first king; δ, flow expansion coefficient ahead of arc; T, temperature; $F = (\delta\rho_0 h_1)^2/4\bar{N}\bar{\sigma}$; $E^2_{\min} = Fv_0^2$; $\bar{h} = (h - h_1)/h_1$; J_0, J_1, zeroeth and first-order Bessel functions of the first kind; I_0, modified zeroth-order Bessel function; $w = h_1\rho v/\bar{M}$; $a^2 = \bar{N}/\bar{M}$. Subscripts: 0, gas parameters far from arc; 1, parameters at edge of arc; x, y, projections on coordinate axes; a, arc.

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THERMODYNAMIC CALCULATIONS OF COMBUSTION PRODUCTS AT HIGH PRESSURES

V. F. Baibuz, V. Yu. Zitserman,
L. M. Golubushkin, and I. G. Malyshev

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A procedure for the calculation of chemical equilibrium in combustion products at high pressures (and high temperatures) is developed on the basis of a model equation of state. The conditions are determined for validity of the ideal-solution and covolume-gas approximations.

Methods for the calculation of equilibria of gas mixtures at high pressures have been discussed at length in the literature. The problem arises often in the study of solid-fuel combustion [1], in organic synthesis technology [2], in geochemistry [3], and in other applications. The fundamental problem is to find a sufficiently universal equation of state that is effective for the mixture at high parameters (up to ~5000°K and 10^3-10^4 bar). Various approximations are used for thermodynamic calculations in this range of the parameters, e.g., the combination of the Lewis—Randall approximation with the virial equation of state [4], or the single-fluid approximation [5, 6], in which the mixture is replaced by a hypothetical substance that is equivalent in some respect. In particular, the application of the virial equation of state in such calculations encounters difficulties associated with the determination of the third-fourth cross virial coefficients of the mixture.

In the present article we propose a procedure for calculating the equilibrium composition of reacting gas mixtures at high parameters on the basis of the equation of state postulated in [7, 8]. This equation of state has the specific attribute that it describes the properties of a high-temperature gas over a wide range of parameters with the use of data only on the second virial coefficients. The well-known mixing rule

$$B_{\mathrm{mx}} = \sum_{i,j} x_i x_j B_{ij} \tag{1}$$

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can be used in the majority of cases to take proper account of the nonadditivity of the properties of the components.

EQUATION OF THE MIXTURE

The following equation of state has been derived [7, 8]:

$$Z = 1 + \frac{B\rho}{1 - \rho/\rho_0}, \tag{2}$$

where $B = B(T_0)$ and $T_0 = T/(1 - \rho/\rho_0)$, for the domain of the parameters $T \geqslant 2\varepsilon/k$ and $\rho/\rho_0 \leqslant 0.6$. For the majority of gases the latter condition corresponds to a pressure of $\sim 10^4$ bar at $T = 2000°K$. The equation of state (2) is based on certain specific characteristics observed in the PVT surface of a real gas in the analysis of the experimental data for pure gases and mixtures, in particular linearities of the ideal curves, i.e., lines along which the magnitude of some property of the real gas is equal to the ideal-gas value of that property. The equation involves only one temperature function (the second virial coefficient) and the parameter ρ_0, which is characteristic of each substance and is of roughly the same order of magnitude as the density of an unstressed crystal. To obtain the equation of state of a mixture it is sufficient to use the mixing rule (1) and the following combination rule for the parameter ρ_0 [7, 8]:

$$1/\rho_{0,\mathrm{mx}} = \sum_{ij} x_i x_j \left(\frac{2}{\sqrt{\rho_{0,i}} + \sqrt{\rho_{0,j}}} \right)^3.$$

If an interaction potential, say the (12, 6) potential, is introduced in this model, each of the second virial coefficients will depend on its argument:

$$B_{ij} = \frac{2}{3} \pi N \sigma_{ij}^3 B_{ij}^* (T_{0,ij}^*),$$

$$T_{0,ij}^* = \frac{kT}{\varepsilon_{ij} (1 - \rho/\rho_{0,\mathrm{mx}})},$$

and the parameter ρ_0 can be related to the potential parameter

$$\frac{2}{3} \pi N \sigma^3 = 2{,}39 \frac{1}{\rho_0}.$$

Using the known potential parameters for the components of the mixture and the analytical expression for the reduced second virial coefficient $B^*(T^*)$ (say, from [9]), we can describe the thermodynamic properties of a mixture of real gases. The errors induced by the application of the (12, 6) potential are eliminated by the introduction of the temperature-dependent parameters ε/k and σ [10].

We obtain expressions for the isothermal increments of the thermodynamic properties on the basis of standard thermodynamic relations:

$$\Delta Y = Y(T, P) - Y_{\mathrm{IdG}}(T, P).$$

The proposed model enables us to circumvent quadratures in the computation of ΔU and ΔH:

$$\Delta U = RT_0 [B(T) - B(T_0)],$$

$$\Delta H = \Delta U + \frac{RT\rho}{1 - \rho/\rho_0} B(T_0).$$

The analogous correction to the Helmholtz function is conveniently computed according to the equation

$$\Delta F = \int_{\rho(P')}^{\rho(P)} \frac{P}{\rho^2} \, d\rho - RT \ln \frac{P}{P'},$$

TABLE 1. Equilibrium Constant K_x (6)

T, K	Initial composition	P, MPa						
		1	10	100	300	500	700	1000
1000	$CO_2 : H_2 = 1 : 1$	0,7	0,72	0,94	1,4	1,8	2,2	2,8
	$CO_2 : H_2 : H_2O = 1 : 1 : 9$	0,7	0,73	1,06	1,9	2,5	3,1	4
3000	$CO_2 : H_2 = 1 : 1$	7,5	7,5	7,7	8,1	8,5	8,9	9,5
	$CO_2 : H_2 : H_2O = 1 : 1 : 9$	7,5	7,5	7,8	8,4	9	9,5	10,3

in which P' is a sufficiently low pressure at which the gas can be regarded as ideal.

The calculations are carried out under the condition that the fugacity f_i of the components is given by the relations

$$\begin{gathered} f_i(T,\ P,\ x) = \gamma_i(T,\ P,\ x) P x_i, \\ RT \ln \gamma_i = \int\limits_0^P \frac{d\rho}{\rho^2} \left[\left(\frac{\partial P}{\partial n_i} \right)_{T,P,n_x} - RT\rho \right] - RT \ln Z. \end{gathered} \tag{3}$$

In the Lewis—Randall approximation these functions can be restricted to data on the pure components:

$$f_i(T,\ P,\ x) = f_i^{\text{pure}}(T,\ P) x_i \tag{4}$$

or

$$\gamma_i(T,\ P,\ x) = \gamma_i^{\text{pure}}(T,\ P). \tag{5}$$

CALCULATION OF THE EQUILIBRIUM COMPOSITION FOR A MIXTURE OF IDEAL GASES

Any equilibrium-composition algorithm requires data on the component chemical potential μ_i. For an ideal gas $\mu_i = \mu_i^0(T) + RT \ln P x_i$, where $\mu_i^0(T)$ is the value of the chemical potential in the standard state. For a real gas $\mu_i = \mu_i^0(T) + RT \ln \gamma_i P x_i$ and the functional dependence of γ_i on the state and composition parameters of the mixture complicates the algorithm enormously. However, if the quantities γ_i are fixed in the calculation of equilibrium, i.e., in the search for the maximum of G, the dependence of μ_i on the composition of the mixture is similar to the dependence of μ_i on the composition of an ideal-gas mixture:

$$\mu_i = \mu_i^* + RT \ln P x_i, \quad \mu_i^* = \mu_i^0 + RT \ln \gamma_i.$$

In the first step of the iterative cycle we can set $\gamma_i = 1$ or estimate the values of the fugacity coefficients in the Lewis—Randall approximation and then refine them successively with the use of relation (3).

The algorithm for the calculation of equilibrium is based on the method, proposed in [11], of successive reduction to equilibrium of the individual reactions and subsequent conversion of the basis. As a first example we consider equilibrium in the system known as "water gas," in which the main reaction is $CO_2 + H_2 \to CO + H_2O$. In the ideal-gas approximation the equilibrium constant of this reaction $K_p^0 = \prod\limits_i x_i^{\nu_i}$ does not depend on the pressure. It depends on the pressure only when the fugacity is taken into account:

$$K_x = \prod_i x_i^{\nu_i} = K_p^0 / K_\gamma,$$

where $K_\gamma = \prod\limits_i \gamma_i^{\nu_i}$

As the pressure is increased, the quantity

$$K_x = \frac{x(CO)\, x(H_2O)}{x(CO_2)\, x(H_2)} \tag{6}$$

varies considerably, more so at lower temperatures (see Table 1). It follows from Table 1

TABLE 2. Results of Calculations for Combustion Products at T = 1000°K

P, MPa	ρ, kg/dm^3	δU	δH	δG	γ_i				
		kJ/kg			CO	H_2O	H_2	N_2	CO_2
100	0,326	—69,9	—15,8	44,4	1,48	0,93	1,38	1,50	1,29
200	0,541	—114,2	5,49	94,7	2,19	0,94	1,81	2,22	1,79
500	0,89	—182,0	131,4	257,5	6,55	1,25	3,59	6,67	5,18
800	1,07	—213,8	285,1	428,8	1*	1,86	6,56	18,7	15,3
1000	1,15	—225,8	395,5	547,2	1*	2,48	9,54	36,6	31,7

*The value $\gamma_i = 1$ is adopted conditionally, since $x_i < 10^{-3}$.

that the equilibrium constant K_x depends not only on the pressure, but also on the ratio of the elements C:O:H in the mixture. However, if the Lewis—Randall approximation were valid, as is frequently presumed in the literature [1, 2], the quantity $K_x = K_p^0/K_\gamma$ would not depend on the composition of the mixture, according to relations (4) and (5). Consequently, the ideal-solution approximation is by no means always valid in gas mixtures.

As a second example we consider equilibrium in the combustion products of a solid fuel with the equivalent formula given in [12]: $O_{34.5}H_{29.8}N_{10.1}C_{23}$. The total number or components in this system is 38, but we have taken into account only the nonideality of 6 to 10 components in the calculations. For the rest, we assumed conditionally that $\gamma_i = 1$ and did not include these components in the sum (1). Typical results of the calculations are given in Tables 2-4.

SIMPLIFIED MODEL OF A MIXTURE

The results of the equilibrium calculations for multicomponent gas mixtures enables us to investigate the validity of the ideal-solution approximation from a fresh point of view when $G^E = V^E = 0$. In this case

$$G_{mx} = \sum_i x_i [\mu_i^{pure}(T, P) + RT \ln x_i],$$

which is equivalent to relations (4) and (5), i.e., to the Lewis—Randall approximation or, alternatively, the approximation of an "ideal mixture of real components" [2]. The results in Table 1 show that this approximation holds quite accurately at T > 2000°K but creates appreciable deviations already at T = 1000°K.

Equation of state (2) can be reduced to:

$$V = \frac{RT}{P} + \frac{B}{1 + (B\rho_0 - 1)\rho/\rho_0}, \tag{7}$$

where $B = B(T_0)$.

Numerical estimates show that the denominator in the second term of Eq. (7) differs from unity at most by 0.1 at $T \geqslant 2000$°K, and so we can deduce a simplified version of the equation of state:

$$V = \frac{RT}{P} + B(T_0). \tag{8}$$

The expression for the excess volume, according to (1), has the form

$$V^E = \sum_{ij} x_i x_j \left(B_{ij} - \frac{1}{2} B_i - \frac{1}{2} B_j\right). \tag{9}$$

If the following relations hold for all pairs i, j:

$$B_{ij} \approx \frac{B_i + B_j}{2},$$

TABLE 3. Results of Calculations for Combustion Products at T = 3000°K

P, MPa	ρ, kg/dm^3	δU	δH	δG	γ_i				
		kJ/kg			CO	H_2O	H_2	N_2	CO_2
100	0,083	—0,48	112,7	114,2	1,14	1,05	1,06	1,14	1,16
200	0,153	0,29	223,4	226,4	1,30	1,10	1,12	1,30	1,34
500	0,309	7,5	543,9	553,2	1,89	1,29	1,33	1,88	2,06
800	0,418	18,2	852,8	869,1	2,71	1,51	1,56	2,70	3,12
1000	0,475	25,9	1053,1	1074,2	3,43	1,68	1,73	3,41	4,11

TABLE 4. Mole Fractions and Fugacity Coefficients at T = 3000°K, P = 500 MPa

Component	x_i	γ_i	Component	x_i	γ_i
H_2O	0,37	1,28	OH	0,0009	1*
CO	0,37	1,89	H_2CO	0,0003	1*
CO_2	0,13	2,03	CH_4	0,0001	1*
H_2	0,13	1,36	CH_3	2×10^{-5}	1*
HCO	0,0015	1,69	O_2	3×10^{-6}	1*
H	0,0009	1*			

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*The value $\gamma_i = 1$ is adopted conditionally owing to the small content of the component.

then

$$V^E = 0; \quad G^E = \int_0^P V^E dP = 0,$$

i.e., we arrive at the Lewis—Randall approximation.

The reduced second virial coefficient B* is known to depend weakly on T* at high temperatures. Accordingly, in the high-temperature range $B_{ij} \approx a\sigma_{ij}^3$, where a is a constant, and the expression $B_{ij} - B_i/2 - B_j/2$ in Eq. (9) can be replaced with acceptable accuracy by the expression $a\left(\sigma_{ij}^3 - \frac{\sigma_i^3 + \sigma_j^3}{2}\right)$. Calculations show that Eq. (9) implies $V^E = 0$ (mixture average).

The specific temperature threshold of validity of the equation of state (8) is determined by means of the parameter $T^* = kT/\varepsilon$.

It follows from tables in the book [4] that B* has roughly a constant value at T* > 10, and the Lewis—Randall approximation can be expected to be valid in this domain.

The values of the parameters ε/k lie in the interval 100-200°K for the majority of component of combustion products, and so the behavior of such a gas mixture above T = 2000°K is described by the simplified equation of state (8). However, if such a mixture contains a large proportion of water vapor (for which $\varepsilon/k \sim 500$°K) or metal vapors (for which also characterized by high values of the parameter ε/k), then $T^* \sim 2$-5, and the deviations from ideal mixing become appreciable. As a result, K_x depends on the composition of the mixture, in particular for the reaction in water gas with a large H_2O content.

It has been noted in ballistic studies [1, 12] that the properties of combustion products are described by a simple equation of state over a wide range of the state parameters, viz:

$$P = \frac{RT}{V - b}, \tag{10}$$

where b is the covolume, which is approximately constant for a given gas over a wide range of T and P.

It follows from a comparison of Eqs. (8) and (10) that $b \approx B(T_0)$, i.e., the covolume is related to B*, and its value is approximately constant for T* > 10. It follows from the equation of state (10) that the internal energy does not depend on the pressure:

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P = 0.$$

This conclusion, in turn, explains the long-known fact that the isochoric temperature of combustion depends weakly on the pressure.

In conclusion we reemphasize the fact that all the approximations used in the present study are associated with a small value of the parameter ε/k for the majority of the components of the mixture, and these approximations are inapplicable if the mixture contains a large quantity of components for which $\varepsilon/k > 500$-800°K.

NOTATION

P, pressure; T, temperature; ρ, density; ρ_0, characteristic parameter of the equation of state (2) for a given substance, approximately equal to the crystal density at 0°K; B, B_{ii}, B_{ij}, B_{mx}, second virial coefficients of the pure gas, the i-th component, the ij-th pair of components (cross coefficient), and the total mixture, respectively; B*, reduced second virial coefficient; $T_0=T/(1-\rho/\rho_0)$, argument of B in Eq. (2); $T^*=kT/\varepsilon$; reduced temperature; Z = PV/RT, compressibility coefficient; ε/k and σ, parameters of the intermolecular Lennard–Jones (12, 6) potential; x_i, mole fraction; Y and ΔY, generalized thermodynamic property and its isothermal increment; U and ΔU, internal energy and its isothermal increment; ΔH, isothermal enthalpy increment; F, Helmholtz energy; G, Gibbs energy; G^E and V^E, excess Gibbs energy and excess volume; K_p^0, K_γ, K_x, equilibrium constants, defined in text; μ_i and μ_i^{pure}, chemical potentials of the i-th component in the mixture and of the pure component, respectively; n_i, number of moles; b, covolume; f_i and γ_i, fugacity and fugacity coefficient; ν_i, stoichiometric coefficient of reaction.

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