 1,285	— 3,667	— 2,546	— 1,479	— 5,15	— 4,389
2400	— 1,648	— 2,11	— 2,19	— 3,529	— 4,078	—0,762	— 4,82	1,7645	— 4,449	— 0,985	— 2,9695	— 2,039	— 1,300	— 4,415	— 3,710
2600	— 1,206	— 2,00	— 1,74	— 2,769	— 3,228	—0,791	— 4,00	— 1,3845	— 3,614	— 0,74	— 2,3845	— 1,614	— 1,150	— 3,80	— 3,150
2800	— 0,811	— 1,63	— 1,31	— 2,115	— 2,495	—0,819	— 3,26	— 1,0575	— 2,8775	— 0,525	— 1,8725	— 1,2475	— 1,019	— 3,28	— 2,649
3000	— 0,470	— 1,31	— 0,999	— 1,548	— 1,858	—0,810	— 2,62	— 0,774	— 2,239	— 0,344	— 1,4290	— 0,929	— 0,907	— 2,825	— 2,217
3200	— 0,168	— 1,011	— 0,700	— 1,051	— 1,290	—0,873	— 2,082	— 0,5255	— 1,686	— 0,1795	— 1,046	— 0,645	— 0,807	— 2,429	— 1,848
3400	+ 0,097	— 0,805	— 0,137	— 0,611	— 0,806	- 0,902	— 1,610	— 0,3055	— 1,208	— 0,0345	— 0,708	— 0,403	— 0,723	— 2,077	— 1,528
3600	+ 0,339	— 0,596	— 0,201	— 0,226	— 0,367	-0,935	— 1,192	— 0,113	— 0,7795	+ 0,094	— 0,411	— 0,1835	— 0,644	— 1,764	— 1,240
3800	+ 0,512	— 0,410	+ 0,001	+ 0,132	+ 0,026	- 0,952	— 0,820	+ 0,066	— 0,397	+ 0,209	— 0,139	+ 0,013	— 0,575	— 1,483	— 0,985
4000	+ 0,728	- 0,212	+ 0,190	+ 0,449	+ 0,379	0,970	- 0,484	+ 0,2245	— 0,0525	+ 0,311	+ 0,1035	+ 0,1895	— 0,513	— 1,230	— 0,755

Note to Table II

The values of $\lg K_1 \div \lg K_3$ and $\lg K_6 - K_{15}$ over the interval 300 - 3,000° K are taken from the monograph by Zel'dovich and Polyarny (16). These authors, in turn, have partly borrowed them from the summary by Lewis and Elbe (21) and partly calculated them by the method outlined in Section 1, Chapter V. The values of $\lg K_4$, $\lg K_5$, and $\lg K_{13}$ over the 300-4,000 ° K range and the values of $\lg K_1 \div \lg K_3$ in the interval of 3,200-4,000° K are taken from the book by A. P. Vanichev (2). On the basis of these data, with the help of formulas (V.20) and (V.35), calculations were made of the remaining constants (with the exception of K_{14}) for 3,200-4,000° K. The values of $\lg K_{14}$ over the 3,200-4,000° K range were computed on the basis of $\Delta \Phi^{*o}$, recorded in the article by Giauque and Clayton (39). The thermodynamic functions and thermodynamic data, on the basis of which calculations were made of the equilibrium constants recorded here, have recently suffered certain changes. This was reflected in particular, in the new list of chemical equilibrium constants provided in the second edition of the book by Lewis and Elbe (49) (see also (42)). In spite of the existence of these new data, we deemed it methodically more advisable to append hereto a list of those equilibrium constants, enthalpies, and entropies, which we have used in calculations of the greater part of the examples incorporated in this book. This was done expecially because these old data differ but little from the new ones. The most considerable difference came as a result of the fact that the majority of investigators prefer nowadays to use the higher values of the heat of OH formation than that of $(\Delta H_0^o)_{\text{form OH}}$ determined by Lewis and Elbe and utilized in the summary recorded herein.

In particular, in the works (49, 42), referred to above, use was made of the value produced by Dwyer and Oldenberg (33) to which corresponds that of $\Delta H_{03}^o = 67.107 \frac{\text{kcal}}{\text{mole}}$. Gaydon, in the recently published second revised edition of his book <u>Energii dissotsiatsii i spektry dvukhatomnykh molekul</u> (Dissociation Energies and Spectra of Diatomic Molecules), recommends the value of 4.45 eV for D_o (OH) which corresponds to $\Delta H_{03}^o = 64.7 \frac{\text{kcal}}{\text{mole}}$.

Table III

Constants of Chemical Equilibrium K_p (p_i in atm)

T (°K)	$K' = \frac{p_{CO}\sqrt{p_{O_2}}}{p_{CO_2}}$	$K'_2 = \frac{p_{H_2}\sqrt{p_{O_2}}}{p_{H_2O}}$	$K' = \frac{p_{OH}\sqrt{p_{H_2}}}{p_{H_2O}}$	$K'_4 = \frac{p_H^2}{p_{H_2}}$	$K'_5 = \frac{p_O^2}{p_{O_2}}$	$K'_6 = \frac{p_{CO_2}\cdot p_{H_2}}{p_{CO}\cdot p_{H_2O}}$	$K'_7 = \frac{p_{H_2}^2\cdot p_{O_2}}{p_{H_2O}^2}$	$K'_8 = \frac{p_H}{\sqrt{p_{H_2}}}$	$K'_9 = \frac{p_{H_2}\cdot p_O}{p_{H_2O}}$	$K' = \frac{p_{OH}}{\sqrt{p_{H_2O}}\sqrt[4]{p_{O_2}}}$	$K'_{11} = \frac{p_H\sqrt[4]{p_{O_2}}}{\sqrt{p_{H_2O}}}$	$K'_{12} = \frac{p_O}{\sqrt{p_{O_2}}}$	$K'_{13} = \frac{p_{NO}}{\sqrt{p_{N_2}}\sqrt{p_{O_2}}}$	$K'_{14} = \frac{p_N}{\sqrt{p_{N_2}}}$	$K'_{15} = \frac{p_{NO}\cdot p_{H_2}}{p_{H_2O}\sqrt{p_{N_2}}}$
300						88520,0									
400						1469,0									
600						27,10									
800						4,074							0,000006		
1000						1,403				0,000003			0,000089		
1200						0,7162				0,000060			0,000541		
1400	0,000001					0,4560		0,000006		0,000501		0,000001	0,001968		
1600	0,000019	0,000006	0,000006			0,3273		0,000061		0,002512		0,000016	0,005188		
1800	0,000201	0,000054	0,000065			0,2630		0,000397		0,008811	0,000003	0,000130	0,01099		
2000	0,001375	0,000302	0,000398	0,000003		0,2198		0,001787		0,02291	0,000031	0,000710	0,02018		0,000006
2200	0,006413	0,001231	0,001820	0,000038	0,000008	0,1919	0,000002	0,006138	0,000001	0,05188	0,000215	0,002845	0,03319	0,000007	0,000041
2400	0,02250	0,003891	0,006157	0,000296	0,000084	0,1730	0,000015	0,01720	0,000036	0,1036	0,001073	0,009142	0,05012	0,000038	0,000195
2600	0,06223	0,01000	0,01820	0,001702	0,000592	0,1607	0,0001	0,04126	0,000243	0,1820	0,00426	0,02133	0,07080	0,000158	0,000708
2800	0,1546	0,02315	0,01571	0,007674	0,003199	0,1517	0,00055	0,08760	0,001326	0,2986	0,01341	0,05656	0,09572	0,000525	0,002244
3000	0,3389	0,01898	0,1003	0,02831	0,01387	0,1415	0,002399	0,1683	0,005768	0,4529	0,03724	0,1178	0,1239	0,001497	0,006068
3200	0,6792	0,09099	0,1995	0,08892	0,05129	0,1310	0,008279	0,2982	0,02061	0,6615	0,08995	0,2265	0,1560	0,003724	0,01419
3400	1,250	0,1567	0,3656	0,2449	0,1563	0,1253	0,02455	0,4949	0,06194	0,9237	0,1959	0,3951	0,1892	0,008375	0,02965
3600	2,183	0,2535	0,6252	0,5913	0,4295	0,1161	0,06127	0,7709	0,1662	1,242	0,3882	0,6551	0,2270	0,01722	0,05754
3800	3,483	0,3890	1,009	1,355	1,062	0,1117	0,1514	1,164	0,4009	1,618	0,7261	1,030	0,2661	0,03289	0,1035
4000	5,346	0,5728	1,549	2,812	2,393	0,1072	0,3281	1,677	0,8861	2,016	1,269	1,517	0,3069	0,05888	0,1758

The least reliable of all is the value of lg K_{14}, since the magnitude of the energy of N_2 dissociation has not yet been unambiguously established. The values of lg K_{14} recorded here are calculated in the assumption that $D_0(N_2) = 169.220 \frac{\text{Kcal}}{\text{mole}}$. According to a different interpretation of the N_2 spectrum, the value for $D_0(N_2)$ amounts to 225 Kcal/mole. Fortunately, both these values are so high (K_{14} being so small), that the selection of the one or the other of them will hardly at all affect the calculations of combustion characteristics.

The values of the logarithms of equilibrium constants for any temperature over the 300-4,000° K range may be obtained with the aid of Table II and the interpolation function of type lg K_p = const. $\frac{1}{T}$. The same function may be used for not too far-reaching extrapolation.

Table IV

Enthalpies of Gases H^{o} $(\frac{\text{Kcal}}{\text{mole}})$

T(°K) \ Gas	H_2	H	H_2O	OH	O	O_2	CO	CO_2	N_2	NO	N	$\frac{5}{2}RT$
0	57,113	79,797	0	34,444	58,68	0	66,760	0	0	21,400	84,61	0
300	59,149	81,286	2,387	36,563	60,170	2,082	68,845	2,256	2,085	23,612	86,100	1,490
400	59,843	81,783	3,203	37,272	60,666	2,792	69,543	3,197	2,781	24,326	86,596	1,986
600	61,241	82,776	4,879	38,681	61,659	4,280	70,969	5,327	4,198	25,788	87,589	2,979
800	62,649	83,769	6,662	40,102	62,652	5,851	72,459	7,696	5,667	27,321	88,582	3,972
1000	64,077	84,762	8,563	41,548	63,645	7,497	74,016	10,233	7,202	28,920	89,575	4,965
1200	65,540	85,755	10,583	43,027	64,638	9,185	75,628	12,886	8,793	30,569	90,568	5,958
1400	67,044	86,748	12,700	41,564	65,631	10,903	77,281	15,624	10,426	32,254	91,561	6,951
1600	68,584	87,741	14,918	46,147	66,624	12,654	78,963	18,424	12,093	33,967	92,554	7,944
1800	70,166	88,734	17,230	47,759	67,617	14,427	80,669	21,273	13,782	35,699	93,547	8,937
2000	71,785	89,727	19,622	49,401	68,610	16,220	82,397	21,159	15,500	37,447	94,540	9,930
2200	73,436	90,720	22,069	51,068	69,603	18,036	84,140	27,072	17,226	39,208	95,533	10,923
2400	75,113	91,713	24,566	52,775	70,596	19,876	85,891	30,014	18,966	40,980	96,526	11,916
2600	76,822	92,706	27,109	54,498	71,589	21,734	87,649	32,983	20,714	42,761	97,519	12,909
2800	78,555	93,699	29,686	56,240	72,582	23,610	89,417	35,967	22,475	44,549	98,512	13,902
3000	80,302	94,692	32,288	58,009	73,575	25,502	91,194	38,970	24,245	46,343	99,505	14,895
3200	82,06	95,68	34,91	59,80	74,58	27,41	92,97	42,00	26,02	48,11	100,50	15,888
3400	83,83	96,68	37,55	61,60	75,57	29,33	94,75	15,01	27,80	49,94	101,49	16,880
3600	85,60	97,67	40,19	63,43	76,56	31,27	96,52	48,04	29,58	51,75	102,48	17,874
3800	87,37	98,66	42,83	65,27	77,55	33,22	98,29	51,08	31,38	53,56	103,48	18,867
4000	89,13	99,66	45,47	67,11	78,54	35,18	100,40	51,12	33,18	55,38	101,47	19,860

Note to Table IV

The enthalpy values over the interval from 0 to 3,000° K were taken from the monograph by Zel'dovich and Polyarny (16), who calculated them for H_2, H_2O, OH, O_2, CO, CO_2, N_2, and NO, while utilizing the summary prepared by Lewis and Elbe (21). The enthalpies for the 3,200-4,000° K interval were computed by the method described in Section 2, Chapter V, on the basis of the data recorded in Vanichev's book (2).

The enthalpies of monatomic gases H, O, and N, borrowed from Zel'dovich and Polyarny (16) and from Vanichev (2), were calculated without consideration of the electron constituent. The reader may define them more precisely by independent calculation on the basis of formulas (App.I.32) and (App.I.37a). The value H° of monatomic nitrogen cannot be vouched for, for the same reason for which we cannot vouch for the certainty of K_{14}. The values of enthalpies for any temperature T over the interval 300-4,000° K may be calculated on the basis of the data in Table IV with the aid of interpolation function (V.59) or by means of a function of the type of (51):

$$H^{\circ}_T = aT + bT^2 + cT^{-1} + d. \qquad \text{(App.IV.1)}$$

In a way similar to that described in Chapter V, it may be shown that

$$c = -\Delta^3 H_1 \frac{(T_1 + 3\Delta T)(T_1 + 2\Delta T)(T_1 + \Delta T) T_1}{6(\Delta T)^3} \qquad \text{(App.IV.2)}$$

$$b = \frac{\Delta^2 H_1}{2(\Delta T^2)} - \frac{c}{(T_1 + 2\Delta T)(T_1 + \Delta T) T_1} \qquad \text{(App.IV.3)}$$

$$a = \frac{\Delta H_1}{\Delta T} - (2T_1 + \Delta T) b + \frac{c}{(T_1 + \Delta T) T_1}; \qquad \text{(App.IV.4)}$$

$$d = H_1 - aT_1 - bT_1^2 - \frac{c}{T_1}. \qquad \text{(App.IV.5)}$$

The same function may be also used for extrapolation.

Table V

Standard Entropies of Gases S^0 $\left(\frac{cal}{mole \cdot deg}\right)$

T (°K) \ Gas	H_2	H	H_2O	OH	O	O_2	CO	CO_2	N_2	NO	N
300	31,27	27,45	45,15	43,97	38,51	49,06	47,36	51,14	45,83	52,24	36,65
400	33,27	28,90	47,47	46,01	40,01	51,12	49,37	53,84	47,83	54,29	38,08
600	36,10	30,89	50,86	48,85	42,15	54,12	52,25	58,17	50,70	57,22	40,09
800	38,12	32,32	53,44	50,89	43,43	56,38	54,40	61,55	52,82	59,12	41,52
1000	39,72	33,44	55,54	52,51	44,72	58,21	56,13	64,37	54,53	61,21	42,63
1200	41,05	34,34	57,38	54,06	45,64	59,74	57,60	66,80	55,97	62,71	43,54
1400	42,20	35,10	59,02	55,40	46,40	61,05	58,88	68,86	57,23	64,01	44,30
1600	43,23	35,77	60,49	56,26	47,10	62,25	59,98	70,73	58,33	65,16	44,97
1800	44,17	36,36	61,86	57,05	47,70	63,30	61,00	72,42	59,34	66,19	45,55
2000	45,03	36,89	63,13	57,92	48,23	64,20	61,92	73,95	60,21	67,12	46,08
2200	45,79	37,35	64,31	58,71	48,71	65,04	62,71	75,32	61,07	67,94	46,55
2400	46,53	37,78	65,38	59,45	49,18	65,82	63,50	76,60	61,83	68,72	46,98
2600	47,22	38,18	66,39	60,14	49,55	66,56	64,22	77,80	62,53	69,44	47,38
2800	47,87	38,56	67,35	60,78	49,93	67,22	64,88	78,91	63,18	70,10	47,75
3000	48,47	38,90	68,25	61,37	50,28	67,85	65,48	79,94	63,79	70,72	48,09
3200	49,04	39,22	69,09	61,94	50,64	68,44	66,06	80,93	64,37	71,30	48,41
3400	49,58	39,52	69,89	62,49	50,94	68,99	66,60	81,84	64,91	71,85	48,71
3600	50,09	39,80	70,63	63,00	51,22	69,51	67,11	82,66	65,41	72,35	49,00
3800	50,57	40,07	71,35	63,50	51,49	70,01	67,58	83,46	65,87	72,83	49,27
4000	51,05	40,32	72,04	63,99	51,76	70,50	68,02	84,19	66,36	73,28	49,52

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Note to Table V

The monatomic nitrogen entropies are calculated on the basis of formula $S^o = \Phi^{*o} + \frac{5}{2}R$ and the values of Φ^*-potential recorded in the article by Giauque and Clayton (39). Consequently, no account was taken of the derivative in Q_e with respect to T.

The entropies of other gases are borrowed from A. P. Vanichev's book (2).

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