AGREEMENT OF MODELS OF CHEMICAL REACTIONS IN GASES
WITH THE SECOND LAW OF THERMODYNAMICS

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In the specified caloric equation of state, the rate constants of the direct and inverse chemical reactions must agree, taking account of the second law of thermodynamics. In particular, the free energy of the chemical-equilibrium gas mixture with specified density and temperature must be minimal. If this condition is not met, the phase portraits of the dynamic systems may be distorted, which is especially significant in analyzing the existence, uniqueness, and stability of solutions close to the bifurcation points. In the present work, corrections to the kinetic (equilibrium) models [1-4] are proposed for accurate agreement with the second law of thermodynamics.

In these models, the composition of the chemically reacting gas is determined by a variable molecular mass μ and the molecular masses in the limiting dissociated and recombined states, the constants μ_{min} and μ_{max}. The total internal energy of the mixture per unit mass in [1-4] is represented as a function of two variables

$$U = U(T, \mu), \tag{1}$$

and the kinetic equation in the form

$$\frac{d\mu}{dt} = W_1 \rho^2 - W_2 \rho, \tag{2}$$

where t is the time; ρ is the density; T is the temperature; W_1, W_2 are functions of T and μ. The following notation is adopted here: F is the free energy; p is the pressure; S is the entropy; u is the mass velocity; c_p and c_V are the specific heat at constant pressure and density. The free energy is a function of the variables T, ρ, and μ; hence

$$dF = -SdT + \frac{p}{\rho^2} d\rho + \left(\frac{\partial F}{\partial \mu}\right)_{\rho,T} d\mu, \tag{3}$$

$$U = F + TS = F - T\left(\frac{\partial F}{\partial T}\right)_{\rho,\mu} = -T^2\left[\frac{\partial (F/T)}{\partial T}\right]_{\rho,\mu}. \tag{4}$$

Integrating Eq. (4) with respect to T for constant ρ and μ gives

$$F = T\omega(\rho, \mu) - T\int U \frac{dT}{T^2}, \tag{5}$$

where ω is an arbitrary function. It follows from Eqs. (3) and (5) that

$$p = \rho^2\left(\frac{\partial F}{\partial \rho}\right)_{T,\mu} = \rho^2 T\left(\frac{\partial \omega}{\partial \rho}\right)_\mu - T\int\left(\frac{\partial U}{\partial \rho}\right)_{T,\mu}\frac{dT}{T^2} \tag{6}$$

or, taking account of Eq. (1) $p = \rho^2 T\left(\frac{\partial \omega}{\partial \rho}\right)_\mu$.

It follows from Eq. (6) and the equation of state of an ideal gas that $(\partial\omega/\partial\rho)_\mu = R/\rho\mu$. Integrating this expression at constant μ, the result obtained is $\omega(\rho, \mu) = R/\mu \ln\rho + \eta(\mu)$ (η is an arbitrary function), which may be substituted into Eq. (5) to give

$$F(\rho, T, \mu) = \frac{RT}{\mu} \ln\rho + T\eta(\mu) - T\int U(T, \mu)\frac{dT}{T^2}. \tag{7}$$

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*Deceased.

It follows from the second law of thermodynamics that, in a state of chemical equilibrium ($d\mu/dt = 0$) at constant T and ρ, the free energy is a minimum

$$(\partial F/\partial \mu)_{\rho, T} = 0,$$ (8)

$$(\partial^2 F/\partial \mu^2)_{\rho, T} > 0.$$ (9)

Using Eqs. (2) and (7), the condition of an extremum in Eq. (8) in a state of chemical equilibrium takes the form

$$\frac{W_2(T, \mu)}{W_1(T, \mu)} = \exp\left[\frac{\mu^2}{R}\left(\frac{d\eta}{d\mu} - \int\left(\frac{\partial U}{\partial \mu}\right)_T \frac{dT}{T^2}\right)\right].$$ (10)

Equation (1) is a necessary condition for the agreement of the kinetic equations of the type in Eq. (2) with the caloric equation of state in Eq. (1). In the particular case when

$$\frac{\partial^2 U}{\partial (1/\mu)^2} = 0$$ (11)

(this condition holds for all the models analyzed below), Eq. (1) reduces to the form

$$\frac{\partial (\varphi W_1/W_2)}{\partial T} = 0,$$ (12)

$$\varphi(T) = \exp\left[\int \frac{\partial U}{\partial (1/\mu)} \frac{dT}{RT^2}\right].$$ (13)

In [1, 2], it was assumed that

$$U = \frac{1}{\gamma - 1}\frac{RT}{\mu} + E\left(\frac{1}{\mu} - \frac{1}{\mu'}\right),$$ (14)

$$\frac{d\mu}{dt} = 4K_+ \rho^2 \frac{\left(1 - \frac{\mu}{\mu_{max}}\right)^2}{\mu} - A_1\rho\left(\frac{\mu}{\mu_{min}} - 1\right)e^{\frac{E}{RT}},$$ (15)

μ' is determined by the origin of the energy axis; K_+ is the generalized recombination rate; E is the dissociation energy; γ is the adiabatic index; A_1 is a function of T, taken to be approximately equal to $\bar{A}_1$ in [1-4]. It follows from Eqs. (12) and (13) that, if Eq. (15) is to agree with the second law of thermodynamics, $A_1 = AT^{1/(\gamma-1)}$ must be assumed in the expression for the internal energy in Eq. (14), where A = const.

In [3], U was described more accurately by replacing Eq. (14) with the following equation

$$U = \frac{3}{2}\left[1 + \left(\frac{1}{2} + e^{-\frac{\Theta_1}{T}}\right)\left(\frac{\mu}{\mu_a} - 1\right)\right]\frac{RT}{\mu} + E\left(\frac{1}{\mu} - \frac{1}{\mu'}\right),$$ (16)

where μ_a is the molecular mass of gas in the atomic state; Θ_1 is the analog of the excitation temperature of the vibrational degrees of freedom, for which the value 2500 K was chosen in [3]. Equations (16) and (15) with $A_1 = \bar{A}_1 = $ const describe model I.

Satisfaction of the consistency conditions in Eqs. (9) and (10) requires that when B = const

$$A_1 = B\exp\left[\frac{3}{4}\int\left(1 - 2e^{-\frac{\Theta_1}{T}}\right)\frac{dT}{T}\right].$$ (17)

An unsolved integral appears in Eq. (17), which hinders its practical use. The integral may be calculated if the vibrational part of the total internal energy in Eq. (16) is approximated by the temperature dependence for the vibrational energy of diatomic molecules (see [6], for example): $E_{vib} \sim \Theta/(e^{\Theta/T} - 1)$. Then

$$U = \left[\frac{3}{4}\left(\frac{\mu}{\mu_a} + 1\right) + \frac{3}{2}\left(\frac{\mu}{\mu_a} - 1\right)\frac{\Theta_2/T}{e^{\Theta_2/T} - 1}\right]\frac{RT}{\mu} + E\left(\frac{1}{\mu} - \frac{1}{\mu'}\right),$$ (18)

where Θ is the characteristic temperature, and Θ_2 the effective temperature, of excitation of the vibrational degrees of freedom.
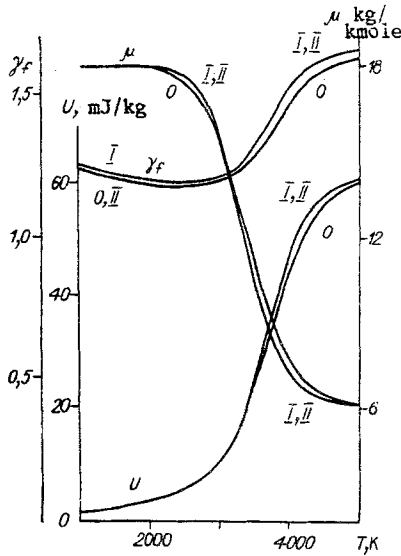
Fig. 1

The consistency condition in Eqs. (9) and (10) gives

$$A_1 = A_2 T^{3/4} \left(1 - e^{-\frac{\Theta_2}{T}} \right)^{3/2}$$

(A_2 = const), and the model kinetic equations takes the form

$$\frac{d\mu}{dt} = 4K_+ \frac{\rho^2}{\mu} \left(1 - \frac{\mu}{\mu_{max}} \right)^2 - A_2 T^{3/4} \left(1 - e^{-\frac{\Theta_2}{T}} \right)^{3/2} \rho \left(\frac{\mu}{\mu_{min}} - 1 \right) e^{-\frac{E}{RT}}. \tag{19}$$

Model II is described by Eqs. (18) and (19).

Analysis of kinetic Eq. (15) shows that, when $K_+ > 0$ and $A_1 > 0$, for any fixed ρ and T, there is a unique state of chemical equilibrium in the range $\mu_{min} < \mu < \mu_{max}$. Taking account of Eqs. (7), (8), and (11), it may be found that $(\partial^2 F/\partial \mu^2)_{\rho,T} > 0$, which corresponds to the condition of minimum free energy in a state of chemical equilibrium. Investigation of Eq. (15), integrated at constant ρ and T, shows that the given equation of state is stable with respect to arbitrary (in the given range) perturbations of μ.

The following expressions for the frozen (subscript f) and equilibrium (subscript e) sound velocities are required for use of model II

$$c_f^2 = \gamma_f \frac{RT}{\mu}, \quad c_e^2 = \gamma_e \frac{RT}{\mu}.$$

Here

$$\gamma_f = 1 + \frac{1}{a} = \frac{c_p^f}{c_V^f}; \quad \gamma_e = 1 + \frac{1 + (2b - a)\Lambda}{a + \Lambda b^2} \neq \frac{c_p^e}{c_V^e};$$

$$a = \frac{3}{4} \left(\frac{\mu}{\mu_a} + 1 \right) + \frac{3}{2} \left(\frac{\mu}{\mu_a} - 1 \right) \left(\frac{\Theta_2}{T} \right)^2 \frac{e^{\Theta_2/T}}{\left(e^{\Theta_2/T} - 1 \right)^2};$$

$$b = \frac{E}{RT} + \frac{3}{4} - \frac{3}{2} \frac{\Theta_2/T}{e^{\Theta_2/T} - 1};$$

$$\Lambda = \frac{(\mu_{max} - \mu)(\mu - \mu_{min})}{2\mu\mu_{max} - \mu_{min}(\mu + \mu_{max})}.$$

The results of calculating the temperature dependences of V, μ, and γ_f in the state of chemical equilibrium of the mixture $2H_2 + O_2$ at p = 1 atm using models I and II are compared with those corresponding to solution of the system of accurate equilibrium equations for elementary reaction using the tables of [5]. The solution of the system of accurate equations is denoted by subscript 0. The limiting dissociated and atomic state of the mixture $2H_2 + O_2$ corresponds to the composition 2H + O, and the limiting recombined state to the composition H_2O. The chemical part of the total internal energy is measured from the limiting recombined

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state with $\mu' = \mu_{max}$ in Eqs. (14), (16), and (18). For the constants of the models, the following values are adopted [1, 2]: $\mu_a = \mu_{min} = 6.005$ kg/kmole, $\mu_{max} = 18.02$ kg/kmole, $E = 4.592 \cdot 10^8$ J/kmole, and $K_+ = 6 \cdot 10^8$ m^6/kmole$^2 \cdot$sec. Analogously to [3], where $\Theta_1 = 2500$ K was chosen for best agreement with the accurate data, the value $\Theta_2 = 4000$ K is adopted here; this is in the range of excitation temperatures of the vibrational degrees of freedom of hydrogen (6100 K) and oxygen (2230 K) [6]. Like the value $A_1 = 1.284 \cdot 10^{13}$ m^3/kmole·sec in [1-4], $A_2 = 5.099 \cdot 10^{10}$ m^3/kmole·sec·K$^{3/4}$ is determined here from the condition of agreement of the solution of the accurate equilibrium equations with ρ, T, and μ at the Chapman—Jouget point ($u = c_f$).

Analysis of the results (Fig. 1) shows that the dependences of U, μ, γ_f on the temperature according to models I and II in the range 1000-5000 K are practically the same, and close to the results obtained using accurate equilibrium equations. Nevertheless, it is preferable to use model II, since it accurately satisfies the second law of thermodynamics.

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COMBUSTION MECHANISM OF SPRAYED LIQUID-FUEL FLAME

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The combustion of liquid fuels sprayed by pneumatic force pumps is widely used in motors and power plants. In [1], it was proven experimentally that a coaxial pneumatic force pump allows liquid and gaseous fuels to be effectively burned. In this connection, there is undoubted interest in theoretical and experimental modeling of the combustion of such fuels, in particular, the mechanism of burnup.

It was shown in [2] that kerosine sprayed a pneumatic force pump burns by a diffusional mechanism, which is very close to the combustion of immersed gaseous hydrocarbon fuels. This conclusion is only valid in a certain range of initial kerosine concentrations. With increase in flow rate of the sprayed (primary) air, the combustion mechanism of a preliminarily mixed mixture should probably appear, and, as in the initial kerosine concentration reaches the stoichiometric level, this process may predominate over the diffusional mechanism. Note that, with a stoichiometric initial concentration of the fuel, the mixture is rapidly depleted on account of mixing with the surrounding air, and does not ignite or else burns ineffectively; therefore, such conditions are of no practical value. In the combustion conditions used in practice, both mechanisms may occur.

The aim of the present work is to investigate experimentally the influence of primary air used to spray liquid fuel on the mechanism of fuel burnup in the flame, which is especially important for correct numerical modeling of the process.

The experimental apparatus and instruments were described in detail in [1, 2].

In the present work, a flame of sprayed kerosine TS-1 sprayed by a coaxial pneumatic force pump, with air and gaseous nitrogen as the spraying gas, is investigated. In the latter case, the primary gas is only a spraying medium, and does not participate in the chemical reaction. Thus, there is a "pure" diffusional flame. The rate of primary-gas emission