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Translation

CHEMICAL THERMODYNAMICS OF COMBUSTION AND EXPLOSION

By

B.N. Kondrikov

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CHEMICAL THERMODYNAMICS OF COMBUSTION AND EXPLOSION

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ANNOTATION

This training manual examines, on the basis of Soviet and foreign literature, the fundamental problems associated with the chemical thermodynamics of combustion and explosion--energy release, the composition of combustion products and the thermodynamic characteristics of fuels and the products of their chemical conversion. It provides simple methods for calculating thermodynamic variables required for assessment of the effectiveness of explosion processes, the danger of spontaneous combustion or explosion and the quantity of toxic products formed by combustion and detonation. Special attention is devoted to the state equation for the initial substances and explosion products at high temperature (thousands of degrees--and ultrahigh pressure--hundreds of thousands of atmospheres).

FOREWORD

The principal unique feature of combustion processes--that which predetermines their technical applications and the danger of spontaneous fires and explosions--is the release of a significant quantity of energy. Hence follows, in particular, the primary significance of the thermodynamic aspects in the study of these processes. At present, however, there are no training manuals which might examine the theoretical problems of combustion and explosion thermodynamics and the methods of calculating the principal thermodynamic variables from the standpoint of the requirements of institutions of higher education specializing in chemical technology. Some books dealing with these problems, for example the remarkable textbook written by Andreyev and Belyayev (1), have long been a bibliographic rarity while others are too voluminous and difficult or fail to satisfy our instruction programs.

The purpose of this training manual is to correct this situation. In addition to examining the commonplace thermodynamic relationships and simple calculation methods, it devotes significant attention to one of the most important problems of the theory of explosive transformation--the state equation for matter at high pressure--tens and hundreds of thousands of atmospheres. In the final analysis the objective is to make it possible for every process engineer to calculate the composition and other characteristics of the products of chemical reactions occurring at high temperature and ultrahigh pressure, something which is now within the means of only a few specialists having access to expensive computer technology (2). Some particular paths of solving this problem are already known, and they are described in this book. We will probably not have to wait long at all for someone to arrive at a general solution similar to that reached for combustion processes at moderate pressure (3,4). Perhaps some of the students for whom this guide is intended will themselves be able to take part in reaching this solution.

1. Concentration. Stoichiometric Relationships

In physics, the principal characteristic describing the concentration of a substance in a given point in space is density ρ (kg/m^3). The reciprocal, $V=1/\rho$, is called the specific volume. If the substance is an individual chemical compound, the product V_iM_i (m^3/mole) is its molar volume. Here, $V_i=1/\rho_i$ is specific volume and M_i is the molecular weight of substance i (kg/mole).

In chemistry. concentration C is usually given as the number of particles (molecules, atoms, radicals, ions) per unit volume ($1/m^3$, moles/m^3, moles/liter). There are other ways of expressing concentration involving simple relationships of ρ, V and C:*

Proportion of substance in mixture by weight (kg_i/kg)	$g_i = C_i M_i V = \frac{C_i M_i}{\rho}$	(I.I.)
Molar proportion ($moles_i/mole$)	$\alpha_{M_i} = \frac{C_i}{\Sigma C_i} = \frac{g_i M}{M_i}$	(I.2.)
Proportion by volume (m^3_i/m)	$\alpha_{V_i} = \frac{C_i M_i V_i}{\Sigma C_i M_i V_i} = \frac{g_i V_i}{\Sigma g_i V_i}$	(I.3.)
Number of moles of the substance per kg of mixture ($moles_i/kg$)	$n_i = C_i V = \frac{g_i}{M_i}$	(I.4.)

Here, $M = 1/\Sigma(g_i/M_i) = \rho/\Sigma C_i$ is the mean molecular weight of the mixture (kg/mole). Symbol Σ means summation in relation to all of the components of the mixture, or in relation to a certain group of the components, for example just the gaseous products. Thus when we compute the composition of combustion products we use

$$N_O = \sum_{\text{gas}} N_i \tag{1.5}$$

where summation is performed only in relation to the gaseous components of the mixture.

If when the components are mixed together they do not interact in such a way to cause a change in volume, then

$$V = \Sigma g_i V_i \ , \ \rho = \Sigma \alpha_{V_i} \rho_i \ ; \alpha_{V_i} = C_i M V_i = \frac{g_i V_i}{V} \quad \text{(I.6.)}$$

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*A convenient way to check the correctness of formulas (1.1)-(1.4), or formulas similar to them, is to consider the units of measurement pertaining to a given component of a mixture of substances. Following reductions, the units of measurement must be in the right combination. For example for formula (1.1), $[g_i] = kg_i/kg = [M_i C_i V] = kg_i \cdot moles_i \cdot m^3/moles_i \cdot m^3 \cdot kg$. It should be considered that in formula (1.4), $\Sigma \frac{M^3_i}{M^3} \overset{(1.4.)}{=} \frac{\Sigma M^3_i}{M^3} = \frac{M^3}{M^3}$. It stands to reason that following such verification, the units of measurement should be reduced to their conventional form.

Relationships (1.6) are always satisfied for mixtures of ideal gases. It would not be difficult to note that the sums Σg_i, $\Sigma \alpha_{M_i}$ and $\Sigma \alpha_{V_i}$ in relation to all components of the mixture are equal to unity. Obviously g and α may also be expressed as percents.

When we use the theory of combustion and explosion to solve thermochemical problems, first we usually determine the elementary (elemental) composition of the mixture. In this case the concentration of element $n_Э$ is determined in moles/kg by the formula:

$$n_{Э_j} = \Sigma Э_j \frac{g_j}{M_j} = \Sigma Э_j n_j \qquad (1.7.)$$

where $Э_j$ is the number of atoms of the given element in the molecule of compound j ($Э$ = C, O, H, N etc., moles/mole). Summation is performed in relation to all components of the mixture. The variable $g_j/M_j = n_j$ represents the number of moles of the given compound per kg of the mixture. On calculating the amount of all [symbol omitted; possibly $n_Э$] elements of which the mixture consists, we get the "empirical formula" for the mixture:

$$C_{n_C}O_{n_{(i)}}H_{n_H}\ldots;$$

the molecular weight of which is 1 kg.

Most systems capable of combustion and explosion contain a fuel and oxygen. The ratio between these ingredients is an important characteristic of the system. Several ways of expressing this ratio are commonly employed in engineering.

In the case of secondary explosives, the best suited variable is the oxygen balance ($K\delta$), expressed as a percent by weight. It is the difference between the quantity of oxygen contained in the system and the quantity necessary for complete combustion--that is, for transformation of all carbon into CO_2, all hydrogen into H_2O, all aluminum into Al_2O_3 and so on. If halogens such as chlorine or florine are present in the system, it is believed that they interact with hydrogen to form hydrogen halides.

$$K\delta = \frac{1.6}{M}\left\{n(0) - \left[2n_C + \frac{n(H) - n_{Cl}}{2} + \frac{3}{2}n_{Al} + n_{Mg}\right]\right\} \quad (I.8)$$

Coefficient 1.6/*M* in this formula is obtained by dividing the molecular weight of oxygen (0.016 kg/mole) by the molecular weight of system *M* and multiplying it by 100 so that the result would be a percentage.

The oxygen balance of a mixture is an additive function of the oxygen balances of its components. We can easily persuade ourselves of this by summing the products $g_j K\delta$ and applying formula (1.7). The oxygen balance of the mixture would be less than zero if there is not enough oxygen in it for complete oxidation, and greater than zero if excess oxygen is present. For a system that is "balanced in relation to oxygen," $K\delta = 0$.

The coefficient of excess oxidant, α_0, is the ratio of the quantity of oxygen in the system and the quantity needed for complete combustion. For the purposes of this handbook, in our calculation of α_0 we will consider only the amount of oxygen remaining following combustion of aluminum to Al_2O_3 and *Mg* to *MgO*, and we will consider only carbon and excess hydrogen (following its interaction with halogens--chlorine and fluorine) as the combustible substances. The formula for calculating α_0 would have the form:

$$\alpha_0 = \frac{n_O - \left(\frac{3}{2}n_{Al} + n_{Mg}\right)}{2n_C + \frac{1}{2}\left(n_H - n_{Hal}\right)} \quad (I.9.)$$

When the system is "balanced in relation to oxygen," $\alpha_0 = 1$, when excess oxygen is present $\alpha_0 > 1$, and when oxygen is lacking $\alpha_0 < 1$.

We also use two derivatives of α_0:

The oxygen coefficient $A_0 = 100\ \alpha_0$
The equivalent ratio $\phi = 1/\alpha_0$

The latter is encountered especially frequently in works on combustion of gas mixtures.

2. Functions of State. Some Thermodynamic Relationships

The equilibrium state of a closed thermodynamic system, in which the effects of electric and magnetic fields are ignored, is characterized by five parameters or functions of state. These are pressure P, volume V, temperature T, ~~internal~~ intrinsic energy E and entropy S. They are related to each other by a fundamental thermodynamic relationship:

$$dE = TdS - pdV \qquad (2.I.)$$

T and P are "intensive"--that is, they do not depend on the quantity of the substance within the system. V, E and S are commonly said to be "extensive"--directly proportional to the quantity of the substance.* However, inasmuch as these variables are in all three terms of equation (2.1), this equation would also be valid if we assume V, E and S to be "intensive"--that is, if we represent them in relation to a mole or unit mass of the substance. As a rule we will henceforth use the relative values of V, E and S (in relation to 1 kg of the given substance).

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*It would be easy to memorize that p and T are "intensive" variables by using the terms "intensive heating" and "intensive pressure" (though of course the latter term is sooner political than technical).

Besides equation (2.1), which is most general in nature, to describe a system we usually use another equation of state--the functional relationship between three (or four) of the variables listed above, characterizing the given concrete substance (or mixture of substances).

To make the calculations simpler we introduce another three functions of state:

Enthalpy ("thermal function") $H = E + pv,\ dH = TdS + vdp$ (2.2)
Gibbs' energy* $G = H - TS;\ dG = -SdT + vdp$ (2.3)
Free energy** $F = E - TS;\ dF = -SdT - pdV$ (2.4)

Variables *E*, *H*, *G* and *F* are called the thermodynamic potentials: Under certain conditions (under which the appropriate potential is a characteristic function) each of them determines the maximum work of the system.

In order to fully define the thermodynamic state of a system, assuming we have the equation of state and the four fundamental relationships (2.1-2.4), we must know three of the eight parameters listed above; for the sake of definiteness they would best be in combinations which would transform thermodynamic potentials into characteristic functions: (E,V,S), (H,P,S), (G,T,P), (F,T,V). In view of the fact that under experimental conditions we are far from always able to determine precisely those functions which are needed at the given moment, and also because we must often deal not with the functions themselves but only with their derivatives, numerous relationships were obtained between functions and derivatives in the course of the development of thermodynamics. These relationships now make up the essence of the mathematical foundation of this science. Some of these relationships are given below.

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*Synonyms: free enthalpy, isobaric isothermic potential, isobaric potential.
**Isochoric-isothermic potential, isochoric potential, Helmholtz energy.

By juggling the variables in equation (2.1) we get the derivatives:

$$\left(\frac{\partial E}{\partial V}\right)_S = -p \quad \text{and} \quad \left(\frac{\partial E}{\partial S}\right)_V = T \qquad (2.5.)$$

Differentiating them once again in relation to another variable (the former in relation to V and the latter in relation to S), equating the obtained mixed second derivatives with one another and considering that $\left(\frac{\partial x}{\partial y}\right) = \left(\frac{\partial y}{\partial x}\right)^{-1}$, we get one of the Maxwell equations

$$-\left(\frac{\partial S}{\partial p}\right)_V = \left(\frac{\partial V}{\partial T}\right)_S \qquad (2.6.)$$

Performing similar operations with equations (2.2-2.4) we get another six relationships identical in form to (2.5), and then another three Maxwell equations. These equations associate the derivatives of entropy in relation to pressure and volume with the derivatives of volume and pressure in relation to temperature. We write them in general (though perhaps somewhat unusual) form:

$$-\left(\frac{\partial S}{\partial p}\right)_{\substack{V\\T}} = \left(\frac{\partial V}{\partial T}\right)_{\substack{S\\p}} \; ; \; \left(\frac{\partial S}{\partial V}\right)_{\substack{p\\T}} = \left(\frac{\partial p}{\partial T}\right)_{\substack{S\\V}} \qquad (2.7.)$$

In each of these equations there are four subscripts, which are used in pairs--either the upper or the lower ones. Considering the symmetry of the subscripts and of the variables, equations of form (2.7) are easy to memorize.

The derivatives $\left(\frac{\partial V}{\partial T}\right)_p$, $\left(\frac{\partial p}{\partial T}\right)_V$ and $\left(\frac{\partial V}{\partial p}\right)_T$ are easily measured experimentally, and they are well known for many substances. They are usually given in handbooks as the following expressions:

$\alpha_p = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$ --isobaric coefficient of expansion (2.8)

$\beta_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$ --isothermic coefficient of compression* (2.9)

$\gamma_V = \frac{1}{p}\left(\frac{\partial p}{\partial T}\right)_V$ --isochoric coefficient of pressure (2.10)

For an ideal gas, $\alpha_p = 1/T$ is the Gay-Lussak law, $\beta_T = 1/p$ is the Boyle-Marictte law and $\gamma_V = 1/T$ is Charles' law. In cases where it is difficult to measure one of the variables, its value may be obtained from the other two by means of the identity:

$$\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_p \left(\frac{\partial V}{\partial p}\right)_T = -1 \qquad (2.II)$$

For example $(\partial p/\partial T)_V = \alpha_p/\beta_T$ (2.I2)

Differentiating function $E(T,V)$, we get another two partial derivatives:

$$dE = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV \qquad (2.I3)$$

The first of them, $\left(\frac{\partial E}{\partial T}\right)_V = C_V$, is the heat capacity of a substance in a constant volume. To understand the meaning of the second, let us examine equation (2.1) at $T = \text{const}$:

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - p, \text{ or } p = T\left(\frac{\partial p}{\partial T}\right)_V - \left(\frac{\partial E}{\partial V}\right)_T \qquad (2.I4)$$

The derivative $(\partial S/\partial V)_T$ is substituted in the second relationship by $(\partial P/\partial T)_V$ in correspondence with Maxwell's equation (2.7).

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*The reciprocal, $V(\partial p/\partial V)_T = K_T$, is called the modulus of cubic compression. Note that the coefficient of cubic compression is three times larger than the coefficient of linear compression,

$$\beta_T = 3\left(-\frac{\partial \ln l}{\partial p}\right)_T$$

This result follows directly from the relationship $V=l^3$.

It follows from equation (2.14) that pressure may be represented as the sum of two components--thermal $T(\partial P/\partial T)_V$ and elastic $-(\partial E/\partial V)_T$.

At absolute zero the thermal component of pressure disappears, with only the elastic component remaining. The dependence of elastic pressure (or elastic energy) on the specific volume of a substance at $T = 0°K$ is called the zero isotherm. According to Nernst's theorem (the third law of thermodynamics) at $T = 0°K$ entropy is zero--that is, it remains constant. Therefore the zero isotherm coincides with the zero adiabat (isentrope).

At absolute zero $-(\partial E/\partial V)_T$ is called the "cold pressure" and represents the elastic or potential component of the forces of interaction between the particles of which the substance consists; it depends only on specific volume:

$$P_x = P_x(V) = -(\partial E/\partial V)_{T=0K} \tag{2.15}$$

It is presumed that at $T>0°K$ function $P_x(V)$ remains constant. Only the thermal (kinetic) part of pressure depends on temperature:

$$P_T = P - P_x = T\left(\frac{\partial P}{\partial T}\right)_V - \left[\left(\frac{\partial E}{\partial V}\right)_T + \left(\frac{\partial E}{\partial V}\right)_{T=0}\right] \tag{2.16}$$

A certain cold energy E_x determined from relationship (2.15) corresponds with cold pressure--$dE_x/dV = P_x$. When we use this equation for the calculations, we usually read energy from the level of zero oscillations.*

The thermal or kinetic component of energy is

$$dE_T = dE - dE_x = dE + P_x dV = C_V dT + \left[\left(\frac{\partial E}{\partial V}\right)_T - \left(\frac{\partial E}{\partial V}\right)_{T=0}\right] dV \tag{2.17}$$

---

*At $T = 0°K$ atoms make so-called zero oscillations, with which energy $h\nu/2$ representing one normal oscillation of frequency ν is associated.

Another widely employed term is

$$\left(\frac{\partial H}{\partial T}\right)_p = C_p \qquad (2.18)$$

which represents the specific heat of the substance at constant pressure. Given a constant volume C_V, we use the following relationship to convert this value (which is easily obtained experimentally) to specific heat:

$$C_p/C_v = \gamma = \beta_T/\beta_S \text{, where } \beta_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S \qquad (2.19)$$

or

$$C_p - C_v = T\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial P}{\partial T}\right)_V = -T\left(\frac{\partial V}{\partial T}\right)_P^2\left(\frac{\partial P}{\partial V}\right)_T = TV\alpha_P^2/\beta_T \qquad (2.20)$$

All cofactors in the last expression (2.20) are positive; therefore $C_P > C_V$ always holds, and $\beta_T > \beta_S$. For an ideal gas,

$$C_p - C_v = R, \quad \beta_T = 1/P, \quad \beta_S = 1/(\gamma P).$$

The values for internal energy, enthalpy, entropy and specific heat for all of the basic products of combustion and explosion (obtained by analysis of spectroscopic data and other means) are collected together in handbooks (3) and (4). Tables of combustion product enthalpy and entropy values may be found in handbooks, for example in the fundamental handbook (3). Enthalpy values are given for an interval between 293.15 and 6,000 °K, with the value at 293.15°K* being 0. Inasmuch as for an ideal gas $\Delta H = \Delta E + R(T - T_0)$, it is easy to obtain the value for the internal energy of a gas from these tables.

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*The accuracy of this number (≈0.003 percent) greatly exceeds experimental accuracy in the theory of combustion and explosion. Usually T_0 is presumed equal to 298°K, and sometimes even 300°K.

Figure 1 shows the dependence of enthalpy on temperature for some substances. It is rather complex in nature, and it is usually expressed analytically by a polynomial containing four to six terms. We can see from Figure 1, however, that this dependence may be expressed by a simple formula in a rather broad interval of temperatures (2,000-3,000°):

$$(\Delta H_T^\circ)_i = (H_T^\circ)_i - (H_{300}^\circ)_i = \xi_i (T - T_i) \quad (2.21)$$

Table 1 gives values for ξ_i and T_i. It also shows the temperature interval within which formula (2.21) holds. Note that ξ_i is an approximation of the molar heat capacity of substance i in the indicated temperature interval (C_{p_i}). The relative deviation of ΔH_T values from the tabulated data is within 0.5 percent as a rule, and in any case it is never greater than 1 percent.

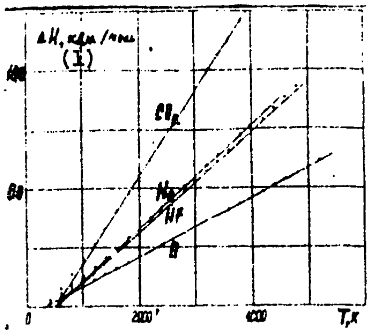

Figure 1. Dependence of the Enthalpy of Some Combustion Products on on Temperature

Key:
1. ΔH, kj/mole.

It follows from Table 1 that for monatomic gases (H, O, N and gaseous C), in the interval from 300 to 3,000°K specific heat C_p is equal to 5/2 R (20.8 j/mole·°K)--that is, it corresponds with the theoretical value for all three forward degrees

Table 1. Dependence of the Enthalpy of Some Combustion and Explosion Products on Temperature $H_{T-300} = \xi_i (T - T_i)$, kj/mole.

	$\Delta T \cdot 10^{-3}$	ξ_i	T_i		$\Delta T \cdot 10^{-3}$	ξ_i	T_i
N_2	2,0-4,0	37,I	500	O	I,0-5,0	2I,0	300
CO	2,0-4,0	37,7	"	H	0,3-4,0	20,8	"
H_2	I,8-3,3	35,4	"	$C_{газ}$	0,3-3,0	20,8	"
O_2	2,0-3,8	39,3	"	N	0,6-4,6	20,9	"
OH	I,8-3,8	36,0	"	NO	I,2-4,0	36,4	400
HCI	I,8-3,8	36,7	"	NaCI	I,8-5,0	40,3	"
HF	I,8-4,0	35,5	"	KCI	0,3-I,0	56,9	300
F	I,2-5,0	42,I	"		I,2-3,0	66,I	0
CO_2	I,6-4,0	6I,I	"	SiO_2	0,8-2,0	75,2	400
N_2O	I,8-3,0	56,9	"		2,2-3,6	98,0	700
HCN	2,0-4,0	6I,3	600	AI_2O_3	I,0-2,2	I30	400
H_2O	2,0-3,8	55,7	700		2,4-6,0	I46	-200[x)]
$C_{конд}$	I,5-3,5	25,7	600	CH_4	I,2-I,6	77,4	500
	3,0-5,0	28,0	300		I,8-2,4	89,I	600

*T_i does not have physical meaning, and therefore, in particular, it may be negative as well.

of freedom (with a consideration for the work of expansion). For diatomic gases in the 2,000-4,000°K interval it is 36-38 j/mole•°K (about 4.25-4.5 R), which corresponds approximately to the sum of energies representing the three forward (3/2 R), two rotational (2/2 R) and two oscillatory (2/2 R) degrees of freedom of a diatomic molecule together with the work of expansion (R).*

In cases where there are no tabulated data, especially in relation to complex organic molecules at high temperature, the specific heat, enthalpy and internal energy may be obtained by calculation. In this case it is presumed that the sum of forward and rotational contributions to specific heat is maximum (5/2 R for

---

*At moderate temperature (from 90 to 370°K for different substances) the value of C_p/R for diatomic gases is close to 3.5 $(\gamma = 1,4)$, which corresponds to excitation of three forward and three rotational degrees of freedom.

linear and 3 R for nonlinear molecules), and that the dependence of specific heat on temperature is defined only by the oscillatory component (the contribution of excited electrons is ignored). The contribution of valent oscillations is accounted for with Einstein's function:

$$\mathcal{E}_i = \frac{(\theta_i/2T)^2}{Sh^2(\theta_i/2T)} \qquad (2.22)$$

$Sh(x) = (e^{x}-e^{-x})/2$--hyperbolic sine function; Θ_i--characteristic temperatures corresponding with characteristic frequencies ν_i of the molecule under examination:

$$\theta_i = \frac{h\nu_i}{K} = \frac{N_A h\nu_i}{R_0}$$

(h and K--Planck's and Boltzman's constants, N_A--Avogadro's number). Values for function $\mathcal{E}_i$ are given in (5). Values of Θ_i are obtained from analysis of spectroscopic data. For example $\Theta_i = 3{,}340$°K for nitrogen, 2,230°K for O_2 and 6,100°K for H_2. The number of characteristic frequencies is greater for polyatomic molecules. For example CO_2 has four--954, 954 [sic], 1,890 and 3,360°K .

An approximate method of calculating the specific heat of polyatomic molecules makes use of just two characteristic frequencies for each chemical bond, $\nu_i^{(1)}$ and $\nu_i^{(2)}$. The formula used for the calculations has the form:

$$C_v/R_0 = A + \sum_1^{b} \mathcal{E}_i^{(1)} + B\sum_1^{b} \mathcal{E}_i^{(2)}, \qquad (2.23)$$

where $A = 5/2$ for linear and 6/2 for nonlinear molecules; $B = (3a-5-b)/b$ for linear and $(3a-6-b)/b$ for nonlinear molecules; a--number of atoms; b--number of chemical bonds in the molecule; $\mathcal{E}_i^{(1)}$ and $\mathcal{E}_i^{(2)}$--Einstein's functions for characteristic temperatures $\Theta_i^{(1)}$ and $\Theta_i^{(2)}$.

Table 2 gives the characteristic temperatures $\Theta_i^{(1)}$ and $\Theta_i^{(2)}$ for frequently encountered chemical bonds. The dependence of the specific heat of some substances on temperature, calculated by formula (2.23), is shown in Figure 2.

Table 2. Characteristic Temperatures of Chemical Bonds

Связь (1)	$\theta_\nu^{(1)}$,K	$\theta_\nu^{(2)}$,K	Связь	$\theta_\nu^{(1)}$,K	$\theta_\nu^{(2)}$,K
C -C (алифатический ряд) (2)	1307	935	H - I (в HI)	3200	-
C -C (ароматический ряд) (3)	2154	862	H - S	3694	1235
C = C	1724	1307	O - O (в O_2)	2230	-
C ≡ C	2990	539	S = O	1797	748
C - H (4)	4315	1510	S - C	992	402
C - O (в CO)	3070	-	N - N	1437	1290
C - O	1480	1610	N - N (в N_2)	3340	-
C = O	2500	1120	N - N (в N_2O)	3190	848
C - N	1437	647	N - N (в N_2O_4)	1402	719
C ≡ N	3190	345	N - H	4740	1724
C - Cl	935	374	N - O (в NO)	2690	-
C - F	1510	1724	N - O	1823	949
C - Br	877	1165	N = O	2112	935
C - I	762	1264	Si - H	3132	1335
H - H (в H_2)	6100	-	Si - O	1510	575
H - O	5030	1940	B - H	3668	1654
H - Cl (в HCl)	4140	-	B - F	1280	992
H - Br (в HBr)	3700	-			

Key:

1. Bond	3. Aromatic series
2. Aliphatic series	4. In

Integrating (2.23), we can find intrinsic energy.

$$\frac{E_{вн}}{R_0} = AT + \sum_1^{l} \theta_i^{(1)}\left(e^{\theta_i^{(1)}/T} - 1\right)^{-1} + B\sum_1^{l} \theta_i^{(2)}\left(e^{\theta_i^{(2)}/T} - 1\right)^{-1} \tag{2.24}$$

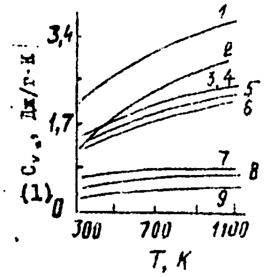

Figure 2. Dependence of Specific Heat on Temperature: *1*--methanol, *2*--toluol, *3*--methylnitrate, *4*--nitroglycol, *5*--nitromethane, *6*--chloroform, *7*--CCl_4, *8*--bromoform

Key:
1. j/gm·°K

The enthalpy of an ideal gas is $H_{id} = E_{id} + RT$.

The specific heats (and entropies) of many organic compounds are given in (6) for a broad interval of temperatures.

Calculations using formulas (2.23) do not account for interaction between molecules, and for condensed substances they usually understate the value of C_V. If an experimental value is available for C_V at temperature T_0, the following formula can be used to determine the dependence of C_V on temperature as a certain approximation:

$$C_v(T) = C_v(T)_{ид} + [C_v(T_0)_{оп} - C_v(T_0)_{ид}] \quad (2.25)$$

Isentropic compressibility β_S (see formula (2.19)) is used to calculate the volumetric speed of sound

$$C_0^2 = \left(\frac{\partial p}{\partial \rho}\right)_S = -V^2\left(\frac{\partial p}{\partial V}\right)_S = V/\beta_S = 1/(\beta_S \rho) \quad (2.26)$$

The speed of sound in an ideal gas is

$$C_0 = \sqrt{\gamma p V} = \sqrt{\gamma R T} \qquad (2.27)$$

The velocity of longitudinal waves in an organic liquid, also determined by equation (2.26), may be calculated using Rao's rule:

$$C_0 = \left(\frac{10^{-6}\rho_0}{M} \Sigma Z_i B_i\right)^3, \text{ m/sec}, \qquad (2.28)$$

where ρ_0--density of the liquid, kg/m^3; M--its molecular weight, kg/mole; Z_i--number of chemical bonds of the given form; B_i--contributions of these bonds:

C - H	95,2	C - N	20,7	N - H	90,7
C - C	4,25	C = C	129	C - NO_2	302,5
C - O	34,5	C = O	186	O - NO_2	360
C - O (ether)	44,5	O - H	99	N - NO_2	330

The speed of sound (of longitudinal waves) in solid organic substances having the density of crystals may also be estimated by formula (2.28) in the absence of experimental data.*

When we use the speed of sound, we can supplement relationship (2.20) by yet another:

$$C_v = \frac{C_p}{1 + (T\alpha_p^2 C_0^2 / C_p)} \qquad (2.29)$$

---

*It should be remembered in this case that waves propagating in isotropic solids may be both longitudinal (compressive strain) and transverse (shear strain). The speed of sound in a thin plate and in a thin rod differs from the speed of sound in a boundless medium and from the velocity of surface waves. The calculation formulas may be found in handbooks (see for example (7)). Estimates may be arrived at very conveniently with the formula $C \simeq \sqrt{E/\rho}$, where E--Young's modulus and ρ--density of the solid. This is the speed of sound in a thin rod, close to the longitudinal speed of sound in a boundless medium.

Here, C_P in the denominator is the specific heat (inasmuch as the square of the speed of sound has the units of specific energy).

Table 3 gives the values of C_P, C_V, α_P and C_0 for a number of substances.

Table 3. Density, Specific Heat, Coefficient of Thermal Expansion and the Speed of Sound for Some Organic Substances

Вещество (1)	ρ_0 (2) г/см³	C_p^0 (3) кДж/кг·К	C_v^0 (3) кДж/кг·К	γ^0	α_p, К⁻¹10³	C_0, м/с (4) по (2.17) (5)	C_0, м/с (4) опыт (6)
Тротил (7) (293К)	1,663	1,373	1,243	1,105	0,32	2195	
(354К)	1,470	1,604	0,983	1,63	1,05	1516	1600
Тетрил (8)	1,73	0,942	0,616	1,15	0,32	2191	
Гексоген (9)	1,816	1,248	1,135	1,10	0,25	2621	
Тэн (10)	1,773	1,67	1,33	1,26	0,5	2431	
Нитроглицерин (11)	1,60	1,67	1,22	1,37	0,85	1714	
Нитрогликоль (12)	1,49	1,67ˣ⁾	1,26	1,33	0,85	1604	
Метилнитрат (13)	1,21	2,035	1,453	1,40	1,3	1275	
Нитрометан (14)	1,13	1,742	1,223	1,42	1,22	1293	1346 1300
Нитробензол (15)	1,207	1,511	1,168	1,293	0,83	1540	1473
Толуол (16)	0,867	1,704	1,235	1,38	1,1	1330	1300
Метанол (17)	0,791	2,571	2,197	1,17	1,2	1112	1122
Хлороформ (18)	1,489	0,967	0,653	1,48	1,23	989	995
Четыреххлористый углерод (19)	1,594	0,858	0,592	1,45	1,236	866	930
Бромоформ (20)	2,89	0,515	0,289	1,78	1,27	744	908

*The value of C_p^0 for nitroglycol is assumed to be the same as for nitroglycerin; formula (2.23) for an ideal gas produces close values for these two substances.

Key:

1. Substance
2. gm/cm³
3. kj/kg·°K
4. m/sec
5. From formula (2.17)
6. Experimental
7. Trotyl
8. Tetryl
9. Hexogen
10. PETN
11. Nitroglycerin
12. Nitroglycol
13. Methylnitrate
14. Nitromethane
15. Nitrobenzene
16. Toluol
17. Methanol
18. Chloroform
19. Carbon tetrachloride
20. Bromoform

The system's entropy may be found by equation (2.1):

$$dS = \frac{dE}{T} + \frac{pdV}{T} = \frac{C_v dT}{T} + \left(\frac{\partial E}{\partial V}\right)_T \frac{dV}{T} + \frac{pdV}{T} = \frac{C_v dT}{T} + \left(\frac{\partial p}{\partial T}\right)_V dV = \frac{C_v dT}{T} + \gamma_v p dV \quad (2.30)$$

In addition to (2.1), we use equations (2.13) and (2.14) to write these equalities.

Integrating (2.30), we get:

$$S - S_0 = \int_{T_0}^{T} \frac{C_v dT}{T} + \int_{V_0}^{V} \left(\frac{\partial p}{\partial T}\right)_V dV \qquad (2.31)$$

The dependence of specific heat C_V on temperature is obtained experimentally, or it is found from formula (2.23). The derivative

$$(\partial p/\partial T)_v = \gamma_v p = \alpha_p/\beta_T \qquad (2.12.)$$

The entropy of an ideal gas (or mixture of gases) may be calculated using equation (2.2):

$$dS = \frac{dH}{T} - \frac{VdP}{T} = \frac{C_p dT}{T} - \frac{VdP}{T} = C_p \frac{dT}{T} - n_0 R_0 \frac{dP}{P} \quad (2.32)$$

or

$$S_T^P - S_{T_0}^0 = \int_{T_0}^{T} C_p d\ln T - R_0 \int_{1}^{P} n_0 d\ln P \qquad (2.33)$$

In an isobaric process,

$$S_T^0 - S_{T_0}^0 = \int_{T_0}^{T} C_p d\ln T \qquad (2.34)$$

In an isothermic process,

$$S_T^p - S_T^0 = -k_0 \int_{p_0}^{p} n_0 \, d\ln p = -k_0 \bar{n}_0 \ln \frac{p}{p_0} \quad (2.35)$$

In an adiabatic (isentropic) process,

$$\int_{T_0}^{T} C_p \, d\ln T - k_0 \int_{p_0}^{p} n_0 \, d\ln p = 0, \text{ or } S_T^0 - S_{T_0}^0 = S_T^p - S_T^0 \quad (2.36)$$

It follows from relationships (2.34)-(2.36) that when adiabatic expansion of a gas occurs, pressure may be calculated if we know the entropy of the gas at atmospheric pressure and at a temperature corresponding to the given degree of isentropic expansion:

$$\ln(p/p_0) = -\frac{1}{n_0 k_0}\left(S_T^0 - S_{T_0}^0\right) \quad (2.37)$$

S_T^0 is the entropy of an ideal gas at the given temperature, and pressure $P_0 = 10^5$ Pa is called the standard entropy. It follows from (237) that change in entropy in an isobaric process may serve as a measure of pressure change in an adiabatic process.

At N_0, $Cp = \text{const.}$ in an adiabatic isentropic process,

$$R \ln(p/p_0) = C_p \ln(T/T_0) \quad \text{or} \quad P/P_0 = (T/T_0)^{C_p/R}$$

Considering that $Cp = \gamma R/(\gamma-1)$ and $P = RT/V$, we can write

$$P/P_0 = (T/T_0)^{\gamma/(\gamma-1)} = (V_0/V)^{\gamma} \quad (2.38)$$

This is Poisson's adiabatic equation.

To complete our list of basic thermodynamic relationships, we need one more function of state that is often used in calculations associated with combustion processes--the reduced thermodynamic potential:

$$\Phi_T^\circ = S_T^\circ - \frac{H_T^\circ - H_0^\circ}{T} \quad . \quad (2.39)$$

As with entropy, the reduced thermodynamic potential is characterized by the fact that it converts to zero at absolute zero for most substances.

3. The Equation of State

3.1. An Ideal Gas

Before writing the equation of state for an ideal gas--one of the fundamental laws of nature*--we will examine partial gas laws from which it was obtained. These laws were obtained as a result of physical measurements made over a period of about two centuries, and as we know, they are of interest on their own. We will adhere not to the chronological but to the logical sequence of presentation and to the commonly accepted modern terminology.

1. Dalton's law (John Dalton, 1766-1844): The pressure of a mixture of several nonreacting gases is equal to the sum of the partial pressures of each of these gases.

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*It would be interesting to note that despite the fact that this law is so fundamental, the equation of state for an ideal gas is purely approximate. From this standpoint this is a typically technical or technological law. Incidentally it does enjoy broad use in engineering.

2. Law of multiple proportions (Prout, 1799; Dalton, 1808): Volumes of gases entering into a reaction relate to one another as small whole numbers.

3. Avogadro's law (Amadeo Avogadro, 1776-1856): Equal volumes of gases at the same temperature and pressure contain the same number of molecules (at given P and T, the molar volumes of all gases are equal).

4. The Boyle-Mariotte law (Boyle, 1662; Mariotte, 1676): At constant temperature, the pressure of a certain mass of gas is inversely proportional to the volume of the gas.

5. The Gay-Lussak law (Joseph Louis Gay-Lussak, 1778-1850): At constant pressure, the volume of a gas is proportional to its absolute temperature.

6. Charles' law (1787): At constant volume, pressure is directly proportional to the absolute temperature of a gas (a different interpretation is: The pressure of a certain mass of gas, when heated 1°C at constant volume, increases by 1/273d of the pressure at 0°C).

Let us write laws (4), (5) and (6) for 1 mole of a gas:

$$\begin{aligned} &(4)\ \text{at } T = \text{Const} \quad && p = \alpha_1 / V_M \\ &(5)\ \text{at } P = \text{Const} \quad && V_M = \alpha_2 T \\ &(6)\ \text{at } V_M = \text{Const} \quad && p = \alpha_3 T \end{aligned}$$

where V_M--molar volume, α_1, α_2, α_3--constants.

Note that inasmuch as at given pressure and temperature, according to Avogadro's law (3) the molar volume of all gases would be the same and constants α_1, α_2 and α_3 would be exactly the same for all gases.

Let us obtain the appropriate partial derivatives from relationships (4)-(6):

$$\left(\frac{\partial p}{\partial V_M}\right)_T = -\frac{p}{V_M};\ \left(\frac{\partial V_M}{\partial T}\right)_p = \frac{V_M}{T};\ \left(\frac{\partial p}{\partial T}\right)_{V_M} = \frac{p}{T} \qquad (3.1.)$$

We immediately see that these derivatives form a general thermodynamic identity:

$$\left(\frac{\partial p}{\partial V_M}\right)_T \left(\frac{\partial V_M}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_{V_M} = -1$$

But this means that the pressure, molar volume and temperature of a gas are associated with each other by a single functional dependence common to all gases:

$$f(p, V_M, T) = 0 \quad \text{or} \quad p = p(V_M, T) \qquad (3.2.)$$

The form of this dependence is easily found by differentiating (3.2):

$$dp = \left(\frac{\partial p}{\partial V_M}\right)_T dV_M + \left(\frac{\partial p}{\partial T}\right)_{V_M} dT = -\frac{p}{V_M} dV_M + \frac{p}{T} dT$$

and integrating the resulting expression:

$$\ln p = -\ln V_M + \ln T + Const, \quad \text{or} \quad pV_M/T = Const = R_0 \qquad (3.3.)$$

Thus we arrive at the famous Clapeyron law--the equation of state of an ideal gas. Constant R_0 may be obtained experimentally; it is the same for all gases.

$R_0 = 8.315$ Pa·m^3/(mole·°K) = 8.315 j/(mole·°K) = 1.987 cal/mole·°K. Substituting the molar volume by specific volume, we get

$$pV = RT \qquad (3.3,a)$$

where $R = R_0/M$--specific gas constant (different for different gases); M--molecular weight of the gas.

If V_C is the volume of the vessel and M is the mass of the gas within it, then

$$V_M = V_C M/m \quad \text{and} \quad pV_C = \frac{m}{M} RT \qquad (3.3,б)$$

This is the Clapeyron-Mendeleev law.

Inasmuch as $1/V_M = C$ is the concentration of a gas,

$$p = CR_0 T \qquad (3.3в)$$

or for a mixture of gases,

$$p_i = C_i R_0 T \qquad (3.3,д)$$

where P_i is the partial pressure of the gas.

In accordance with Dalton's law $P = \Sigma P_i$, since $C = \Sigma C_i$ (the total number of molecules in a given volume is equal to the sum of the numbers of molecules in the different gases). Other relationships for partial pressure are:

$$p_i = \alpha_{Vi} p = \alpha_{ni} p = (n_i/n_0) p \qquad (3.4.)$$

Partial pressures enter directly into the expression for the equilibrium constants of an ideal gas:

$$K_p = e^{-\frac{\Delta G_T^0}{RT}} = \frac{\Pi p_i^{\nu_i}}{\Pi p_j^{\nu_j}} = e^{\frac{\Delta \Phi_T^0}{R}} \qquad (3.5.)$$

Here Π--multiplication symbol; ν_i and ν_j--stoichiometric coefficients of correspondingly the reaction products (the right side of the reaction equation) and the initial substances; ΔG_r and $\Delta \Phi_R$*--change in Gibbs' energy and in the reduced thermodynamic potential as a result of the reaction:

$$\Delta G_r = -\Phi_r^* T = \Delta H_r - T\Delta S_r$$

3.2. Real Gases

3.2.1. Noble's and Abel's Equation

When the temperature of combustion products is high (1,000°K and above) the equation for an ideal gas may be used with relatively small error (up to 2 percent) at pressures up to several hundred atmospheres.

At higher pressure (up to several thousand atmospheres) we use a simplified van der Waals equation*:

$$p(V - V_k) = RT \text{, or } \frac{pV}{RT} = \frac{1}{1 - V_k/V} \qquad (3.6.)$$

where V--specific volume of combustion products at pressure P and temperature T; V_K--so-called covolume, which accounts for the volume of the molecules themselves in gaseous products (V_K is about four times as large as the total volume of gas molecules) and, in the case of gaseous suspensions, the volume of the condensed substance. V_K is expressed in cubic meters per kilogram of explosion products. If g_i is the proportional weight of condensed product i and V_0 is the specific volume of gases under normal conditions, then

$$V_k = 0,001 V_0 + \Sigma g_i V_i \qquad (3.7.)$$

---

*We should note the fact that the first to discover and explain the difference in behavior of real and ideal gases was M. V. Lomonosov; this is sometimes called Lomonosov's equation (8).

The following terms are introduced for the internal ballistics of gunbarrel systems (in relation to which we mainly employ equation (3.6)):

$$RT_V = f_n, \quad 1/V = \Delta$$

T_V--temperature generated by combustion of powder in an enclosed space in adiabatic conditions. The variable f_n, which is expressed in the units of specific energy,* is called the "powder power," and variable Δ is referred to as the "loading density." Equation (3.6) takes the form:

$$p = \frac{\Delta f_n}{1 - V_k \Delta} \qquad (3.8.)$$

Formula (3.8), which was obtained experimentally at the end of the last century, is called the Noble-Abel equation (sometimes Abel's equation).

If gas pressure is greater than several thousand atmospheres the dependence of covolume on pressure must be considered. Assuming that covolume is a function of just specific volume alone at high temperature, M. Cook obtained a single dependence, $V_K(V)$, for the explosion products of 14 explosives in an interval of V values from 0.2 to 1.4 cm^3/gm (a specific volume of 0.2-0.4 cm^3/gm--that is, a density of 5-2.5 gm/cm^3--corresponds to the explosion products of lead azide, mercury fulminate and mixtures of trotyl with a large quantity of lead nitrate). The dependence $V_K(V)$ can be expressed approximately by the following formula (Johanson and Person, 1970):

$$V_k = V_k^0 e^{-V^0/V} \qquad (3.9.)$$

---

*At constant heat capacity $f_n = (\gamma - 1)E$, where $\gamma = C_p/C_V$; E--specific intrinsic energy of the gas.

There are two constants in this formula that are expressed in units of specific volume:

$$V_K{}^0 = 1.0 \text{ cm}^3/\text{gm} \qquad \text{and} \qquad V^0 = 0.4 \text{ cm}^3/\text{gm}$$

3.2.2. Equation of State With Virial Coefficients

If we write equation (3.6) in the form

$$\frac{PV}{RT} = \frac{1}{1 - V_K/V} = 1 + \frac{V_K}{V}\,\frac{1}{1 - V_K/V} = 1 + \frac{V_K}{V} + \left(\frac{V_K}{V}\right)^2 + \ldots \qquad (3.10.)$$

(we use the expansion $(1-x)^{-1} = 1+x+\ldots$ at $x \ll 1$ to obtain the latter equality), it is easy to see ~~that~~ the relationship between the Noble-Abel equation and an equation of state for a gas containing virial coefficients:

$$\frac{PV}{RT} = 1 + \frac{B_2}{V} + \frac{B_3}{V^2} + \ldots, \qquad (3.11.)$$

obtained on the basis of Boltzman's virial theorem (the theorem on expansion of the function of state into a series in relation to small powers of density). Here, B_1, B_2 etc. are the second, third and subsequent virial coefficients depending on temperature and not depending on pressure. The second virial coefficient in the model of rigid spherical molecules is equal to the covolume (that is, it is four times larger than the volume of the molecules themselves), and the third and fourth virial coefficients are proportional to the corresponding powers of the second:

$$\frac{PV}{RT} = f(V) = 1 + \frac{B_2}{V} + 0{,}625\frac{B_2^2}{V^2} + 0{,}287\frac{B_2^3}{V^3} + 0{,}193\frac{B_2^4}{V^4} \qquad (3.12.)$$

The second virial coefficient in this equation, B_2, is obtained by summing the contributions made to its magnitude by gaseous explosion products:

Table 4 gives values for coefficients B_{2i}.

Table 4. Second Virial Coefficients for Gaseous Substances, B_{2i}, cm^3/gm, at 3,500°K

NH_3	NO	CO_2	N_2	CO	N_2O	H_2	O_2	CH_4	H_2O
15,2	21,2	37,0	34,0	33,0	63,9	14,0	30,5	37,0	7,9

3.2.3. The Becker-Kistyakovskiy-Wilson Equation

Substituting $B_2/V=X$ in equation (3.11), we get (ignoring all but the first three terms of the polynomial)

$$\frac{pv}{RT} = 1 + X(1+\beta' X) \simeq 1 + Xe^{\beta' X} \quad (3.13.)$$

Here $\beta' = B_3/B_2^2$; the latter equality is obtained by using the expansion $E^{\beta' X} \simeq 1+\beta' X$.

When we use the potential for interaction between molecules in the form

$$E_r = a_1/r^{n_1} - a_2/r^{n_2}$$

the second virial coefficient may be expressed in the form

$$B_2 = KT^{-3/n_2},$$

where K is proportional to the covolume and represents the sum of the products of the corresponding values of each of the gaseous explosion products times their molar proportions in the mixture. In order to keep pressure increasing to infinity as the temperature tends toward zero and keep $(\partial P/\partial T)_V$ positive, constant T' had to be added within the range of specific volumes of interest to us. The expression for X is found to contain three constants, the selection of which must be made with a consideration for experimental data (the fourth constant contained in equation (3.13) is β':

$$X = \frac{K'}{V(T+T')^{\alpha'}} = \frac{\varkappa' \sum n_i k_i}{V(T+T')^{\alpha'}} \qquad (3.14.)$$

Equation (3.13) with parameter X, given in form (3.14), is called the Becker-Kistyakovskiy-Wilson (BKW) equation. It is broadly employed in the USA (2) to calculate the detonation characteristics of explosives. Good results were obtained for trotyl and hexogen using the constants shown in Table 5.

Table 5. Constants in the BKW Equation of State Used to Calculate Detonation Characteristics of Trotyl and Hexogen

	β'	$\varkappa'$	α'	T'	k_i			
					H_2O	CO_2	CO	N_2
TNT	0,096	12,69	0,50	400	250	600	390	380
Hexogen	0,16	10,91						

3.3. Gases at Ultrahigh Pressure and Condensed Substances

One shortcoming of all of the forms of the equation of state given above is that they do not contain the cold and elastic components of pressure and intrinsic energy. In all cases except (3.13), at $T = 0$ pressure becomes zero independently of V_C--the specific volume of the substance. But the theory of the structure of matter indicates that at absolute zero, pressure and intrinsic energy are functions of volume, and when the latter changes (especially when it decreases) they change a very great deal.

The general form of an equation of state taking account of this circumstance was given earlier as relationships (216) and (217):

$$P = P_x + P_T \quad \text{and} \quad E = E_x + E_T$$

where P_X and E_X--potential and elastic or "cold" components of pressure and intrinsic energy, associated by the relationship $dE_x/dV = (\partial E/\partial V)_{T=0} = -P_x$; P_T and E_T--thermal (that is, depending on temperature) components of pressure and intrinsic energy.

The dependence of the elastic energy of a solid on specific volume (Figure 3) has qualitatively the same form as the curves describing the dependence of the energy of interaction of two atoms in a molecule on the distance between them. The dependence of elastic pressure on specific volume is also shown in Figure 3.

The value for specific volume at $T = 0°K$, $V_{0°K}$, corresponds to mechanical equilibrium. Cold pressure at this point would be equal to zero.* The forces of attraction and repulsion balance each other out. Elastic energy is minimal in this case.

When a substance is heated, it undergoes thermal expansion: Thermal pressure, which is always assumed to be positive, arises. Elastic pressure becomes negative in this case: It compensates for the action of the stretching forces that increase specific volume. In terms of absolute value,

$$|P_x| = |P_T|.$$

Negative pressure can be estimated from the heat of sublimation of the substance. By definition, the area beneath the curve representing cold expansion of a solid between zero volume and infinity is equal to the energy of sublimation:

$$E_s = \int_{V_{0K}}^{\infty} P_x \, dV = P_{x\,max} \cdot \Delta V$$

---

*We ignore external (atmospheric) pressure when examining condensed substances.

Assuming that bonding forces diminish significantly as the interatomic distance doubles (that is, when $\Delta V \approx 10V_{0^\circ K}$), we get

$$|P_{x\,\max}| \sim E_s/10V_{0K} .$$

For iron: $E_S = 94$ kcal/mole $= 7.0 \cdot 10^6$ j/kg
For aluminum: $E_S = 55$ kcal/mole $= 8.5 \cdot 10^6$ j/kg

This means that for iron and aluminum, $|P_{X\max}|$ is, respectively, $\approx 6 \cdot 10^9$ and $\approx 2.5 \cdot 10^{-9}$ Pa (that is, $60 \cdot 10^3$ and $25 \cdot 10^3$ atm).

The forces of repulsion, which increase dramatically as atoms come closer together, play the main role in relation to compression. Therefore when $V < V_{0^\circ K}$, pressure and energy increase quickly. When the specific volume of iron is decreased by a factor of 1.5, elastic energy E_X increases by $2.4 \cdot 10^6$ j/kg while elastic pressure attains $1.33 \cdot 10^{11}$ Pa.

3.3.1. Debye's Theory

The derivation of the equation of state of a condensed substance (9) is based on the following premises.

If temperature is not too high the atoms of a solid are locked within cells formed by their closest neighbors, and they make harmonic oscillations relative to their equilibrium positions. Exit from such a cell would require surmounting a potential barrier equal in order of magnitude to the substance's energy of evaporation or sublimation. For many substances this energy corresponds to an increase in temperature on the order of several thousand degrees. When compression occurs, the height of the potential barrier grows intensively as a result of growth in repulsive forces, and it becomes even harder for the atoms to leave their cells. In this case the properties of a liquid begin to approximate those of a solid. Thus atoms continue to make harmonic oscillations over a broad interval of pressures and temperatures.

In an elastic solid, three independent oscillation directions exist in relation to each wave--one longitudinal and two transverse. Assume that an isotropic elastic medium is contained within a rectangular box with sides a_1, a_2, a_3 in line with coordinate axes x_1, x_2, x_3. Then those stationary waves propagating along axis x_i for which half the wavelength is a whole multiple of a ($\lambda/2 = a_i/l_i$, or $2/\lambda = l_i/a_i$, where l_i is a whole number) correspond to box dimension a_i. The general limitation for waves traveling in an arbitrary direction is

$$(2/\lambda)^2 = (l_1/a_1)^2 + (l_2/a_2)^2 + (l_3/a_3)^2.$$

For a given type of oscillations (longitudinal for example) the number of possible wavelengths greater than λ_0 would be equal to the number of positive whole numbers l_1, l_2, l_3 satisfying the condition:

$$\left(\frac{l_1}{a_1}\right)^2 + \left(\frac{l_2}{a_2}\right)^2 + \left(\frac{l_3}{a_3}\right)^2 \leq \left(\frac{2}{\lambda_0}\right)^2,$$

that is, it is equal to the quantity of integral points within an ellipsoid:

$$\left(\frac{l_1}{b_1}\right)^2 + \left(\frac{l_2}{b_2}\right)^2 + \left(\frac{l_3}{b_3}\right)^2 = 1,$$

the coordinates l_i of which are positive whole numbers and the semiaxis of which is $b_i = 2\,a_i/\lambda_0$. The volume of such an ellipsoid is $\frac{4}{3}\pi b_1 b_2 b_3$. If we divide the ellipsoid in Cartesian coordinates by planes x_1x_2, x_1x_3 and x_2x_3 we get eight octants, the volume of each of which is $(\pi/6)b_1b_2b_3$. One of these octants corresponds to positive values of b_i (the one located in space $(l_1, l_2, l_3) > 0$). The number of possible wavelengths greater than λ_0 is

$$\frac{\pi}{6}\,\frac{8a_1a_2a_3}{\lambda_0^3} = \frac{4\pi}{3}\,\frac{V}{\lambda_0^3},$$

where V is the volume of the box. Thus the number of stationary longitudinal waves is directly proportional the volume of the box $V = a_1a_2a_3$. The velocity of a wave in an isotropic medium does not depend on direction, and when $\lambda_0 \ll (a_1, a_2, a_3)$, it does not depend on wavelength either. The relationship between the velocity of a longitudinal wave on one hand and frequency ν and length λ on the other has the conventional form $C_l = \lambda\nu$ (a quantity ν of waves with length λ would fit within C_l). The number of possible frequencies less than ν_0 in this case would be

$$\frac{4\pi}{3}\cdot\frac{\nu^3}{c_l^3}V.$$

Similarly if the velocity of all transverse waves is C_t, then considering the existence of two independent transverse oscillations, we find that the total number of frequencies less than ν_0 is

$$\frac{4\pi}{3}\cdot\frac{\nu_0^3}{c_l^3}V + 2\,\frac{4\pi}{3}\,\frac{\nu_0^3}{c_t^3}V = \frac{4\pi V\nu_0^3}{c^3},$$

where $c^3 = 3\left(\frac{1}{c_l^3} + \frac{2}{c_t^3}\right)^{-1}$ --average velocity of waves for oscillations of all types.

Differentiating expression (3.15), we get the number of simple oscillations with frequencies in the interval between ν and $\nu + d\nu$:

$$\frac{12\pi V}{c^3}\,\nu^2 d\nu \qquad (3.16.)$$

Let us interpret each such oscillation as one of a harmonic oscillator, the zero energy of which is adopted as the energy of its lowest quantum state. The oscillatory statistical sum of such an oscillator would be

$$\chi_{\text{кол}} = (1 - e^{-h\nu/kT})^{-1} \qquad (3.17.)$$

The sum total in relation to the states of all oscillators, $Z(T)$, is the derivative of a function having the form (3.17), the powers of which are determined from (3.16):

$$\chi(T) = \prod_0^{\infty} (1 - e^{-h\nu/kT})^{-\frac{12\pi V}{c^3}\nu^2 d\nu} \qquad (3.18.)$$

Expressing (3.18) as a logarithm and correspondingly substituting the product by a sum and the sum by an integral, we get

$$\ln \chi(T) = -\frac{12\pi V}{c^3}\int_0^{\nu_0} \nu^2 \ln(1 - e^{-h\nu/kT})\,d\nu \qquad (3.19.)$$

We integrate in (3.19) in relation to all stationary frequencies from 0 to ν^0 (in compliance with Debye's theory we assume that there are no frequencies higher than ν^0).

A real solid consisting of N material points may have not more than $3N$ oscillation frequencies. Basing ourselves on this condition, we can estimate ν^0. We find from (3.15)

$$\frac{4\pi V\nu_0^3}{c^3} = 3N \quad \text{or} \quad \nu_0^3 = \frac{N}{V}\,\frac{3c^3}{4\pi} \qquad (3.20.)$$

This frequency is characteristic of the given elastic medium. It is called the Debye frequency, and it depends on the number of particles per unit volume and on the mean velocity of elastic waves. Computations show that at $\nu \leq \nu^0$ the wavelength corresponds to several thousand elementary cells, and consequently interpretation of the medium as an elastic continuum is fully valid.

Let us introduce Debye's temperature:

$$\theta_D = \frac{h\nu_0}{k} = \frac{hc}{k}\cdot\left(\frac{3N}{4\pi V}\right)^{1/3} \qquad (3.21.)$$

The oscillatory sum (3.19) takes the form:

$$\ln Z(T) = -9N\int_0^1 \eta^2 \ln\left(1-e^{-\frac{\theta_D}{T}\eta}\right)d\eta = -9N\left(\frac{T}{\theta_D}\right)^3\int_0^{\theta_D/T}\xi^2\ln\left(1-e^{-\xi}\right)d\xi \qquad (3.22.)$$

where $\eta = \nu/\nu_0$ and $\xi = h\nu/kT = \theta_D\eta/T$ are integration variables.

Statistical physics provides this expression for free energy, $F(T)$:

$$F(T) = -kT\ln Z(T) \qquad (3.23.)$$

Ignoring the contribution made by free and bound electrons and the orientation of nuclear spins, we get the following for the free energy of an elastic solid:

$$F = E_n + E_{nk} + 9NkT\int_0^1 \eta^2 \ln\left(1-e^{\frac{\theta_D}{T}\eta}\right)d\eta \qquad (3.24.)$$

$E_n + E_{nk} = E_x$ is the contribution made by the potential energy of atoms in zero oscillation state at $T = 0$°K. Using (3.16), (3.20) and (3.21) we find the contribution made by the energy of zero oscillations:

(3.20.) и (3.21.):

$$E_{HK} = \int_0^{\nu_0} \frac{1}{2} h\nu \cdot \frac{12\pi V}{c^3}\nu^2 d\nu = \frac{3}{2}\frac{\pi h V \nu_0^4}{c^3} = \frac{9}{8} N h\nu_0 = \frac{9}{8} R\Theta_D \qquad (3.25.)$$

For many solids, energy E_{HK} is small in comparison with crystal bond energy. It plays a noticeable role in molecular crystals, and it is so great for helium that at normal pressure, even at $T = 0°$, helium remains liquid.

It follows from the thermodynamic identity (2.4) that

$$E = F - T\left(\frac{\partial F}{\partial T}\right)_V = -T^2\left(\frac{\partial (F/T)}{\partial T}\right)_V ; \quad p = -\left(\frac{\partial F}{\partial V}\right)_T \qquad (3.26)$$

Keeping in mind that E_Π, E_{HK}, ν_0, ν and consequently η do not depend on temperature, we find from (3.24) that

$$E = -T^2\left[-\frac{E_\Pi}{T^2} - \frac{E_{HK}}{T^2} - 9NK\int_0^1 \frac{\eta^3 \frac{\Theta_D}{T^2} e^{-\frac{\Theta_D \eta}{T}} d\eta}{1 - e^{-\Theta_D \eta/T}}\right] = E_\Pi + E_{HK} + 9R\Theta_D \int_0^1 \frac{\eta^3 d\eta}{e^{\Theta_D \eta/T} - 1}$$

or $$E = E_\Pi + E_T^{(i)} + E_{HK} + 3RTD\left(\frac{\Theta_D}{T}\right) \qquad (NK = R) \qquad (3.27)$$

where $$E_T^{(i)} = 3RTD(\Theta_D/T) \qquad (3.28)$$

is the component of intrinsic energy contributed by thermal oscillations of particles at the junctions of the crystalline lattice.

$$D\left(\frac{\Theta_D}{T}\right) = 3\left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} \frac{\xi^3 d\xi}{e^\xi - 1} \qquad (3.29)$$

is Debye's function (see (5)).

At low ($\Theta_D/T \gg 1$) and high ($\Theta_D/T \ll 1$) temperatures expression (3.29) is integrated analytically. At low temperature Debye's function $D \simeq (T/\Theta_D)^3$. At high ($\Theta_D/T \ll 1$), $D = 1$. In the intervening temperature interval (3.29) can be integrated numerically.

We calculate pressure using (3.24) in correspondence with the second expression of (3.26):

$$p = -\frac{\partial E_x}{\partial V} - \frac{\partial E_{nk}}{\partial V} + 9RT\frac{\partial \theta_D}{\partial V}\frac{\partial}{\partial \theta_D}\int_0^1 \xi^2 \ln\left(1 - e^{-\frac{\theta_D \xi}{T}}\right)d\xi =$$

$$= -\frac{dE_x}{dV} - \frac{9}{8}R\frac{\partial \theta_D}{\partial V} + 9RT\frac{\partial \theta_D}{\partial V}\int_0^1 \frac{\xi^3 \frac{1}{T}\,d\xi}{e^{\theta_D \xi/T} - 1} =$$

$$= P_x + P_{nk} + 9R\frac{\partial \theta_D}{\partial V}\int_0^1 \frac{\xi^3 d\xi}{e^{\theta_D \xi/T} - 1} = P_x + 9R\frac{\partial \theta_D}{\partial V}\left(\frac{T}{\theta_D}\right)^4\int_0^{\theta_D/T}\frac{\xi^3 d\xi}{e^{\xi} - 1}$$

or

$$p = P_x + 3R\frac{T}{\theta_D}\frac{\partial \theta_D}{\partial V}D(\theta_D/T) = P_x + \frac{\Gamma}{V}E_T;\quad p - P_x = \frac{\Gamma}{V}(E - E_x), \qquad (3.30)$$

where

$$\Gamma = \Gamma(V) = -\frac{\partial \ln \theta_D}{\partial \ln V} = -\frac{\partial \ln \nu_D}{\partial \ln V} \qquad (3.31)$$

is Gryunayzen's parameter, a dimensionless variable depending on volume and (in the approximation under examination here) not depending on temperature.

Formula (3.30) or the Mi-Gryunayzen equation, written using the symbols of (3.28), (3.29) and (3.31), is the sought equation of state.

Pressure resulting from zero oscillations of a solid is

$$P_{nk} = \frac{9R\theta_D \Gamma}{8V} = \frac{9}{8}R\rho\theta_D\Gamma$$

Under normal conditions this pressure attains several kilobars, and it increases as the volume of the solid decreases. Correspondingly we can also obtain, for a solid, the contribution made by zero oscillations to the modulus of cubic compression:

$$K_{nk} = -V\frac{dP_{nk}}{dV} = \frac{9}{8V}R\theta_D\Gamma\left(\Gamma + 1 - \frac{\partial \ln \Gamma}{\partial \ln V}\right)$$

The characteristic Debye temperature--θ_D--is a significant element of the equation of state for a crystalline substance. It may be determined from the dependence of atomic heat capacity on temperature:

$$C_V^{(1)} = \left(\frac{\partial E}{\partial T}\right)_V = \frac{\partial E_T^{(1)}}{\partial T} = 9R\theta_D \int_0^1 \frac{\xi^4 \frac{\theta_D}{T} e^{\theta_D \xi/T} d\xi}{(e^{\theta_D \xi/T} - 1)^2} = 9R\left(\frac{\theta_D}{T}\right)^2 \int_0^1 \frac{\xi^4 e^{\theta_D \xi/T} d\xi}{(e^{\theta_D \xi/T} - 1)^2} =$$
$$= 9R\left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{\xi^4 e^{\xi} d\xi}{(e^{\xi} - 1)^2} = 3RD_1\left(\frac{\theta_D}{T}\right) \qquad (3.32)$$

where $D_1(\Theta_D/T)$ is another Debye function (see Appendix 4 in (5)). This function also varies from zero to one as the temperature rises from zero to infinity. At low temperature ($\Theta_D/T>10$) it equals $78(T/\Theta_D)^3$, which corresponds to the relationship $C_V \propto T^3$, obtained by Debye back in 1912. At high temperature $C_V \approx 3R_0 \approx 25$ j/mole•°K. This is the well known Dulong-Petit law. Of course the latter was obtained for specific heat at constant pressure C_P, but according to expression (2.20), in terms of gram-atoms the difference between C_P and C_V is not very large, averaging just ~1.6 j/mole•°K.

Θ_D in (3.32) is found as a reducing parameter from the experimental dependence of heat capacity on temperature (see Appendix 5 in (5)).

Another way for calculating Θ_D requires interpretation of a crystal as an elastic isotropic medium. An isotropic solid has two coefficients of elasticity--the compressibility coefficient β_T and Poisson's constant σ_Π. The speeds of sound C_l and C_T are expressed in terms of β_T and σ_Π as follows:

$$C_l^2 = \frac{3(1-\sigma_\Pi)}{(1+\sigma_\Pi)\beta_T\rho}, \quad C_t^2 = \frac{3(1-2\sigma_\Pi)}{2(1+\sigma_\Pi)\beta_T\rho} \quad \text{or} \quad \frac{1}{\theta_D^3} = \frac{4\pi V}{9N}\left(\frac{k}{h}\right)^3\left(\frac{1}{C_l^3} + \frac{2}{C_t^3}\right) \qquad (3.34)$$

When we know β_T, σ_Π and ρ, we can find Θ_D.

The table below compares Θ_D values obtained by these two approaches for four metals.

Characteristic Debye Temperatures

	ρ г/см^3 (1)	$\beta_T \cdot 10^{11}$ м^2/Па (2)	$\sigma_п$	(3) θ_D, K из $C_V(T)$	(4) θ_D, K по (3.34)
Al	2,7I	I,36	0,337	398	402
Cu	8,96	0,74	0,334	3I5	332
Ag	I0,53	0,92	0,379	2I5	2I4
Pb	II,32	2,0	0,446	88	73

Key:

1. gm/cm^3
2. m^2/Pa
3. From
4. According to

The closeness of the values is doubtlessly very good for a theory derived so approximately.

Crystals Consisting of Molecules

The formulas of Debye's theory may be applied directly only to crystals consisting of atoms of the same sort. If a crystal consists of N molecules, each with s atoms, then in addition to $3N$ oscillations distributed as per Debye's theory, to describe the state of the crystal we would have to add $3N(s-1)$ oscillations associated with the internal degrees of freedom of the molecules (it is usually assumed that motion within molecules and relative motion of molecules within the crystalline lattice do not depend on each other). We will interpret internal degrees of freedom as simple harmonic oscillations of the same frequency, and correspondingly we represent their contribution as Einstein's statistical sum:

$$\prod_{i=1}^{3s}\left(1-e^{-\theta_i/T}\right)^{N}$$

The logarithm of the statistical sum would be:

$$\ln Z(T) = -9N\left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \xi^2 \ln\left(1-e^{-\xi}\right) d\xi - N\sum_{i=1}^{3s} \ln\left(1-e^{-\theta_i/T}\right)$$

Free and intrinsic energy would correspondingly equal

$$F = E_x + 9RT\left(\frac{T}{\theta_D}\right)^{3}\int_0^{\theta_D/T}\xi^2 \ln(1-e^{-\xi})\,d\xi + RT\sum_{i=1}^{35}\ln(1-e^{-\theta_i/T}) \qquad (3.35)$$

$$E = E_x + 3RTD(\theta_D/T) + RT\sum_{i=1}^{35}\frac{\theta_i/T}{e^{\theta_i/T}-1} = E_x + E_T^{(1)} + E_T^{(2)}, \qquad (3.36)$$

where $E_T^{(2)}$ is the energy contribution of thermal oscillations of atoms in the molecules. Differentiating (3.36) with respect to T, we get the specific heat

$$C_v = C_v^{(1)} + C_v^{(2)} = 3RD_1(\theta_D/T) + \sum_{i=1}^{35}\frac{(\theta_i/T)^2 e^{\theta_i/T}}{(e^{\theta_i/T}-1)^2} \qquad (3.37)$$

Comparing (3.37) with (2.22) and (2.23), we find that in the approximation under examination here, the expression for specific heat of a molecular crystal at $\Theta_D/T \ll 1$ is similar to the relationship for heat capacity of an ideal gas consisting of nonlinear molecules. If we assume that the internal degrees of freedom of a molecule depend weakly on pressure and volume, and if we ignore the influence of V on Θ_i, then in accordance with (3.26) and (3.30) we get the following expression for pressure:

$$p = p_x + \frac{3RT}{V}\frac{\partial \ln \theta_D}{\partial \ln V} D\left(\frac{\theta_D}{T}\right) = p_x + \frac{\Gamma}{V}E_T^{(1)}$$

or

$$p - p_x = \frac{\Gamma}{V}\left(E - E_x - E_T^{(2)}\right) \qquad (3.38)$$

The third term of the expression for free energy (3.35) does not contribute to pressure.

Debye's theory is one of the fundamental theories of physics. Naturally, however, in view of the structural complexity and diversity of condensed substances, its conclusions must be approximate in nature. This is especially true of the in-between range in which the frequency distribution function (3.16) obtained for long-wave low-temperature oscillations applies to the entire interval of temperatures, up to the extreme highest, at which point the solution once again becomes statistically valid (10). Also important is the fact that the theory does not account for the anisotropy typical of crystalline substances or the relatively high mobility of particles in a fluid. As was noted earlier, the latter becomes less significant at high pressure, which limits the mobility of particles so much that the state of both a liquid and even a gas could be described by equations such as (3.30) and [equation number illegible; possibly (3.38)]. We will henceforth need only these two equations. A reader wishing to acquaint himself with the equation for the state of crystals with ionic and complex lattices and consider the influence of free and bound electrons would need to refer to more-detailed handbooks (9).

Gryunayzen's Parameter Γ

Gryunayzen's parameter, which is fundamental to an equation of state for a condensed substance, may be obtained by differentiating (3.38) with respect to energy at constant volume:

$$\frac{V}{\Gamma}\left(\frac{\partial P}{\partial E}\right)_V = 1-\left(\frac{\partial E_T^{(2)}}{\partial E}\right)_V = 1-\left(\frac{\partial E}{\partial E_T^{(2)}}\right)_V^{-1} = 1-\left(\frac{\partial (E_X+E_T^{(1)}+E_T^{(2)})}{\partial E_T^{(2)}}\right)_V^{-1} =$$

$$= 1-\left(1+\left(\frac{\partial E_T^{(1)}}{\partial E_T^{(2)}}\right)_V\right)^{-1} = 1-\left(1+\frac{C_V^{(1)}}{C_V^{(2)}}\right)^{-1} = 1-\frac{C_V^{(2)}}{C_V} = \frac{C_V^{(1)}}{C_V}$$

$$\text{or}\quad \Gamma = C_V\frac{V}{C_V^{(1)}}\left(\frac{\partial P}{\partial E}\right)_V = \frac{V}{C_V^{(1)}}\left(\frac{\partial P}{\partial T}\right)_V = -\frac{V}{C_V^{(1)}}\left(\frac{\partial P}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P = \frac{V\alpha_P}{C_V^{(1)}\beta_T} = \frac{\alpha_P}{\rho\beta_T C_V^{(1)}} \qquad (3.39)$$

In the general case $C_V^{(1)}$ is determined by formula (3.32). At $(\Theta_D/T) \ll 1$, we can assume $C_V^{(1)} = 3R$. The values of α_P, β_T and ρ are known for many substances under normal conditions. Therefore there is usually no difficulty in calculating $\Gamma(V_0)$.

Slater's formula can be used to calculate Gryunayzen's parameter at high pressure. This formula was derived with the assumption that all frequencies in an isotropic solid are proportional to the speed of sound $\left[C_x = V(-\partial p_x/\partial V)^{1/2}\right]$ and inversely proportional to the distance between particles $r \sim V^{1/3}$:

$$\nu \sim -V^{2/3}\left(\frac{\partial p_x}{\partial V}\right)^{1/2}$$

From whence we get

$$\Gamma = \frac{\partial \ln \nu}{\partial \ln V} = -\frac{V}{2}\,\frac{\partial^2 p_x/\partial V^2}{\partial p_x/\partial V} - \frac{2}{3} \qquad (3.40)$$

The following formula gives values closer to experimentally obtained values for ionic crystals and metals:

$$\Gamma = -\frac{V}{2}\,\frac{\partial^2(p_x V^{2m/3})/\partial V^2}{\partial(p_x V^{2m/3})/\partial V} + \frac{1}{3}(m-2) \qquad (3.41)$$

In this case $m=1$ for metals in most situations, while for ionic crystals $m=2$. In many cases the dependence of Gryunayzen's parameter on the specific volume of a solid is close to a direct proportion:

$$\frac{\Gamma}{V} = \frac{\Gamma(V_0)}{V_0} = \mathrm{Const} \qquad (3.42)$$

Potential Components of Energy and Pressure (11)

The energy of a crystalline lattice is determined by forces acting between its elements. These include attraction forces--Coulomb, van der Waals and valent, and forces of repulsion--Coulomb or quantum.

Coulomb attraction dominates in ionic lattices. Its energy has the form $-\alpha q/r$, where q is the least charge of the ion, r is the least distance between ions and α is Madelung's constant. Forces of repulsion are produced in ionic crystals by overlapping of the electron shells of the ions. These are quantum forces which decrease exponentially with distance. The potential of an ionic crystal may be written as:

$$E_n = 3(a_1/a_2)V_0 \exp\left[a_2\left(1-\frac{r}{r_0}\right)\right] - 3a_3V_0\left(\frac{V_0/r}{r}\right) \qquad (3.43)$$

where a_1, a_2 and a_3 are constants and $r \simeq V^{1/3}$.

The potential part of pressure is

$$P_n = -\frac{dE_n}{dV} = a_1\left(\frac{r_0}{r}\right)^2 \exp\left[a_2\left(1-\frac{r}{r_0}\right)\right] - a_3\left(\frac{r_0}{r}\right)^4 \qquad (3.44)$$

The potential part of the modulus of cubic compression is:

$$K_n = -V\frac{dP_n}{dV} = \frac{a_1}{3}\left(\frac{r_0}{r}\right)^2\left(a_2\frac{r}{r_0}+2\right)\exp\left[a_2\left(1-\frac{r}{r_0}\right)\right] - \frac{4}{3}a_3\left(\frac{r_0}{r}\right)^4 \qquad (3.45)$$

The forces of attraction in molecular crystals are van der Waals forces. Their dependence on distance is $-\Psi(r)/r^6$, where $\Psi(r)$ is some function of distance. As in ionic crystals, forces of repulsion are produced by overlapping of electron shells.

Potential energy has the form

$$E_n = 3(a_1/a_2)V_0 \exp\left[a_1\left(1-\frac{r}{r_0}\right)\right] - \frac{a_3}{2}V_0\left(\frac{r_0}{r}\right)^6 \qquad (3.46)$$

Potential pressure is

$$P_n = a_1\left(\frac{r_0}{r}\right)^2 \exp\left[a_2\left(1-\frac{r}{r_0}\right)\right] - a_3\left(\frac{r_0}{r}\right)^9 \qquad (3.47)$$

The potential part of the modulus of compression is

$$K_n = \frac{a}{3}\left(\frac{r_0}{r}\right)^2\left(a_2\frac{r}{r_0}+2\right)\exp\left[a_2\left(1-\frac{r}{r_0}\right)\right] - 3a_3\left(\frac{r_0}{r}\right)^9 \qquad (3.48)$$

In the case of metals the forces of attraction are produced by Coulomb interaction of free electrons with positive ions as well as by the volume energy of free electrons. In both cases energy is proportional to r^{-1}. Coulomb forces of repulsion may be combined into a single term together with forces of attraction. Repulsion forces stemming from overlap of electron shells have the same form as in previous cases. Fermi kinetic energy of free electrons also causes repulsion. It is proportional to r^{-2}.

The resultant potential is

$$E_n = a_1 \exp\left[a_2\left(1-\frac{r}{r_0}\right)\right] + a_3\left(\frac{r_0}{r}\right)^2 - a_4\left(\frac{r_0}{r}\right) \qquad (3.49)$$

In alkali metals the forces of repulsion are produced mainly by Fermi kinetic energy of conducting electrons: The first term in (3.49) may be ignored. In a number of cases exponential repulsion plays the main role, and the second term of (3.49) may be ignored. In the latter case the components of pressure and the modulus of cubic compression are determined by formulas (3.44) and (3.45).

Many authors use exponential potential:

$$\varphi(r) = \frac{a}{r^n} - \frac{b}{r^m} \qquad (3.50)$$

where, as in the previous cases, the positive term represents forces of repulsion and the negative term represents forces of attraction. Obviously as r decreases the repulsion forces decrease faster than the attraction forces ($n>m$). In most cases $n=9$-14; for molecular crystals $m=6$, and for ionic crystals $m=1$.

Leonard-Johns used potential (3.50) at $m=6$ to describe the behavior of compressed gases and (in the free volume theory) to arrive at an equation of state for fluids. The theory of free volume gives us the potential for spherical apolar molecules (3.50) in the form

$$E(r) = \frac{\varepsilon_m}{S/6-1}\left(\frac{S}{6}\right)^{\frac{S}{S-6}}\left[\left(\frac{r_0}{r}\right)^S - \left(\frac{r_0}{r}\right)^6\right], \qquad (3.5I)$$

where ε_m--maximum energy of interaction, and r_0--effective collision radius, for which $E(r)=0$. At $S=12$ this is the so-called Leonard-Johns potential (6-12).

For it,

$$E_n = 4\varepsilon_m\left[\left(\frac{V_*}{V}\right)^4 - \left(\frac{V_*}{V}\right)^2\right] \; ; \; P_n = \frac{8\varepsilon_*}{V}\left[2\left(\frac{V_*}{V}\right)^4 - \left(\frac{V_*}{V}\right)^2\right]$$
$$K_n = \frac{8\varepsilon_*}{V}\left[10\left(\frac{V_*}{V}\right)^4 - 3\left(\frac{V_*}{V}\right)^2\right] \qquad (3.52)$$

These expressions are much simpler than (3.46)-(3.48).

We can also calculate Gryunayzen's parameter:

$$\Gamma = 3\left(1 + \frac{1}{10(V_*/V)-3}\right) - \frac{2}{3}$$

The relationship between V_*, $V_{0°K}$ and V_0 is diagrammed in Figure 3.

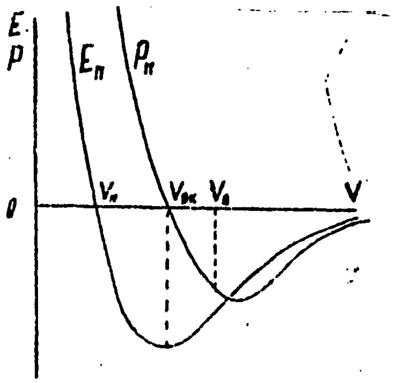


Figure 3. Dependence of Potential Components of Intrinsic Energy and Pressure on the Specific Volume of a Substance

4. Chemical Equilibrium in the Products of Combustion and Explosion

4.1. Moderate Pressure

Table 6 shows the basic equilibrium reactions in the explosion and combustion products of commonly encountered explosive systems (C, H, N, O, Cl, P). The enthalpies of these reactions and the expressions for the equilibrium constants are given. Partial pressures of gaseous substances are expressed in atmospheres. The partial pressures of condensed substances are given in dimensionless units. The formulas for the dependence of equilibrium constants on temperature were obtained by plotting the tabulated data in coordinates $1/T$-[symbol illegible]. For all reactions except (1), straight lines are obtained with good accuracy within a broad interval of temperatures (500-[number and units illegible]). The constants for the reaction were obtained in a 2,000-4,000°K interval.

Table 6. Basic Equilibrium Reactions in Combustion and Explosion Products; Value of Coefficients A and B in the Formula lg $Kp = A-(B/T)$

No.	Reaction Equations ΔH_r	A	B
I	$CO_2 + H_2 \rightleftharpoons CO + H_2O$	I,23	II00
2	$CO_2 + C_K \rightleftharpoons 2CO$	8,73	8480
3	$H_2O \rightleftharpoons OH + \frac{I}{2} H_2$	3,65	I4800
4	$CH_4 + H_2O \rightleftharpoons CO + 3H_2$	I3,06	II580
5	$CH_4 \rightleftharpoons C_K + 2H_2$	5,75	4740
6	$NH_3 \rightleftharpoons \frac{I}{2} N_2 + \frac{3}{2} H_2$	6,00	27I0
7	$\frac{I}{2} N_2 + \frac{I}{2} O_2 \rightleftharpoons NO$	0,65	4750
8	$HCI \rightleftharpoons \frac{I}{2} H_2 + \frac{I}{2} CI_2$	-0,35	4970
9	$HF \rightleftharpoons \frac{I}{2} H_2 + \frac{I}{2} F_2$	-0,I0	I4260
IO	$N_2 \rightleftharpoons 2N$	7,20	499I0
II	$O_2 \rightleftharpoons 2(O)$	7,I0	26490
12	$H_2 \rightleftharpoons 2H$	6,30	23470
13	$CI_2 \rightleftharpoons 2CI$	6,40	I3220
14	$F_2 \rightleftharpoons 2F$	6,70	8700
I5	$CO_2 \rightleftharpoons CO + \frac{I}{2} O_2$	4,30	I45I0

Note: The equilibrium constant for the reaction (i) $aA + bB \rightleftharpoons dD + fF$

has the form $K_i = \frac{n_D^d \cdot n_F^f}{n_A^a \cdot n_B^b} \left(\frac{P}{n_0}\right)^{f+d-a-b}$

For example, $K_3 = \frac{n_{OH}\sqrt{n_{H_2}}}{n_{H_2O}}\sqrt{\frac{P}{n_0}}$; $K_4 = \frac{n_{CO} \cdot n_{H_2}^3}{n_{CH_4} \cdot n_{H_2O}} \left(\frac{P}{n_0}\right)^2$.

Thermochemical calculations are now usually made using the equilibrium constants for atomization reactions. These constants may be used on their own: It is presumed that the initial substance had broken down into atoms, which then group together in correspondence with the atomization reaction constants into the appropriate groups--molecules or radicals. On the other hand these constants can be used to derive the equilibrium constant for any equilibrium chemical process. For example for reaction (1) (Table 6),

$$CO_2 + H_2 \rightleftharpoons CO + H_2O$$

the equilibrium constant is calculated as

$$K_I = \frac{p_{CO}\, p_{H_2O}}{p_{CO_2}\, p_{H_2}} = \frac{K^a_{CO_2} K^a_{H_2}}{K^a_{CO} K^a_{H_2O}},$$

where K_i^a are the atomization constants of the appropriate substances: For example

$$K^a_{CO_2} = \frac{p_O^2\, p_C}{p_{CO_2}}.$$

The values of K_i^a are taken from handbook (3).

It follows from Table 6 that at moderate pressure the equilibrium of reactions 3, 7, 11 and 12 is shifted leftward to a temperature of about 3,000°K and the equilibrium of reactions 8-10 is shifted leftward to a temperature of up to 5,000°K. When the temperature is not too high (up to about 3,000°K) and pressure is high (above 10^7 Pa) there is little OH in the products, and almost no N, O and H at all. The equilibrium of reaction 2, 4-6, 13 and 14 is shifted right at high temperature. Methane and ammonium do not form at high temperature and moderate pressure in systems of conventional composition. Higher temperature promotes formation of these substances while simultaneously blocking dissociation as described by the equations (reactions 3 and 10-14).

For practical purposes aluminum and magnesium experience combustion reactions in the entire range of combustion conditions. These reactions are not shown in Table 6. It may be presumed that when oxygen is sufficient aluminum transforms quantitatively into Al_2O_{3k}, while M_g transforms into MgO_k. In the presence of chlorine and fluorine Na, K and α_i transform into the appropriate halides, while in the absence of these elements they transform into oxides, hydroxides or carbonates.

Finally the equilibrium of the reaction of water gas establishes itself in accordance with the size of the equilibrium constant of reaction 1 at the given temperature and concentration of carbon, hydrogen and oxygen in the system.

4.2. High Pressure

At high pressure, in the range within which the equation of state for an ideal gas becomes inapplicable, the expression for the equilibrium constant becomes more complex. In an isothermic process

$$dG = Vdp^{\,x)} \qquad (4.I)$$

At $V = RT/P$ (Clapeyron's equation) we get

$$dG = RT\,d\ln p \quad \text{and} \quad \Delta G = RT\ln(p/p_0) \qquad (4.2)$$

This is the source of the simple relationship (3.5).

At high pressure $V \neq RT/P$, relationship (4.2) breaks down, and a dependence arises between the equilibrium constant (3.5) and pressure. The effect of pressure on the equilibrium constant may be determined by Lewis' method by substituting partial pressure in (3.5) by fugacity:

$$f = \varphi(T)e^{\frac{\Delta G}{RT}} \quad \text{or} \quad d\ln f = \frac{dG}{RT} = \frac{VdP}{RT} \qquad (4.3)$$

---

x) $dG = d(H - TS) = Vdp - SdT$, at $T = Const$ we get (4.I)

Integrating, we get

$$\ln(f/f_0) = \frac{1}{RT}\int_{P_0}^{P} V\,dP$$

We introduce the coefficient of activity $\gamma_a = f/P$; $(\gamma_a^0 = f_0/P_0)$:

$$\ln(\gamma_a/\gamma_a^0) = \ln(P_0/P) + (1/RT)\int_{P_0}^{P} V\,dP \qquad (4.4)$$

We represent volume as $V = RT/P - \Delta V$ (correspondingly, $\Delta V = (RT/P) - V$), and we account for the fact that as $P_0 \to 0$, $\gamma_a^0 \to 1$ and $\ln \gamma_a^0 \to 0$. Then

$$\ln \gamma_a = -\frac{1}{RT}\int_0^P \Delta V\,dP \qquad (4.5)$$

Usually the coefficient of activity is found by approximate integration of (4.5). Having the isotherm $V(P)$ for a real gas, we plot the curve $\Delta V = RT/P - V = \Delta V(P)$. The area between this curve and the abscissa from 0 to P is proportional to the logarithm of the activity coefficient at pressure P. For oxygen at 0°C and carbon dioxide at 60°C, at a pressure of $2 \cdot 10^7$ Pa $\gamma_a = 0.87$ and 0.45 respectively, while for carbon monoxide at $1.2 \cdot 10^8$ Pa, $\gamma_a = 2.22$. If a simple analytical expression is obtained for the isotherm of a real gas, the coefficient of activity may be found by quadrature.

Thus expressing $V(P)$ as in formula (3.6):

$$V = \frac{RT}{P} + V_k \quad \text{и} \quad \Delta V = -V_k = \mathrm{Const}$$

we get

$$\ln \gamma_a = +\frac{PV_K}{RT} = +\frac{P_0V_0}{RT_0}\cdot\frac{V_K}{V_0}\cdot\frac{P}{P_0}\cdot\frac{T_0}{T} = +\frac{V_K}{V_0}\,\frac{P}{P_0}\,\frac{T_0}{T}$$

At $V_K/V_0 = 1.10^3$, $P/P_0 = 5{,}000$ and $T_0/T = 1\cdot10^{-1}$, we get $\ln \gamma = +0.5$; $\gamma = 1.65$.

When we find the equation of state with virial coefficients (3.12) applicable,

$$V = \frac{RT}{P}\sigma(x),$$

where

$$\sigma(x) = 1 + x + 0{,}625x^2 + 0{,}287x^3 + 0{,}193x^4$$

$$x = B_2/V, \qquad B_2 = \Sigma n_i B_{2i}.$$

B_{2i}--second virial coefficient for 1 mole of the given reaction product (see Table 4),

$$\ln \gamma_i = \int_0^x \frac{\sigma - 1}{x}\,dx - \ln \sigma + \frac{nB_{2i}}{B_2}(\sigma - 1) \qquad (4.6)$$

Knowing the activity coefficient γ_{ai} and substituting partial pressure by fugacity in the formula for the equilibrium constant (3.5), we get

$$K_f = \Pi f_i^{\nu_i} = \Pi(f_i^{\nu_i}/p_i^{\nu_i})p_i^{\nu_i} = \Pi\gamma_{ai}^{\nu_i}\,\Pi p_i^{\nu_i} = K_a\,\Pi p_i^{\nu_i} \qquad (4.7)$$

Here the Π symbolizes multiplication of fugacities (or partial pressures) of the reagents to a power consistent with the reaction's stoichiometric coefficient ν_i (for substances in the right side of the reaction equation $\nu_i>0$, and for substances in the left side $\nu_i<0$).

Thus at high pressure we can use the partial pressures (and molar fractions) of the components to calculate equilibrium processes, but the equilibrium constant of the appropriate reaction, K_p (at a given temperature), must be divided by $K_a = \Pi \gamma_{ai}^{\nu_i}$, where the coefficients of activity γ_{ai} are calculated with formula (4.5) and the signs of the stoichiometric coefffients ν_i are determined by the rule given at the end of the previous section.

For the reaction of water gas (No 1, Table 6):

$$CO_2 + H_2 \rightleftharpoons CO + H_2O$$

$$\frac{P_{CO}\cdot P_{H_2O}}{P_{CO_2}\cdot P_{H_2}} = K' = K_p \frac{\gamma_{a\,CO_2}\cdot \gamma_{a\,H_2}}{\gamma_{a\,CO}\cdot \gamma_{a\,H_2O}}$$

For the CO_2 dissociation reaction (No 2):

$$\frac{P_{CO}P_{O_2}^{1/2}}{P_{CO_2}} = \frac{n_{CO}\sqrt{n_{O_2}P/n_0}}{n_{CO_2}} = K_2' = K_2 \frac{\gamma_{a\,CO_2}}{\gamma_{a\,CO}\sqrt{\gamma_{a\,O_2}}}$$

At very high pressure and for reactions in condensed phase, it would be more convenient to use equation (4.4), integrating it in parts:

$$\ln\frac{\gamma_a}{\gamma_a^0} = \frac{1}{RT}\left[(PV - p_0V_0) - \int_{V_0}^{V} P\,dV\right] - \ln P/P_0$$

As follows from section 3.3., functions $P(V)$ are usually given in explicit form while functions $V(P)$ are given in implicit form.

If we write pressure in the form (3.30) and (3.52) at $\Gamma/V = \Gamma_0/V_0$, $V_0 >> V$ and

$$P = P_x(V) + \frac{\Gamma(V)\,C_V^{(1)}T}{V} - \frac{16\,E_x V_x^4}{V^5} - \frac{8\,E_x V_x^2}{V^3} + \left(\frac{\Gamma_0}{V_0}\right)C_V^{(1)}T,$$

then we get the following simple formula for the coefficients of activity from (4.8):

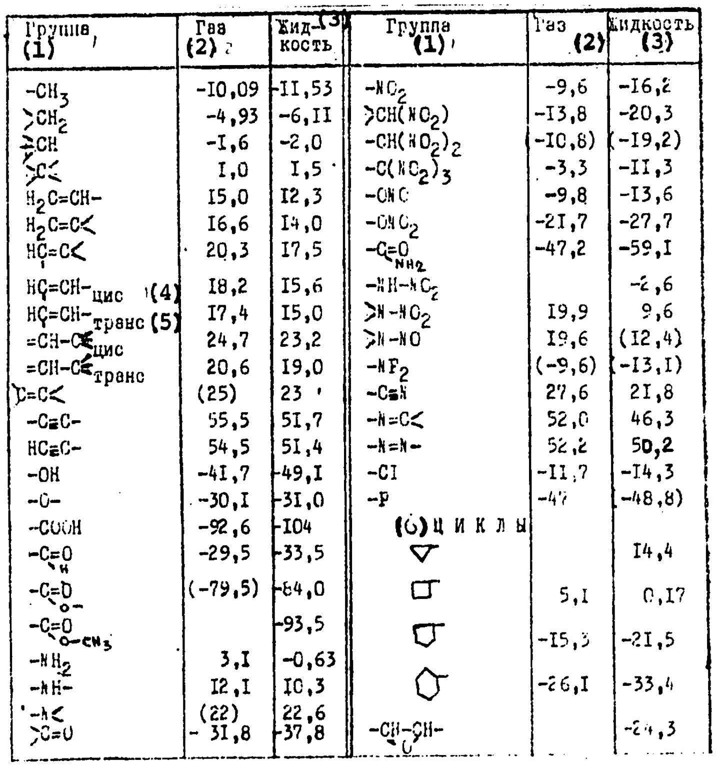
$$\ln\frac{\gamma}{\gamma_q^{T_0}} = \frac{4\varepsilon}{RT}\left[5\left(\frac{V_*}{V}\right)^4 - 3\left(\frac{V_*}{V}\right)^2\right] + \Gamma_0 C_v^{(1)}/R - \ln\frac{P}{P_0} \qquad (4.9)$$

5. Enthalpy of Formation

Besides the equation of state , the equilibrium constants and the dependence of intrinsic energy or enthalpy on temperature, to calculate the thermodynamic relationships in combustion and explosion products we need to know the enthalpy of formation of the initial substances and the reaction products. The enthalpies of formation of organic compounds--the principal ingredients of combustible and explosive systems--are obtained mainly by measuring the heats of combustion reactions in a calorimetric bomb. Values obtained in this fashion are tabulated in handbooks (3,6,12). Some of the values used most often are given in the Appendix in (5). At the same time in view of the tremendous diversity of organic compounds on one hand and the complexity and high cost of reliably determining enthalpy of formation on the other, methods of calculating this variable are under intensive development.

All existing methods of calculating enthalpy of formation , as well as a number of other thermodynamic variables (entropy, Gibbs' energy, specific heat), are based on the principal of additive contributions by groups and bonds. Table 1 in the Appendix compares some methods in application to a number of organic substances, as studied in a degree project conducted by I. Ye. Esterman (1977). It also gives the results of his calculations for group contributions obtained by Esterman and V. M. Reykova from an analysis of formerly published experimental values of ΔH_f. These contributions are brought together in tables 7 and 8. Table 1 in the Appendix gives the differences (in kcal/mole) between the ΔH_f values obtained

Table 7. Contributions of Functional Groups to Enthalpy of Formation of Aliphatic Compounds (From Data Cited by I. Ye. Esterman and V. M. Raykova)



Группа (1)	Газ (2)	Жидкость (3)	Группа (1)	Газ (2)	Жидкость (3)
$-CH_3$	-I0,09	-II,53	$-NO_2$	-9,6	-I6,2
$>CH_2$	-4,93	-6,II	$>CH(NO_2)$	-I3,8	-20,3
$\geq CH$	-I,6	-2,0	$-CH(NO_2)_2$	(-I0,8)	(-I9,2)
$>C<$	I,0	I,5	$-C(NO_2)_3$	-3,3	-II,3
$H_2C{=}CH-$	I5,0	I2,3	$-ONO$	-9,8	-I3,6
$H_2C{=}C<$	I6,6	I4,0	$-ONO_2$	-2I,7	-27,7
$H\underset{\vert}{C}{=}C<$	20,3	I7,5	$-C{=}O$ NH_2	-47,2	-59,I
$H\underset{\vert}{C}{=}CH-$ цис (4)	I8,2	I5,6	$-NH-NO_2$		-2,6
$H\underset{\vert}{C}{=}CH-$ транс (5)	I7,4	I5,0	$>N-NO_2$	I9,9	9,6
$=CH-C\leq$ цис	24,7	23,2	$>N-NO$	I9,6	(I2,4)
$=CH-C\leq$ транс	20,6	I9,0	$-NF_2$	(-9,6)	(-I3,I)
$>C{=}C<$	(25)	23	$-C\equiv N$	27,6	2I,8
$-C\equiv C-$	55,5	5I,7	$-N{=}C<$	52,0	46,3
$HC\equiv C-$	54,5	5I,4	$-N{=}N-$	52,2	50,2
$-OH$	-4I,7	-49,I	$-Cl$	-II,7	-I4,3
$-O-$	-30,I	-3I,0	$-F$	-47	(-48,8)
$-COOH$	-92,6	-I04	(6) Циклы		
$-C{=}O$ H	-29,5	-33,5	▽		I4,4
$-C{=}O$ $O-$	(-79,5)	-84,0	□	5,I	0,I7
$-C{=}O$ $O-CH_3$		-93,5	⬠	-I5,3	-2I,5
$-NH_2$	3,I	-0,63			
$-NH-$	I2,I	I0,3	⬡	-26,I	-33,4
$-N<$	(22)	22,6			
$>C{=}O$	-3I,8	-37,8	$-CH-CH-$ O		-24,3

Note: Contributions obtained from the enthalpy of formation of one compound are given in parentheses. Contributions are given in kcal/mole, 1 kcal = 4.184 kj.

Key:
1. Group
2. Gas
3. Liquid
4. Cis
5. Trans
6. Rings

experimentally (usually the averages of several sources) and values obtained by calculation. Comparative calculations using six to eight methods were made for 100 compounds. From one to three compounds were chosen by chance to represent many of the examined series. Omissions of figures in the table mean that ΔH_f^0

Table 8. Contributions by Functional Groups of Liquid Aromatic Compounds

Заместители со слабым взаимодействием (1)		Заместители с сильным взаимодействием (2)		
$-CH_3$	-11,53	$-NO_2$		(-10,4)
$-O-$	-31,7	$>N-NO_2$		+23,2
$-OH$	-49,1	$-NH_2$		-6,3
$C\ll^{O}_{H}$	-33,9	$>NH$		+4,4
$>C=O$	-36,6	$>N-$		+16,8
$-COOH$	-101	$-NH-NH_2$		+18,4
$-C\ll^{O}_{NH_2}$	(-58)	C_6H_5	газ (3)	21,64
$-C\ll^{O}_{NH-}$	(-47,6)		жидк (4)	14,41
$-C\equiv N$	(+24,5)	C_6H_x	газ	$35,49-2,77x$
$-Cl$	-11,5		жидк	$28,06-2,73x$
$-F$	-49,5			

Key:
1. Substituents exhibiting weak interaction
2. Substituents exhibiting strong interaction
3. Gas
4. Liquid

Table 9. Energy of Interaction Between Functional Groups in Aromatic Compounds

	Ortho-	Meta-	Para-
NO_2, NO_2	8,8	2,3	0,8
CH_3, NO_2	1,9	1,3	-1,3
OH, NO_2	1,4	-1,4	-2,8
$-O-$, NO_2	2,1		1,4
NH_2, NO_2	0,8	0,5	-4,0
NH, NO_2	2,2		-3,4
$COOH$, NO_2	3,7	0,85	0,50
CH_3, OH	-2,2		
Cl, Cl	1,6	0,9	
F, F	2,9	2,3	1,3

All values are given in kcal, 1 kcal = 4.184 kj could not be calculated by the given method for the particular compound. We can see from the table that the accuracy of Esterman's method is at least no worse than that of those published to date. Its advantage lies in the possibility of obtaining ΔH_f both for gases and for liquids and in the great assortment of contributions by functional groups.

In the case of solids the enthalpy of melting must be subtracted from the liquid's enthalpy of formation. If it is not available in the handbook for the given compound, Val'den's rule may be used: $\Delta H_m = 56.5 T_m$, j/mole.

In the case of compounds with several functional groups, the action of the groups upon one another must be accounted for. Groups exhibiting strong interaction are separated in Table 8 from those exhibiting weak interaction. The effects of group interaction in aromatic compounds are described in Table 9.

Nitrogroups interact with one another especially strongly.

The increase in enthalpy of formation associated with presence of two or more nitro groups in the same molecule should also be accounted for in calculations associated with the aliphatic series. It has been noted in this case that the interaction effect, which expresses itself as growth of ΔH_f that is greater than can be explained by "additive" growth (as calculated using the data in Table 7), weakly depends on the aggregate state of the substance (be it a gas or a liquid), but it decreases intensively as the NO_2 groups move farther apart. For neighboring nitro groups the interaction effect is 16-20 kj per paired interaction, while for crosswise nitro groups attached to neighboring carbon atoms $[C(NO_2)-CH_2-C(NO_2)]$ the interaction effect is about 4 kj. Nitro groups that are farther apart parctically do not interact with each other $(\Delta(\Delta H) \approx 0$: 1 kj per paired interaction).

6. Calculation of the Composition and Thermodynamic Characteristics of Combustion and Explosion Products

6.1. Statement of the Problem

The main problem of thermodynamic calculation is to determine the equilibrium composition and functions of state of the combustion and explosion products. Inasmuch as the enthalpy or intrinsic energies of the products are given as the dependencies of these variables on temperature and the expressions for the equilibrium constants include pressure, the main parameters of state considered in such calculations are temperature and pressure. Knowing the equilibrium composition and functions of state of combustion products at given P and T, we can solve a large number of technical problems. The main ones are: 1) calculating the composition, heat, temperature and other thermodynamic characteristics of combustion products in adiabatic conditions at $P = \text{const.}$ (1a) and at $V = \text{const.}$ (1b); 2) calculating expansion of combustion and explosion products (change in composition of the products and in the functions of state during expansion, calculating the rate of flux and the work of expansion); 3) calculating the cooling of combustion products at $V = \text{const.}$; 4) calculating the thermodynamics of processes in shock waves.

The first of the above problems entails thermodynamic description of combustion (or more precisely, its end results) in isobaric and isochoric processes. The second provides information on isentropic expansion of gaseous products formed in the course of an isobaric, isochoric or some other combustion process.* The third problem is associated with isochoric cooling of combustion and explosion products. These idealized situations are very close to real situations in a number of cases.

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*Note that all of these processes are adiabatic.

Combustion proceeds at practically constant pressure in air, in the combustion chamber of a jet engine operating under steady-state conditions and in apparatus used to measure the rate of combustion of explosives and powders, aptly named a "constant pressure bomb." An isochoric process occurs when powder is burned in a manometric bomb and, as a certain approximation, in the barrel of an artillery weapon. The end products of a gas's combustion in a constant volume bomb* and, once again as a certain approximation, in the cylinder of an internal combustion engine, and the products of detonating an explosive in a Bikhel' bomb (see below) are consistent with those obtained as a result of an isochoric process.

Isentropic expansion of a gas is typical of what occurs in the nozzle section of a rocket engine, of processes following detonation of an explosive charge in air, and of the discharge of powder combustion products out of a gun barrel. It stands to reason that losses due to friction and heat exchange may be ignored in far from all of these cases, but adiabatic and isentropic processes are basically the most significant.

When solving these problems we should turn special attention to the range of pressures and temperatures within which the given process is examined. At pressures up to thousands of atmospheres and temperatures above 1,000° the behavior of combustion products may be described with good accuracy (not less than [symbol illegible]) using the equations of state of an ideal gas. When powder burns in a fire weapon and in conventional artillery, pressure attains 4,000-5,000 atm. At such pressures we should use the equation of state containing virial coefficients. When

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*Combustion of a gas in a bomb of constant volume proceeds at constant temperature for the most part. It is only after all of the gas burns and the reaction products in the bomb mix together that temperature and pressure in keeping with an isochoric combustion process (the Mache effect) are established.

condensed explosives are detonated, a pressure on the order of tens and hundreds of thousands of atmospheres is generated. In this case we would have to use the Mi-Gryunayzen equation (3.30). However, as the combustion or detonation products expand, the pressure within them drops, and beginning with a value on the order of 1,000 atm the equation for an ideal gas once again becomes applicable. Thus the simplest method of thermodynamic description of combustion and explosion products enjoys a very broad area of application.

Precise thermodynamic calculation of combustion and expansion processes is extremely cumbersome, and it requires high-speed computers. A detailed description of such calculations in application to combustion of powder in a rocket chamber is given in (13), and it is described in application to liquid-fueled rocket engines in the handbook (4).

It should be noted, however, that in many cases the accuracy of such calculation is intentionally excessive. On one hand the enthalpies of formation of the initial substances--fuels, oxidants, explosives and the ingredients of explosives and solid rocket propellents, which are industrial-grade products usually of complex composition with a low degree of purity, are only extremely moderate in their reliability. On the other hand while the error of calculating a combustion process with a computer is within hundredths of a percent, the deviation of a combustion process from the calculated values (resulting from absence of equilibrium, deviations from ideal conditions, losses not considered by the calculations) is several percent as a rule, and frequently it is 10 percent and more, for example in the case of calculations for detonation of explosive charges. For this reason engineers still make broad use of simplified variants of thermodynamic calculation that may be performed manually or with small computers, and they will be used for a long period to come. One such method will be analyzed below.

6.2. Composition and Thermodynamic Characteristics of Combustion Products at Low ($P \leqslant 10^8$ Pa) Constant Pressure

The calculations are made with the assumption of an adiabatic system, existence of thermodynamic equilibrium and applicability of the equation of state for an ideal gas.

To perform the calculations, we need to know:

1) The elemental composition of the initial system;

2) the enthalpy of formation of the initial substances and the expected transformation products;

3) the equilibrium constants for the hypothesized reactions;

4) dependence of enthalpy, intrinsic energy or the specific heat of products on temperature;

5) pressure.

Systems containing the following elements are subjected to analysis: C, H, O, N, Al, Mg, Cl, F. When the composition of the system changes, the system remains the same but the calculation formulas must be reexamined.

We find the "empirical formula"--the elemental composition of 1 kilogram of fuel or explosive system. We make the calculations using formula (1.7). By subsequently summing the products of the number of moles and their atomic weight, we verify the calculations. The accuracy of our calculations is generally within several tenths of a percent. The total weight must not deviate from 1 kg by more than 1 gm.

We determine the "enthalpy of formation" of the initial system (once again in relation to 1 kg of the mixture). Enthalpy is an additive function of state, and therefore

$$\Delta H_{f,in} = \Sigma r_j \Delta H_{fj}, \qquad (6.1)$$

where $n_j = g_j/M_j$--the number of moles of the given compound in 1 kg of the explosive system;

$\Delta H_j = \Delta H^0_{f,j}$ --enthalpy of formation of compound j. The latter is found from tables given in (3,6,9), or it is calculated with the help of tables 7-9, or it is taken from other handbooks.

For substances containing oxygen we calculate the oxygen balance (1.8) or the coefficient of excess oxidant (1.9).

We calculate the composition of the transformation products in the zero approximation on the assumption that reactions No 3 and 7-15 are shifted fully leftward while reactions No 4-6 are shifted fully to the right--that is, that NO, NH_3, CH_4 and dissociation reaction products do not form.

When aluminum or magnesium is present in the initial substance, Al_2O_3 and MgO form (in the presence of boron or silicon we get B_2O_3 and SiO_2). Excess oxygen in the initial system oxidizes carbon and hydrogen. Nitrogen and excess oxygen are present as N_2 and O_2.

Chlorine and fluorine react with hydrogen to produce HCl and HF, and excess halogen (if it is present) is liberated as Cl_2 and F_2.

Excess carbon takes the form of carbon black.

Thus there are no difficulties in setting up the equation for the combustion reaction in the zero approximation: Oxygen is consumed first to form Al_2O_3 and MgO, and then to form CO, CO_2 and H_2O. If oxygen is lacking, hydrogen, carbon and then the metal are liberated in elemental form.

Hydrogen is used up to form HCl and HF, and then H_2O, while excess hydrogen is liberated as H_2.

Here are some examples of writing the equations for combustion reactions proceeding at not too high a pressure, in the zero approximation.

Trotyl:

$$C_7H_5N_3O_6 \rightarrow 6CO + C + 2,5H_2 + I,5N_2$$

Dinitrochlorobenzene:

$$C_6H_3N_2O_4CI \rightarrow HCI + 4CO + 2C + H_2 + N_2$$

Nitroglycerin:

$$C_3H_5N_3O_9 \rightarrow 3CO_2 + 2,5H_2O + I,5N_2 + 0,25O_2$$

Hydrazine:

$$N_2H_4 \rightarrow 2H_2 + N_2$$

Mixture of dichloroethane and nitric acid (51:49):

$$I,5HNO_3 + C_2H_4CI_2 = C_2H_{3,5}O_{4,5}CI_4 \rightarrow 2CO_2 + 3,5HCI + 0,25CI_2 + 0,75N_2$$

It would be more convenient to calculate the composition of complex mixtures in gram-atoms of the components per 1 kg of the mixture. For example ammonal 80/20 contains 80 percent ammonium nitrate by weight and 20 percent aluminum by weight. Assuming that ammonium nitrate and aluminum are pure and rounding off the atomic weights, our calculations produce the following figures, per kg:

$$n_{NH_4NO_3} = 0,8/0,080 = 10, \quad n_{AI} = 0,2/0,027 = 7,4 \; (n_H=40, \; n_N=20, \; n_{(O)}=30, \; n_{AI}=7,4).$$

In the zero approximation the combustion reaction is:

$$10\,NH_4NO_3 + 7,4\,AI \rightarrow H_{40}N_{20}O_{30}AI_{7,4} \rightarrow 3,7\,AI_2O_3 + I8,9H_2O + I,IH_2 + I$$

A slight complication arises when CO, CO_2, H_2 and H_2O are present simultaneously among the combustion products (this happens if

$$\alpha < I, \quad n_C < [n_{(O)} - 3/2n_{AI} - n_{Mg}], \text{and } n_H > [n_{CI} + n_F]).$$

The ratio between the concentrations of these substances is determined by the equilibrium equation for the water gas reaction (No 1, Table 6). Considering this equation and the equations for the carbon, oxygen and hydrogen balance,

$$n_{CO} + n_{CO_2} = n_C \ ; \ n_{CO} + 2n_{CO_2} + n_{H_2O} = n_C + n_{CO_2} + n_{H_2O} = n_{(0)} \ ; \ 2n_{H_2} + 2n_{H_2O}$$

we get a simple formula for the concentration of CO_2:

$$n_{CO_2} = \frac{\sqrt{a^2 + Kb} - a}{K} , \qquad (6.2)$$

where $a = \frac{1}{2}\left\{\left[n_C + (n_H^0/2)\right]K_I - n_{(0)}^0 K\right\}$; $b = n_C(n_{(0)}^0 - n_C)$

$K = K_I - 1$; $n_{(0)}^0 = n_{(0)} - \frac{3}{2}n_{Al} - n_{Mg}$; $n_H^0 = n_H - n_{Cl} - n_F$,

in which case $n_{(0)}^0 > n_C$ and $n_H^0 > 0$

The dependence of constant K_1 on temperature is given by formula (1) in Table 6, or it can be read from Table 10.

Table 10. Dependence of the Equilibrium Constant for the Water Gas Reaction on Temperature

T,K	300	600	1000	1500	2000	2500	3000	3500	40
K_I	0,000	[illegible]	0,73	2,67	4,66	6,07	7,13	7,83	8,

At constant ~~temperature~~ pressure the temperature of combustion required for selection of K_1 may be estimated by means of the approximate formula:

$$T_{op.} = 500 + 10^3 A/B , \qquad (6.3)$$

where $A = 255n_{(0)} - 142n_C + 787n_{Al} + 602n_{Mg} + 92,5n_{Cl} + 269n_F + \Delta H$ kj/kg

$B = 17,4n_C + 20,3n_{(0)} + 17,7n_H^{(0)} + 18,5n_N + 73,2n_{Al} + 57n_{Mg} + 36,7n_{Cl} + 35,5n_F$

Knowing the composition of the transformation products, we can determine the temperature of the combustion products at constant pressure ($T_p{}^0$) on the condition that the enthalpy of the reaction at 298°K is equal to the difference between the enthalpies when the combustion products are cooled from T_p to 298°K:

$$\Delta H_r = \sum n_i\left[H(T_0) - H(T_p)\right] = -\sum n_i \Delta H(T_p) \qquad (6.4)$$

$$\Delta H_r = 10^3\left[393{,}5n_{CO_2} + 110{,}5n_{CO} + 241{,}8n_{H_2O} + 1675n_{Al_2O_3} + 602n_{MgO} + 92{,}3n_{HCl} + 269n_{HF} + \Delta H_{fuel}\right]\cdot \text{j/kg}$$

The data in Table 1 are sufficient for determination of $\sum n_i \Delta H(T_p)$ in the zero approximation:

$$\sum n_i \Delta H(T_p) = \sum n_i \xi_i (T_p - T_i) = (T_p^0 - 500)B_1 + (T_p^0 - 700)55{,}6n_{H_2O} + (T_p^0 + \lambda)(\xi n)_{Al_2O_3}, \quad \text{cal/kg}$$

where $B_1 = 61{,}1n_{CO_2} + 37{,}7n_{CO} + 37{,}1n_{N_2} + 35{,}4n_{H_2O} + 39{,}3n_{O_2} + 36{,}7n_{HCl} + 35{,}5n_{HF} + 56{,}9n_{MgCl_2}$

At $1000 < T_p < 2200K$ $\quad \lambda = -400K, \quad \xi = 130$ j/mole·°K

At $2400 < T_p < 6000K$ $\quad \lambda = +200K, \quad \xi = 146$ j/mole·°K

We can obtain the adiabatic temperature of the reaction at constant pressure from equality (6.4):

$$T_p^0 = \frac{\Delta H_r + \sum n_i \xi_i T_i}{\sum n_i \xi_i} = 500 + \frac{1}{B_2}\left\{\Delta H_r + 11130n_{H_2O} - (500 + \lambda)(\xi n)_{Al_2O_3} + 5440n_C\right\}, \quad (6.5)$$

where $\quad B_2 = B_1 + 55{,}6n_{H_2O} + (\xi n)_{Al_2O_3} + 27{,}1\,n_C$

The specific gas constant is

$$R = n_0 R_0, \quad n_0 = \sum_{газ} n_i \qquad (6.6)$$

The specific heat of the products in the vicinity of T_p is:*

$$C_p = 10^{-3}\sum n_i \xi_i = 10^{-3}B_2; \quad C_v = C_p - R; \quad \gamma = C_p/C_v \qquad (6.7)$$

---

*When the error in the size of $\Delta H(T)$ (and correspondingly of $\overline{C}_p$ and $\overline{C}_V$) given by the formulas of Table 1 is small (<1 percent), the error in the size of $C_p(T)$ and $C_V(T)$ may be much greater (by several orders of magnitude). Therefore the C_p and C_V values given by formulas (6.7) should be interpreted only as tentative. It stands to reason that the error decreases when we calculate r.

The mean specific heat of products in the interval from 298°K to T_p^0 is:

$$\bar{c}_p = \frac{-\Delta H_r}{T_p - 298} 10^{-3}; \quad \bar{c}_v = \bar{c}_p - R; \quad \bar{\Gamma} = \bar{c}_p/\bar{c}_v \qquad (6.8)$$

The adiabatic temperature of the reaction at constant volume is:

$$T_v^0 = \Gamma \, T_p^{0*} \qquad (6.9)$$

The heat of combustion Q_p and the heat of "explosion" Q_V are:**

$$Q_p = -10^{-3} \Delta H_r , \quad Q_v = Q_p + n_0 R_0 T_0 = Q_p + 2{,}47 n_0, \text{ kj/kg} \quad (6.10)$$

The "heat of explosion in the presence of liquid water" is:

$$Q_l = Q_v + 44{,}0 \, n_{H_2O} , \quad \text{kj/kg} \qquad (6.11$$

The proportion of condensed combustion products by weight is:

$$g_k = 0{,}012 n_C + 0{,}102 \, n_{Al_2O_3} + 0{,}0403 \, n_{MgO} \qquad (6.12)$$

The average molecular weight of gaseous products is:

$$\bar{M} = (1 - g_k)/n_0 , \quad \text{kg/mole} \qquad (6.13$$

The values given here for heats Q_p, Q_V and Q_l require clarification. The fact is that the first two are conditional. Q_p is that quantity of heat which would be released upon cooling of combustion products from T_p to $T_0 = 298$°K at constant pressure without change in the composition of the products (or as it is put in another way, at a completely "frozen" equilibrium). Q_V is also conditional. It is used only to describe the thermal effect of the burning of condensed substances,

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*For the derivation of formula (6.9), see below, p 68).

**In a thermodynamic system the enthalpy of a combustion reaction is a large negative value in terms of its modulus. Inasmuch as specialists in combustion and explosion have become accustomed to the fact that the heat of combustion is characteristically positive, it would be useful to introduce the variables $Q_p = -\Delta H_r$ and $Q_V = -\Delta H_r + RT_0$.

and it includes, in addition to Q_p, work against the forces of external pressure in the presence of isobaric expansion from the initial volume, which may be adopted equal to 0, to the volume which the gaseous combustion products occupy at 298°K. This work is $p_0V_0 - n_0R_0T_0 \approx 2{,}47n_0$ kj/kg.

Q_l is more realistic. It is the quantity of heat released upon cooling of combustion products in a calorimetric bomb (that is, at constant volume). Besides heat Q_V, it includes the heat of condensation of water vapor at 298°K (44.0 kj/mole). The heats of condensation and dissolution of HCl and HF and the heats of fusion of Al_3O , MgO and other substances, the phase constants of which differ at combustion temperature and normal temperature, should be treated in similar fashion.

In the case of CHNO systems, which form neither free carbon nor free oxygen when burned ($\alpha_0<1$, $n_{\delta}>n_C$), Q_l exhibits a unique feature: In view of the practical thermal neutrality of the water gas reaction, as calculated in terms of liquid water, it does not depend on the extent to which the equilibrium is shifted upon cooling. And in fact, when the temperature decreases the equilibrium of reaction 1 in Table 6 shifts leftward, in the direction of CO_2 formation. The rate of this reaction decreases simultaneously as well, such that at a certain temperature that is not too low (about 1,500°K) the typical cooling time becomes much shorter than the time of the reaction, and the equilibrium "freezes." Depending on the cooling conditions (the volume of the bomb, the pressure within it) the temperature and consequently the "frozen composition" of the combustion products of a certain combustible substance may be different. However, in view of the thermal neutrality of the reaction $CO_2+H_2 \rightleftarrows CO+H_2O_{liquid}$, the resulting effect (the value of Q_l) would remain the same. Other reactions, for example 2, 4 and 7 in Table 6, do not exhibit this capability: Their final thermal effects depend on the depth of transformation at which the reaction stops. This situation is capitalized upon in the so-called (De Pou) method of determining the heat of explosion. Most smokeless powders do not form carbon (soot) and oxygen when burned. And yet many powder components may produce soot (or O_2) when burned in the absence of air. If we measure the contribution of these substances to the heat of combustion of powder directly, the obtained heat would depend strongly on the testing conditions, and moreover it would differ significantly from the heat released upon combustion of the given substance in a powder mixture. In order to avoid this uncertainty we burn the substance under analysis in a mixture with a high-calorie powder, the heat of combustion of which is well known, and at a ratio of ingredients that would satisfy the condition $\alpha_0 < 1, n^0_{(b)} > n_t$. The composition of combustion products is governed by the equation for the water gas reaction, it does not depend on the cooling conditions, and the thermal effect characterizes the contribution made by the given ingredient to the heat of explosion of any powder having a composition that satisfies the condition given above. This contribution may be easily calculated *a priori*. Let substance i consist of carbon, hydrogen, nitrogen and oxygen. Then the following basic reactions would proceed in the combustion products of this substance mixed with a high-calorie powder:

$$(1)\begin{cases} C + CO_2 \rightarrow 2CO + 172{,}4 \\ C + H_2O_{\text{ж}} \rightarrow CO + H_2 + 175{,}3 \end{cases} \quad \Delta H_{cp} = +174 \text{ kj/mole C}$$

$$(2)\begin{cases} \frac{1}{2}O_2 + CO \rightarrow CO_2 - 283 \\ \frac{1}{2}O_2 + H_2 \rightarrow H_2O_{\text{ж}} - 286 \end{cases} \quad \Delta H_{cp} = -284{,}5 \text{ kj/mole O}$$

The hydrogen reaction in the combustion products ($H_2 + CO_2 \rightarrow H_2O + CO$), as calculated in relation to liquid water, is almost thermally neutral. Nitrogen is inert in this approximation.

The contribution of carbon and oxygen to the heat of the combustion reaction Q_l is equal to the enthalpies of reactions (1) and (2). The contribution of substance i (in kj per 10 gm--that is, in relation to 1 percent of this substance in the powder mixture) or the so-called "thermochemical constant beta" is:

$$\beta_{Ti} = \frac{285 n_{(O)i} - 174 n_{Ci} + \Delta H_{fi}}{100 M_i}, \quad \text{kj/\%}$$

For aluminum and magnesium the contribution to Q_l is calculated using these reactions:

$$\begin{cases} 2Al + 3CO_2 = Al_2O_3 + 3CO - 826{,}6 \\ 2Al + 3H_2O_{\text{ж}} \quad Al_2O_3 + 3H_2 - 817{,}9 \end{cases} \quad H_{cp} = (-411) \quad \text{kg/mole Al}$$

$$\begin{cases} Mg + IICO_2, \quad MgO + IICO - 318{,}9 \\ Mg + H_2O_{\text{ж}} \quad MgO + H_2 - 316{,}0 \end{cases} \quad H_{cp} = (-318) \quad \text{kj/mole Mg}$$

The thermochemical constants are:

$$\beta_{T\,Al} = 152 \text{ kj/\%} \qquad \beta_{T\,Mg} = 132 \text{ kj/\%}$$

The β_{Ti} values obtained in this fashion may be used to quickly estimate the effectiveness of a particular substance as an ingredient of smokeless powder (or secondary explosive having a composition satisfying the condition $\alpha_0 < 1$, $n_{\delta} > n_C$).

To conclude this section we will present the derivation of formula (6.9). A reaction proceeding at constant volume satisfies the relationship:

$$Q_V = \sum \Delta E_i (T_V),$$

where Q_V--heat of reaction at $V = \text{const.}$, $\Delta E_i (T_V)$--intrinsic energy of combustion products at $T = T_V$. Considering (6.10), we write

or
$$Q_v = Q_p + RT_0 = \sum n_i H_i(T_v) - R(T_v - T_0) = \sum n_i f_i (T_v - T_i) - RT_v + RT_0$$

Hence
$$Q_p = \sum n_i f_i (T_v - T_i) - RT_v$$

$$T_v = \frac{Q_p + \sum n_i f_i T_i}{\sum n_i f_i - R} = \frac{Q_p + \sum n_i f_i T_i}{C_v}$$

Having in mind that

$$\frac{Q_p + \sum n_i f_i T_i}{C_p} = T_p, \qquad (6.5)$$

we finally arrive at

$$T_v = T_p \frac{C_p}{C_v} = r' T_p \qquad (6.14)$$

Note that although the "instaneous" specific heats C_p and C_v are calculated with a significant error, as is noted in the footnote on p 65, the error of r is much smaller and the reliability of T_v is practically the same as of T_p.

It should be emphasized that the well known formula $T_v = \bar{r} T_p$ is wrong when the composition of the combustion products remains constant. Its derivation does not account for the fact that the average specific heats in the interval T_p-T_v increase, and as function $H(T)$ approaches linearity they increase in such a way that we arrive at formula (6.14). If as a result of the water gas reaction the composition of the products changes, growth in specific heat in response to increasing temperature slows down, and we can then use the formula $T_v = \bar{r} T_p$ (which is easily obtained from the equalities

$$Q_p = \bar{C}_p(T_p - T_0), \quad Q_v = \bar{C}_v(T_v - T_0), \quad Q_v = Q_p + RT_0, \quad \bar{C}_p = \bar{C}_v + R\ )$$

6.3. Refined Calculation of the Thermodynamic Characteristics of Combustion Products

The principal values obtained in calculation of the thermodynamic characteristics of combustion products are adiabatic temperature T_P (or T_V), $R = n_0 R_0$ and $r = C_P/C_V$. As was noted earlier, acquisition of these values by calculation in the zero approximation would be sufficient in a number of cases of evaluating the performance of explosive or powder. The dependability of this approach is verified by calculating the concentration of the dissociation and reaction products (3-7). At temperatures below 2,000°K and high pressure formation of methane, ammonium and (in the presence of excess carbon) carbon dioxide is most probable, while at high temperature NO, Cl_2, OH, O_2, H and O form. Reduction of the pressure promotes formation of the last four substances. The concentrations are found by formulas given in Table 6. For example,

$$n_{OH}^{(0)} = K_1(T_p^0)\, n_{H_2O}^{(0)} \sqrt{\frac{n_0^{(0)}}{p\, n_{H_2}^{(0)}}} \quad ; \quad n_{CH_4}^{(0)} = \frac{p\,(n_{H_2}^{0})^2}{K_5(T_p^0)\, n_0} = \frac{n_{CO}^{(0)}\,(n_{H_2}^{(0)})^3}{K_4\; n_{H_2O}^{(0)}} \cdot \left(\frac{p}{n_0}\right)^2$$

If the concentration of the products of dissociation and of additional reactions is not large (less than 0.05 moles/kg for example), the zero approximation may be thought of as sufficient: The error of all of the principal calculated parameters would be less than 1 percent. If the concentrations of the secondary products are sizeable, the calculations should be continued further.

After we determine $n_i^{(0)}$ we set up the balance equations for the different elements and calculate the new values of the n initial elements ($n_j^{(0)}$). Using these values we repeat the calculation of the composition of the principal combustion products similarly as we have done in the zero approximation, after which we once again calculate the enthalpy of the reaction and the adiabatic temperature. We repeat the calculations until such time that the temperature remains constant within 10-20°K.

Another way of calculating T_p (or T_V) is to select, on the basis of the zero approximation, two temperature values close to the anticipated true value, and calculate the composition first at one value and then at the other, after which the true temperature and other characteristics of the reaction can be determined by linear interpolation (or extrapolation for a slight distance, up to 100°K).

In this case if the error of determining the heat and temperature of combustion can be within 1 percent, we can use approximate relationships for the enthalpy of the products, as given in Table 1. If greater accuracy is required we would need to use the $\Delta H(T)$ given in (3).

Table 2 of the Appendix compares the composition and thermodynamic characteristics of combustion products calculated in the zero approximation for a number of secondary explosives; the figures were obtained by computer calculation at a pressure of 300 atm. The computer calculations were run on the basis of 40 equilibrium reactions. Of the obtained products, the table contains only those for which the concentration was about 0.1 moles/kg and higher.

For 18-19 of the explosives, the approximate and precise calculations of all indicators showed good consistency at $0.35<\alpha_0<0.85$ at a temperature of $2{,}000 \leqslant T_p \leqslant 3{,}500$°K. It should be noted that most practically employed powders not containing high-calorie metals and halogens fall within this interval in terms of composition and temperature.

Temperature $T_V{}^0$ obtained for secondary explosives in the zero approximation can be related to the computer calculated temperatures (T_V) by a simple formula:

$$T_v = 700 + 0{,}80\, T_v^0 ,$$

which is valid for $0.36<\alpha_0<1.1$.

We arrive at a similar formula for nitromethane mixed with tetranitromethane and nitric acid:

$$T_v = 280 + 0{,}88\, T_v^0$$

To calculate the characteristics of the discharge of gases from the nozzle of a rocket engine we need to know the entropy of the combustion products. Entropy is calculated on the basis of the composition of the combustion products using tables showing the dependence of standard entropies S_T^0 on temperature (3).

In the zero approximation the following formula can be used if the temperature is sufficiently high:

$$S_T^P = S_{T_1}^0 + \int_{T_1}^{T} \frac{dH}{T} - R\ln\frac{P}{P_0} = S_{T_1}^0 + \sum n_i \xi_i \ln\frac{T}{T_1} - R\ln\frac{P}{P_0}$$

where $S_{T_1}^0$ is the standard entropy of a mixture of gases (to include the entropy of mixing) at atmospheric pressure and at the temperature T_1 at which the rule $\Delta H_i = \xi_i (T-T_i)$ begins to be satisfied. T_1 = 2,000°K would be a convenient choice. The $S_{i\,2000}^0$ values for some combustion products are given in

Table 11. Entropy $S_{i\,2000}^0$ of Some Combustion Products (cal/mole·°K, 1 kcal = 4.84)

O	48,0745	OH	57,8997	SiO_2	40,100
H	36,8483	NO	65,2264	(2001K)	40,109 41,029
F	47,7675	CO	61,8098		
Cl	49,5706	HF	55,293		
N	46,0706	HCl	58,835	Al_2O_3	64,879
$C_г$	47,2295	HCN	69,662	(2303K)	69,706 81,864
$C_к$	9,665	H_2O	63,314		
N_2	60,2739	N_2O	75,848	MgO	27,953
O_2	64,2119	CO_2	73,892	(3075K)	33,920 39,936
H_2	45,0081	NH_3	69,643		
F_2	64,138	CH_4	73,095		
Cl_2	70,160				

6.4. Thermodynamic Characteristics of the Products of a High Pressure Explosion

At pressures from thousands to several tens of thousands of atmospheres we perform the thermodynamic calculations with an equation of state containing virial coefficients. The results arrived at by the calculations described in section 6.2 are a zero approximation in this case. The equilibrium constants of the principal reactions (1) or (2) are found at the temperature of the zero approximation (T_P^0 or T_V^0) using the data in Table 6, and the coefficients of activity r_a of the reagents are found using formula (4.6). Then we use formula (4.7) to find coefficient K_a and a new equilibrium constant for the volume within which combustion proceeds. Using the new equilibrium constants we calculate the composition and principal thermodynamic characteristics of the combustion products. When the result differs significantly from the results obtained using the formulas in section 6.2, we repeat the calculations in relation to the new temperature values. An example of the calculations can be found in textbook (1).

At higher pressure we would have to use the Mi-Gryunayzen or the Becker-Kistyakovskiy-Wilson (BKW) equation. Equilibrium constants K_0 calculated by Zubarev and Telegrin (14) using an equation of the form (3.30) for reactions (1) and (2) are given in Table 12. Consistently with change in the equilibrium constants, as pressure rises the concentrations of CO_2 and H_2O grow while the concentrations of CO and H_2 drop. In this case the concentration of hydrogen decreases faster than that of CO. And in fact, we get the following for reactions (1) and (2) with respect to the constant values given in Table 12:

$$K'_{10} = \frac{n_{CO} \cdot n_{H_2O}}{n_{CO_2} \cdot n_{H_2}}; \quad K'_{20} = \frac{n_{CO_2}^2}{n_{CO}^2}.$$

Hence it follows that the concentration of CO is $(K'_{2C}\cdot n_{CO_2})^{1/2}$ times smaller than the concentration of CO_2 (when this relationship is disturbed in favor of CO, elemental carbon would be released).

The relationship between concentrations of H_2O and H_2 is:

$$n_{H_2O}/n_{H_2} = K'_{10}(n_{CO_2}/n_{CO}) = K'_{10}(K'_{20}\cdot n_{CO_2})^{1/2}$$

At high pressure (about 10 GPa) and excessively high temperature (up to 4,000°K) both constants are much greater than unity, and correspondingly the ratio n_{H2}/n_{H2O} is very small. Therefore significant quantities of molecular hydrogen are formed only when an excess quantity of hydrogen is present in the explosive. At high pressure (assuming a high charge density), formation of hydrogen in response to detonation of conventional explosives may be ignored.

The general formulas for calculating the composition of the explosion products of HCNO explosives are:

$$\begin{cases} n_{CO} + n_{CO_2} + n_C = n^0_C; \\ 2n_{H_2O} + 2n_{H_2} = n^0_H; \\ n_{H_2O} + 2n_{CO_2} + n_{CO} = n^0_{(O)}, \end{cases} \quad \frac{n_{CO}\cdot n_{H_2O}}{n_{CO_2}\cdot n_{H_2}} = K'_{1C}; \quad \frac{n_{CO_2}}{n^2_{CO}} = K'_{2C}, \qquad (6.15)$$

where n^0_C, n^0_H and $n^0_{(O)}$ are the concentrations of the elements in the initial explosive, moles/kg (or moles/mole). Equating $n^0_C = a$, $n^0_{(O)} = b$, $n^0_H = 2h$ and $n_{CO} = x$, and dropping some of the subscripts from the equilibrium constants, we get

$$n_{CO_2} = K_2 x^2; \quad n_{H_2O} = b - x(1 + 2K_2 x); \quad n_{H_2} = h - n_{H_2O}.$$

Substituting these expressions in the equation for K_1', we find

$$K_1 = \frac{b - x(1+2K_2x)}{K_2x\left(h - b + x(1+2K_2x)\right)}, \quad \text{or} \quad x = \frac{1}{4K_2}\left[\sqrt{1+8K_2b - \frac{8hK_1K_2}{K_1K_2+\frac{1}{x}}} - 1\right] \quad (6.16$$

Equation (6.16) is solved by the method of successive approximations. This is more convenient than solving a third power equation.

In cases where the concentration of hydrogen in explosion products may be ignored, system (6.15) simplifies to

$$x + n_{CO_2} + n_{CO} = a;\quad n_{H_2O} = h;\quad x + 2n_{CO_2} = b - h,\quad n_{CO_2} = K_2x^2.$$

Hence

$$n_{CO_2} = \frac{1}{2}(b - h - x) = K_2x^2,\quad x = \frac{1}{2K_2}\left(\sqrt{1+8K_2(b-h)} - 1\right). \qquad (6.17)$$

This expression may be used as a zero approximation when the assumption that hydrogen is absent in the products is doubtful.

Table 12. Equilibrium Constants K' for Reactions (1) and (2) (See Table 6) at High Pressure (14)

Реакция (1) (1)	(3) Температура, К				
P, ГПа (2)	2000	3000	4000	5000	6000
5	8,78	11,8	12,7	13,6	14,3
10	19,3	21,6	16,3	17,8	17,8
20	$1,33 \cdot 10^2$	72,5	45,8	37,0	29,3
40	$4,22 \cdot 10^3$	$7,17 \cdot 10^2$	$2,61 \cdot 10^2$	$1,36 \cdot 10^2$	94,5
60	$1,34 \cdot 10^5$	$6,11 \cdot 10^3$	$1,17 \cdot 10^3$	$4,23 \cdot 10^2$	$2,24 \cdot 10^2$
Реакция (2)					
5	$3,69 \cdot 10^2$	5,34	0,214	$5,24 \cdot 10^{-2}$	$2,19 \cdot 10^{-2}$
10	$9,27 \cdot 10^3$	18,8	2,16	0,434	0,146
20	$6,75 \cdot 10^5$	$1,61 \cdot 10^2$	33,8	4,41	1,30
40	$3,01 \cdot 10^8$	$1,31 \cdot 10^5$	$9,74 \cdot 10^2$	87,7	14,4
60	$1,57 \cdot 10^{10}$	$2,44 \cdot 10^6$	$1,14 \cdot 10^4$	$7,9 \cdot 10^2$	$1,14 \cdot 10^2$

Key:
1. Reaction
2. GPa
3. Temperature, °K

Table 13. Composition of Secondary Explosive Detonation Products: Calculations are made with the BKW equation of state (moles/mole explosive) at detonation wave pressure and temperature (T_D, P_D)

ВВ (1)	Плотность, г/см³ (2)	(γ) n	H_2O	H_2	CO_2	CO	N_2	$C_к$
Гексоген (3)	1,86	2,98	3,00	-	1,49	0,022	3,00	1,49
$C_3H_6N_6O_6$	1,0	2,48	2,80	0,111	0,67	1,855	2,98	0,45
ТЭН (4)	1,77	[illegible]	4,00	-	3,89	0,223	2,00	0,89
$C_5H_8N_4O_{12}$	[illegible]	2,06	[illegible]	0,167	2,81	2,12	1,93	0,0
[illegible] (5)	1,64	[illegible]	2,50	-	[illegible]	0,188	1,50	5,15
[illegible]	[illegible]	(1,1[illegible])	1,76	0,207	[illegible]	2,86	1,49	3,45

Key:
1. Explosive
2. Density, gm/cm^3
3. Hexogen
4. PETN
5. [One word illegible]

If $n_C = 0$ (for conventional explosives this is observed only at large values of α_0, close to unity), the relationship between n_{CO}, n_{CO_2}, n_{H_2O} and n_{H_2} is governed by the equation for the water gas reaction. Formula (6.2) is used in the calculations.

Finally at $\alpha_0 \geqslant 1$ the composition of the detonation products is written in the same way as for the zero approximation at moderate pressure:

$$n_{CO_2} = n_C^0 ; \; n_{H_2O} = n_H^0/2 ; \; n_{N_2} = n_N^0/2 ; \; 2n_{O_2} = n_O^0 - 2n_C^0 - (n_H^0/2).$$

If metals are present in the system--Al, Mg, B and others, it is presumed that they burn up in the detonation products to produce the appropriate oxides (Al_2O_3, MgO, B_2O_3 etc.). As is the case with moderate pressure, we begin the calculations with transformation of the metal into its oxide. Remaining oxygen is consumed in oxidation of carbon and hydrogen. At high detonation pressure formation of metal nitrides is possible. We will not examine these reactions here.

In the presence of chlorine and fluorine HCl and HF form in the products of hydrogen-containing explosives. Formation of a certain quantity of CF_4 has also been demonstrated to be possible. We will not consider this substance in our calculations.

Table 13 shows the results of calculating the composition of the detonation products of some explosives at different initial charge densities. We can see that as density decreases (and consequently as the detonation pressure decreases) the concentration of CO and H_2 in the explosion products increases while the concentration of CO_2, H_2O and C_K decreases. At very low but practically fully attainable initial charge density the composition of the detonation products is consistent with that calculated on the assumption that the equation of state for an ideal gas is applicable.

One interesting feature of the state of the products of detonation occurring at ultrahigh pressure is that the following relationship is satisfied within a rather broad interval of pressures:

$$p = aV^{-n}, \text{ where } n = 2,5 - 3,5 \qquad (6.18)$$

is a polytropic equation. When the charge density and pressure decrease, *n* decreases. From the standpoint of the theory of free volume this means that forces of repulsion play the principal role in equations such as (3.50) for detonation products. The role of the thermal component and the forces of attraction, which depend weakly on volume, is smaller. The Lennard-Jones potential (6-9) probably provides the most accurate description of the true state of combustion products (this is indicated by calculations made by Zubarev and Telegin (14)). In this case the relationship we get for pressure is $p = (a/V^4) - (b/V^2) + T$; at small , the second and third terms of this relationship somewhat weaken the dependence of $P(V)$ on the first.

6.5. Expansion of the Detonation Products of Condensed Substances

In the first approximation, detonation products undergo polytropic expansion (6.18). In this case the pressure drops very abruptly: At $n=3$ it is proportional to the ninth power of distance. As pressure decreases the polytropic index decreases and the rate of pressure decline slows down. At coordinates $\lg V - \lg P$ the curve $P(V)$ may be approximated by two straight lines. The slope of the first in the high pressure range is n, and the slope of the second is r. Change in slope occurs at pressures on the order of 1,000-2,000 atmospheres.

The effective polytropic index (usually $2<n_{eff}<3$) is used to calculate the work of expansion of explosive charges in a casing.

In view of the consequent intense change in the constants for reactions (1) and (2) (Table 6), it is extremely difficult to calculate the composition of combustion products as it changes in the course of expansion. In this connection attempts have been made since long ago to experimentally determine the heat and composition of explosive detonation products. The first apparatus intended for this purpose was the Bikhel' bomb--a sealed vessel with walls 10-20 cm thick and a capacity of 20-50 liters. The internal cavity of the bomb is sealed with a lead lining, and it is covered by a massive lid with 10-12 huge nuts tightened down by a 1.5-meter wrench. A charge weighing 50-200 gm was suspended in the center of the bomb and exploded by means of an electric detonator. Prior to the experiment air was evacuated from the bomb by a vacuum pump to a residual pressure of several dozen mm Hg. More-compact and convenient devices appeared later on, but their principle of operation essentially remained the same. The results of experiments with a freely suspended charge are shown in Table 14.

Table 14. Results of Experiments With a Detonation Calorimeter (Using a Charge Without a Casing) and of Calculations Using the Equation of State for an Ideal Gas

		(1) Состав продуктов, моль/мольВВ							
	CO	H_2O	H_2	N_2	CO_2	$C_к$	HCN	NH_3	CH_4
			Тротил (4)						
(2) Опыт	5,89	0,17	2,31	I,36	0,063	I,0I	0,024	0,022	0,01
(3) Расчет I500K	5,97	0,007	2,I0	I,49	0,009	0,8I	0,0I8	0,0005	0,49
Расчет I800K	6,00	0,003	2,36	I,47	0,003	0,90	0,056	0,0003	0,05
			Октоген (5)						
Опыт	2,65	2,50	I,53	4,0I	I,44	0	0,0006	0	0
Расчет I500K	2,36	2,36	I,64	4,00	I,65	0	$2 \cdot I0^{-6}$	0	0
Расчет I800K	2,52	2,52	I,48	4,00	1,49	0	$2 \cdot I0^{-5}$	0	0
			Бензотрифуроксан (6)						
Опыт	6,03	0,03	0,039	2,98	0,006	0	0,007	0,002	0
Расчет I355K	5,87	0,00I	0,22	3,00	0,022	0,I3	0,004	0	0,00
Расчет I660K	5,90	$4 \cdot I0^{-4}$	0,23	2,97	0,004	0,I0	0,0I5	0	0,00

Key:

1. Composition of products, moles/mole explosive
2. Experimental
3. Calculated
4. Trotyl
5. Octogen
6. Benzotrifuroxane

Table 15. Results of Experiments With a Detonation Calorimeter (Using Charges in a Massive Gold Casing) and of Calculations Using the Mi-Gryunayzen Equation of State (3.30) (2)

	(1) Состав продуктов, моль/моль/ВВ							
	CO	H_2O	H_2	N_2	CO_2	$C_к$	NH_3	CH_4
	(4) Тротил $\rho_0 = I,63$ $\Delta H_r = 4574$							
(2) Опыт 9	2,00	I,60	0,38	I,I8	I,20	3,4I	0,20	0,007
	I,98	I,60	0,46	I,32	I,25	3,65	0,I62	0,I
(3) Расчет I805K	I,96	I,64	0,40	I,50	I,39	3,80	-	0,23
	(5) Октоген $\rho_0 = I,89$ $\Delta H_r = 6I90$							
Опыт	I,06	3,I6	0,30	3,68	I,92	0,97	0,40	0,032
Расчет I760K	0,93	3,06	0,34	3,97	2,0I	0,8I	0,063	0,26
	(6) Бензотрифуроксан $\rho_0 = I,66$ $\Delta H_r = 5905$							
Опыт	2,87	0,09	0,0I	2,93	I,56	I,57	0,005	0
Расчет I575K	2,05	0,I2	0,036	2,99	I,87	2,07	0,002	0,037

Note: ΔH_r for liquid water, kj/kg; ρ_0--gm/cm^3.

*Old data.

**Calculated using the BKW equation (3.13).

Key:

1. Composition of products, moles/mole explosive
2. Experimental
3. Calculated
4. Trotyl
5. Octogen
6. Benzotrifuroxane

It should be pointed out immediately that these results may produce the completely wrong impression as to the composition of explosion products at high pressure--at tens and hundreds of thousands of atmospheres. When detonation products expand, especially without expenditure of energy, the pressure within them drops very strongly, while the temperature remains practically constant (in principle, it may even grow). An equilibrium in keeping with a relatively low pressure establishes itself within the space of the bomb. In this case the composition of the explosion products is calculated with the equation of state for an ideal gas, as described in section 6.2. Examples of such calculations, shown in Table 14, demonstrate that they are fully in agreement with experimentally obtained values.

In order to hinder secondary reactions at low pressure the explosive charge is placed in a massive casing made from a soft metal (lead or copper). When the explosion occurs the casing disintegrates, and minute fragments fly apart in all directions at high velocity. Energy is expended upon disintegration of the casing and propulsion of its fragments, the explosion products cool quickly, and secondary reactions are slowed down. In order to prevent interaction of explosion products with [one line illegible] at the University of California (USA), the casing was made from gold. The results of experiments with trotyl in a gold casing are given in Table 15, together with old German data. These results differ from those obtained with freely suspended charges: The explosion products of benzotrifuroxane include a large concentration of CO_2, while the explosion products of trotyl contain much CO_2 and H_2O. In the case of octogen--a substance richer in oxygen--the difference in the results shown in tables 14 and 15 is smaller. But these researchers were unable to completely inhibit the reactions proceeding during expansion or establish the composition of products formed in the detonation wave. This problem has still not been solved. The one thing that we have been able to do is to compare the composition of expanding explosion products determined experimentally with calculations performed according to several of the available methods. These calculation results are also given in Table 15. It follows from them that following an explosion in a massive casing, the equilibrium probably freezes at a temperature of 1,500-1,800°K, approximately the same as with a conventional calorimetric bomb, though of course at much higher pressure (0.5-5 GPa). Concurrently the consistency of the calculated and experimental results also demonstrates how reliable the theoretical models are.

It may be concluded in general that the thermodynamic methods of calculating detonation processes in condensed explosives are for the moment much less developed than the methods of calculating processes occuring during combustion of fuels. The main difficulty is associated with the absence of a reliable and universal equation of state for mixtures of gaseous and condensed substances experiencing a temperature of several thousand degrees and a pressure of hundreds of thousands of atmospheres. However, this area of science is developing quickly, and we can anticipate arisal of new interesting and important results in the next few years.

APPENDIX

Table 1. Comparison of Methods of Calculating the Enthalpies of Formation of Some Organic Substances: The difference (kcal/mole) ΔH_F(experiment-$-\Delta H_F$(calculated) determined by different methods is given.

Соединение (1)		ΔH°298 эксп. (2)	Франклина (3)	Бенсона (4)	Андерсена (5)	Лейдлера (6)	Караша (7)	Эстермана (8)
(11) н-пропан	(9) г	-25,11	0,06	0,00	0,03	-0,03	-	0,00
	(10) ж	-29,17	-	-	-	0,05	-5,26	0,00
(12) н-декан	г	-59,62	0,03	0,14	-0,04	-0,77	-	0,00
	ж	-71,94	-	-	-	-0,95	4,98	0,00
(13) н-эйкозан	г	-108,92	-0,01	0,34	-0,14	-1,73	-	0,00
	ж	-133,04	-	-	-	-2,33	4,58	0,00
(14) Среднее по 18 н-парафинам			±0,02	0,17	±0,06	-0,88	4,92	0,00
(15) 1-бутен	г	- 0,06	-0,01	-0,02	0,00	-0,19	-	0,00
	ж	- 5,19	-	-	-	0,01	6,09	0,00
(16) 1-децен	г	-29,64	-0,04	0,05	-0,06	-0,79	-	0,00
	ж	-41,48	-	-	-	-0,47	6,21	0,00
(17) 1-эйкозен	г	-78,94	-0,08	0,25	-0,15	-1,79		0,00
	ж		-	-	-			
(18) [illegible] по 18 [illegible] соедин.			±0,05	±0,11	-0,08	0,99	6,15	0,00
(19) [illegible]	г	[illegible]	-0,22	-0,27	-0,47		0,42	-0,02
		- 2,96						0,14
(20) [illegible]бензол	г	- 3,10	-0,27	-0,27	-0,53			-0,06
	ж	-15,28	-	-	-		0,26	0,06

Методы

Соединение		ΔH	Франклина	Бенсона	Андерсена	Лейдлера	Караша	Эстермана
(21) [illegible]тетрадекан	г	-52,60	-0,51	-0,27	-0,13			-0,26
(22) Среднее по 13 н-алкил-бензолам			-0,36	-0,27	-0,17			-0,14
(23) Этанол	г	-56,79	0,16	-0,33	1,05	2,15	-	-0,04
	ж	-66,71	-	-	-		0,75	-0,01
(24) [illegible]	г	-81,64	-0,06	-0,43	0,80	1,45		-0,24
	ж	-97,31	-	-	-		0,50	-0,06
(25) Среднее по 11 спиртам			±0,13	-0,43	0,80	1,45		-0,24
							0,50	00,06
(26) Пропионовая к-та	г	-107,71	1,94	1,02	4,43	3,74		-0,09
	ж	-121,61	-	-	-		0,60	0,00
(27) Валериановая к-та	г	-117,75	1,75	0,88	4,23	3,36		-0,27
	ж	-133,83	-	-	-		0,72	0,00
(28) [illegible]новая к-та	г	-137,83	1,37	0,60	3,83	2,60		-0,63
	ж	-150,27	-	-	-		0,56	0,00
(29) Пропионовый альд.	г	-45,14	3,81	-0,51	4,15	1,16		[illegible]
	ж	-52,95	-	-	-		4,36	[illegible]
(30) [illegible]наль	г	-64,30	4,35	0,13	4,67	1,32		[illegible]
	ж	-74,50				2,93	7,09	1,52
(31) [illegible]анон-2	г	-66,87	-0,25	-0,31	-0,44	1,72		0,13
	ж	-76,47				4,84		1,01
(32) 1-хлорбутан	г	-35,26		0,38	-0,22			1,40
	ж	-45,2					2,19	1,00

[Key on following page]

Соединение		ΔH_f	Методы					
			Франклина	Бенсона	Андерсена	Лейдлера	Караша	Эстерманна
(33) и-хлорпропан	г	-31,1		-0,47	-1,04			0,57
	ж	-35,0					1,32	0,09
(34) и-фторпропан	г	-67,2		-0,37	-2,14			0,29
(35) пропиламин	г	-17,3	-0,13	-0,47	0,42	0,83		-0,47
	ж	-24,6					4,74	-0,42
(36) этилнитрат	г	-36,85	-3,40	1,13	-	1,05		0,72
	ж	-45,5				1,30	0,80	-0,17
(37) пропилнитрат	г	-41,60	-3,23	1,33	-	1,13		0,90
	ж	-51,27				1,50	1,10	0,17

Key:

1. Compound
2. Experimental
3. Franklin's
4. Benson's
5. Andersen's
6. Leidler's
7. Karash's
8. Esterman's
9. Gas
10. Liquid
11. *n*-Propane
12. *n*-Decane
13. Eicosane
14. Average for 18 *n*-paraffins
15. iso-Butene
16. [Illegible]
17. iso-Eicosane
18. Average for 18 unsaturated compounds
19. Ethylbenzene
20. Butylbenzene
21. Phenyltetradecane
22. Average for 13 monoalkylbenzenes
23. Ethanol
24. Heptanol
25. Average for 11 alcohols
26. Propionic acid
27. Valeric acid
28. Nonanoic acid
29. Propionic aldehyde
30. Heptenal
31. Hexanone-2
32. [Illegible]
33. iso-Chloropropane
34. iso-Fluoropropane
35. Propylamine
36. Ethylnitrate
37. Propylnitrate

Table 2. Thermodynamic Characteristics of the Combustion Products of Secondary Explosives

(1) именование, формула, тальпия образования (/кг), коэффициент бытка окислителя,	n_0	H_2	H_2O	N_2	CO	CO_2	CH_4	$C_{тв}$	T_p	$\bar{\gamma}$	T_v
(2) нитротолуол (-326; 0,II4)	43,75 34,79	25,52 I2,49	- 2,98	3,65 3,62	I4,58 9,63	- I,00	- 5,00	36,46 35,40	I077 I424	I,282 I,I7I	I38I I668
(3) нитротолуол $_4N_2$ (-356; 0,235)	43,92 35,53	I6,47 5,82	- 2,82	5,49 5,33	2I,96 I5,82	- I,85	- 3,87	I6,47 I7,00	I550 2007	I,282 I,I86	I987 2380
(4) тил N_3 (-262; 0,364)	44,03 44,92	II,0I I0,36	- 0,I8	6,60 6,6I	26,42 26,55	- 0,09	- 0,25	4,40 4,I5	2034 2042	I,3I2 I,306	2669 2668
(5) нитро-м-ксилол $_6N_3$ (-297; 0,308)	45,6I 44,42	I4,5I I2,72	- 0,4I	6,22 6,I6	24,88 24,I3	- 0,I9	- 0,65	8,29 8,I2	I8II I864	I,302 I,290	2358 2404
(6) нитроанилин $_6N_4$ (-3I6; 0,429)	43,84 43,04	8,77 8,2I	- 0,I9	8,77 8,59	26,30 25,65	- 0,II	- 0,09	- -	2094 2I02	I,337 I,332	2800 280I
(7) нитробензол N_3 (-I83; 0,444)	42,23 42,02	7,04 6,76	- 0,I3	7,04 6,95	28,I5 27,85	- 0,09	- -	- -	2366 2368	I,329 I,327	3I44 3I43
(8) нитродифениламин $_{I2}N_7$ (-I05; 0,453)	40,98 40,80	5,69 5,46	- 0,II	7,97 7,89	27,32 27,05	- 0,09	-	-	24I0 24I2	I,325 I,324	3I93 3I92
(9) ксанитродифенил $_{I2}N_6$ (+96,4; 0,462)	40,08 39,87	4,7I 4,52	- 0,08	7,07 6,99	28,29 28,04	- 0,08	- -	- -	2658 2600	I,3I9 I,322	3506 3436
(10) илнитрат $C_2H_5O_3N$ (-2II4; 0,462)	54,90 55,0I	I8,67 I8,56	8,78 8,86	5,49 5,49	I9,77 I9,79	2,20 2,2I	- -	- -	I9I5 I906	I,3I7 I,3I6	2522 2507
(11) етрил N_5 (+III; 0,485)	4I,79 4I,83	6,4I 6,36	2,30 2,29	8,7I 8,7I	23,I9 23,I3	I,I8 I,I9	- -	- -	2793 2784	I,293 I,307	36II 3638

	n_0	H_2	H_2O	N_2	CO	CO_2	CH_4	$C_{тв}$		T_p	$\bar{\gamma}$	T_v
(12) ,4-тиленгликольдинитрат C_4H_8 (-I640; 0,500)	49,97 50,05	I3,44 I3,4I	8,77 8,8I	5,55 5,55	I9,88 I9,94	2,33 2,32	- -	- -		2293 2290	I,29[illegible] I,283	2974 2939
(13) инитробензойная к-та (-I548; 0,5I6)	38,89 38,94	4,08 4,07	I,75 I,76	5,83 5,84	25,09 25,I2	2,I4 2,I4	- -	- -		2I37 2I3I	I,3I2 I,3I7	2804 2755
(14) ринитрофенол N_3 (-94I; 0,5[illegible]9)	39,28 39,32	4,28 4,24	2,27 2,29	6,55 6,55	24,09 24,I2	2,I0 2,08	- -	- -		2506 2504	I,30I I,292	3260 3263
(15) Диэтиленгликольдинитрат $C_4H_8O_7N_2$ (-2I83; 0,563)	45,89 45,96	8,77 8,67	II,63 II,72	5,I0 5,I0	I6,72 I6,82	3,67 3,39	-	-		2526 2495	I,275 I,325	322I 3739
(16) ,4,6-Тринитрорезорцин N_3 (-2764; 0,593)	36,7[illegible] 36,75	2,53 2,55	3,59 3,6I	6,I2 6,I2	I9,9I I9,94	4,57 4,35	-	-		2535 2533	I,28I I,282	3247 3248
(17) нитрогликоль (-35I6; 0,6I5)	46,70 46,76	9,I5 9,I0	I4,20 I4,23	4,67 4,67	I4,20 I4,28	4,48 4,44	-	-		2I26 2II9	I,277 I,284	27I5 27I5
(18) I,3-пропиленгликольдинитрат (-I967; 0,667)	42,I5 42,30	4,82 4,90	I3,25 I3,I2	6,02 6,02	I3,25 I3,22	4,82 4,86	- 0,09	-		2960 2938	I,254 I,255	37I9 3687
(19) I,2-пропиленгликольдинитрат N_2 (-2092; 0,667)	42,I5 42,[illegible]7	4,88 4,89	I3,I9 I3,II	6,02 6,02	I3,I9 I3,I8	4,88 4,89	- 0,07	- -		290I 2879	I,255 I,256	364I 36I5
							OH	NO	O_2			
(20) нитрофлороглюцин N_3 (-II46; 0,667)	34,47 34,58	I,26 I,24	4,48 4,45	5,74 5,75	I5,97 I5,96	7,0I 6,8I	0,23	-	-	3435 3340	I,25I I,248	4297 4I68
(21) ексоген (+322; 0,667)	40,52 40,9I	3,5I 3,54	9,99 9,62	I3,5I I3,46	9,99 I0,I2	3,5I 3,37	- 0,36	- 0,I	- -	35II 3375	I,260 I,256	4424 4239
(22) ритриндинитрат (-2765; 0,778)	35,44 36,28	2,I4 I,27	I4,33 I2,3I	5,49 5,48	8,84 7,39	7,63 9,I8	- 0,37	- 0,I	- 0,07	308I 3I69	I,232 I,225	3796 3884
(23) тилнитрат (-20I0; 0,857)	38,94 39,92	I,43 I,37	I8,04 I6,86	6,49 6,36	5,06 6,II	7,92 6,86	- I,II	- 0,25	- 0,II	3663 328I	I,22I I,273	4473 4I77

[Key on following page]

	n_0	H_2	H_2O	N_2	CO	CO_2	OH	NO	[illegible]	[illegible]	[illegible]	[illegible]
(24) [illegible] $C_5H_8O_{12}N_4$ (-1681; 0,857)	34,79 36,06	0,73 1,04	11,93 11,04	6,33 6,17	5,60 6,95	10,22 8,87	- 0,96	- 0,32	- 0,43	[illegible] [illegible]	[illegible] [illegible]	[illegible] [illegible]
(25) Нитрогликоль $C_2H_4O_6N_2$ (-1632; 1)	32,88 36,02	- 0,55	13,15 11,95	6,58 6,29	- 3,54	13,15 9,61	- 1.22	- 0,55	- 1.40	4561 [illegible]	1,198 [illegible]	[illegible] [illegible]
(26) Нитроглицерин $C_3H_5O_9N_3$ (-1640; 1,059)	31,93 34,55	- 0,36	11,01 9,99	6,61 6,27	- 3,01	13,21 10,20	- 1,21	- 0,67	1,10 2,07	4215 3326	1,200 1,200	[illegible] [illegible]
(27) Эритриттетранитрат $C_4H_6O_{12}N_4$ (-1736; 1,091)	31,45 33,49	- 0,30	9,93 8,99	6,62 6,26	- 2,83	13,24 10,42	- 1,20	- 0,73	1,66 2,46	4080 3419	1,203 1,207	4909 4127
(28) Маннитгексанитрат $C_6H_8O_{18}N_6$ (-1479; 1,125)	30,96 34,17	- 0,26	8,85 8,25	6,63 6,47	- 2,83	13,27 10,94	- 1,25	- 0,85	2,21 2,99	4156 3436	1,203 1,216	[illegible] 4179
(29) Нитрометан CH_3NO_2 (-1502; 0,571)	49,15 49,21	10,81 10,80	13,76 13,91	8,19 8,19	13,76 13,73	2,62 2,65	- -	- -	- 0,1	2628 2615	1,277 1,275	3356 3334

Note: The first number in the parentheses following the name of the explosive is ΔH_{F298}, kj/kg, and the second is α_0. For each explosive, the upper row of numbers represents the results of calculations using the approximation method given in this book, and the lower row represents the results of precise computer calculation at $P = 3 \cdot 10^7$ Pa. Because products having a low concentration are ignored in the computer calculations, n_0 may be greater than the sum of the moles of gases shown in the table. n_0 represents the number of moles of gaseous products (moles/kg).

Key:

1. Name, formula, enthalpy of formation (kj/kg), coefficient of excess oxidant
2. *m*-mononitrotoluol
3. 2,4-Dinitrotoluol
4. Trotyl
5. Trinitro-*m*-xylol
6. Trinitroaniline
7. Trinitrobenzene
8. Hexanitrodiphenylamine
9. Hexanitrodiphenyl
10. Ethylnitrate
11. Tetryl
12. 1,4-Butyleneglycol dinitrate
13. Trinitrobenzoic acid
14. Trinitrophenol
15. Triethyleneglycol dinitrate
16. 2,4,6-
16. 2,4,6-Trinitroresocine
17. Mononitroglycol
18. 1,3-Propyleneglycol dinitrate
19. 1,2-Propyleneglycol dinitrate
20. Trinitrofluoroglucin
21. Hexogen
22. Glycerin dinitrate
23. Methylnitrate
24. PETN
25. Nitroglycol
26. Nitroglycerin
27. Erythritol tetranitrate
28. Mannitol hexanitrate
29. Nitromethane

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