Hence

$$\frac{Re_{\text{vib}}^2}{Gr_0} \simeq 11. \qquad (9)$$

The range of data in [1] and [2] did not permit verification of (9). However, using arguments similar to above but modifying the equations for geometry [10], the data of [11] for free convection from horizontal cylinders executing large amplitude transverse vibrations gave an average value of $[Re_{\text{vib}}^2/Gr_0]_{\text{forced}} \simeq 80$ whereas prediction gave approximately 120, the discrepancy is to be expected because of the simplifying assumptions made including neglect of turbulence. This indicates that the right hand side of (9) should be approximately seven. The method discussed here would not be applicable for $Gr_0 \geqslant 1{\cdot}5 \times 10^8$ as a turbulent boundary layer would exist on the stationary plate.

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GENERALIZED FREE ENERGY METHOD FOR EQUILIBRIUM COMPOSITIONS IN COMPLEX MIXTURES

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Knowledge of thermodynamic and transport properties is essential for high temperature heat-transfer studies. In the process of property calculations the equilibrium composition of the reacting components must be determined. White, Johnson and Dantzig [1] have published a simple and effective free energy method for determining the equilibrium composition at a specified temperature and pressure. In this note we generalize the above method to include the condensed phase and electrically charged particles. Furthermore, the rate of change of the moles with respect to temperature is derived, a quantity used in specific heat calculations. Following White, Johnson and Dantzig let:

$$X = (x_1, x_2, \ldots x_n; x_1^0, x_2^0, \ldots x_n^0; x_1^1, x_2^1, \ldots x_n^1; \ldots x_1^N, x_2^N, \ldots x_n^N; x_e)$$

be the set of mole numbers where

x_j = moles of jth species of condensed phase;

x_j^0 = moles of jth species of neutral gas;

x_j^i = moles of jth species of i fold ionized gas;

x_e = moles of electrons.

The free energy of the mixture can be written as

$$F(X) = \sum_{j=1}^{n} [f_j(X) + \sum_{i=0}^{N} f^i_j(X)] + f_e(X) \tag{1}$$

where

$$f_j(X) = x_j C_j, \qquad C_j = \left(\frac{F}{RT}\right)_j;$$

$$f^i_j(X) = x^i_j \left(C^i_j + \ln\frac{x^i_j}{x}\right), \quad C^i_j = \left(\frac{F}{RT}\right)^i_j + \ln P;$$

$$f_e(X) = x_e \left(C_e + \ln\frac{x_e}{x}\right), \quad C_e = \left(\frac{F}{RT}\right)_e + \ln P;$$

P = total pressure in atmospheres;

$$x = x_e + \sum_{j=1}^{n} \sum_{i=0}^{N} x^i_j.$$

The entropy of the mixing term for the condensed phase is assumed to be zero.

The determination of equilibrium composition is equivalent to finding the non-negative set of values x_j, x^i_j, and x_e, which minimizes equation (1) with the constraining equations of conservation of atoms and electrical charge.

$$\sum_{j=1}^{n} (a_{jk} x_j + \sum_{i=0}^{N} a^i_{jk} x^i_j) = b_k \quad (k = 1, 2, \ldots m) \tag{2}$$

$$\sum_{j=1}^{n} \sum_{i=0}^{N} i x^i_j = x_e \tag{3}$$

where b_k is the total number of moles of atom k. a_{jk} is the number of atoms of the kth atom in the jth species.

To minimize $F(X)$ subject to (2) and (3), let

$$G(X) = F(X) + \sum_{k=1}^{m} \pi_k [b_k - \sum_{j=1}^{n} (a_{jk} x_j + \sum_{i=0}^{N} a^i_{jk} x^i_j)] + \theta(x_e - \sum_{j=1}^{n} \sum_{i=0}^{N} i x^i_j) \tag{4}$$

where π_k's and θ are Lagrange multipliers. To minimize $G(X)$ set

$$\frac{\partial G(X)}{\partial x_j} = 0, \quad \frac{\partial G(X)}{\partial x^i_j} = 0, \quad \frac{\partial G(X)}{\partial x_e} = 0.$$

Equation (4) may be linearized by expansion into a Taylor series about an arbitrary point $Y(y_1, y_2, \ldots y_n; y^0_1, y^0_2, \ldots y^0_n; y^1_1, y^1_2, \ldots y^1_n; \ldots y^N_1, y^N_2, \ldots y^N_n; y_e)$. After this, differentiation leads to the following equations.

$$\sum_{j=1}^{n} [a_{jk}(x_j - y_j) + \sum_{i=0}^{N} a^i_{jk}(x^i_j - y^i_j)] + D_k = 0 \tag{5}$$

$$\sum_{j=1}^{n} \sum_{i=0}^{N} i(x^i_j - y^i_j) - (x_e - y_e) = 0 \tag{6}$$

and

$$C_j - \sum_{k=1}^{m} \pi_k a_{jk} = 0 \tag{7}$$

$$\Delta^i_j = x^i_j - y^i_j = -f^i_j(Y) + y^i_j(u + \sum_{k=1}^{m} \pi_k a^i_{jk} + i\theta) \tag{8}$$

$$\Delta_e = x_e - y_e = -f_e(Y) + y_e(u - \theta) \tag{9}$$

where

$$D_k = \sum_{j=1}^{n} (a_{jk} y_i + \sum_{i=0}^{N} a^i_{jk} y^i_j) - b_k;$$

$$f^i_j(Y) = y^i_j \left(C^i_j + \ln\frac{y^i_j}{y}\right);$$

$$f_e(Y) = y_e \left(C_e + \ln\frac{y_e}{y}\right);$$

$$u = \frac{x}{y} - 1;$$

$$y = y_e + \sum_{j=1}^{n} \sum_{i=0}^{N} y^i_j.$$

In (5), we have introduced the quantities D_k, which were first suggested by Levine [2] to simplify the computer programing.

Calculating $x_e + \sum_{j=1}^{n} \sum_{i=0}^{N} x^i_j$ from (8) and (9) the result is

$$\sum_{k=1}^{m} \pi_k \sum_{j=1}^{n} \sum_{i=0}^{N} a^i_{jk} y^i_j = f_e(Y) + \sum_{j=1}^{n} \sum_{i=0}^{N} f^i_j(Y). \tag{10}$$

Now let:

$$r_{hk} = r_{kh} = \sum_{j=1}^{n} \sum_{i=0}^{N} (a^i_{jh} a^i_{jk}) y^i_j \quad (h, k = 1, 2, \ldots m).$$

Substituting (8) into (5), also (8, 9) into (6) together with (7) and (10) gives $n + m + 2$ linear simultaneous equations in the unknowns θ, π_1, π_2, $\ldots \pi_m$, Δ_1, Δ_2, $\ldots \Delta_n$ and u, where $\Delta_j = x_j - y_j$

$$\begin{aligned}
&\alpha_1 u + a_{11}\,\Delta_1 + a_{21}\,\Delta_2 + \ldots + a_{n1}\,\Delta_n + r_{11}\pi_1 + r_{12}\pi_2 + \ldots + r_{1m}\pi_m + \beta_1\theta = H_1\\
&\alpha_2 u + a_{12}\,\Delta_1 + a_{22}\,\Delta_2 + \ldots + a_{n2}\,\Delta_n + r_{21}\pi_1 + r_{22}\pi_2 + \ldots + r_{2m}\pi_m + \beta_2\theta = H_2\\
&\ldots\\
&\alpha_m u + a_{1m}\,\Delta_1 + a_{2m}\,\Delta_2 + \ldots + a_{nm}\,\Delta_n + r_{m1}\pi_1 + r_{m2}\pi_2 + \ldots + r_{mm}\pi_m + \beta_m\theta = H_m\\
&\qquad\qquad \alpha_1\pi_1 + \alpha_2\pi_2 + \ldots + \alpha_m\pi_m = A\\
&\qquad\qquad a_{11}\pi_1 + a_{12}\pi_2 + \ldots + a_{1m}\pi_m = C_1\\
&\qquad\qquad \ldots\\
&\qquad\qquad a_{n1}\pi_1 + a_{n2}\pi_2 + \ldots + a_{nm}\pi_m = C_n\\
&\qquad\qquad \beta_1\pi_1 + \beta_2\pi_2 + \ldots + \beta_m\pi_m + \eta\theta = B
\end{aligned} \tag{11}$$

where

$$\begin{aligned}
\alpha_k &= \sum_{j=1}^{n}\sum_{i=0}^{N} a^i_{jk} y^i_j;\\
\beta_k &= \sum_{j=1}^{n}\sum_{i=0}^{N} i a^i_{jk} y^i_j;\\
\eta &= y_e + \sum_{j=1}^{n}\sum_{i=0}^{N} i^2 y^i_j;\\
H_k &= \sum_{j=1}^{n}\sum_{i=0}^{N} a^i_{jk} f^i_j(Y) - D_k;\\
A &= f_e(Y) + \sum_{j=1}^{n}\sum_{i=0}^{N} f^i_j(Y);\\
B &= -f_e(Y) + \sum_{j=1}^{n}\sum_{i=0}^{N} i f^i_j(Y).
\end{aligned}$$

In order to calculate the equilibrium compositions, one starts by guessing the initial solution $Y(y_1, y_2, \ldots y_n;\ y^0_1, y^0_2, \ldots y^0_n;\ y^1_1, y^1_2, \ldots y^1_n; \ldots y^N_1, y^N_2, \ldots y^N_n;\ y_e)$ permitting $\theta, \pi_1, \pi_2, \ldots \pi_m, \Delta_1, \Delta_2, \ldots \Delta_n$ and u to be determined from equation (11). Δ^i_j and Δ_e are then calculated from (8) and (9) and these values used to make new estimates of the composition. Thus, the incremental change of y_j is $\lambda\Delta_j (0 \leqslant \lambda \leqslant 1)$, etc., using the largest value of λ satisfying the conditions:

1. All mole numbers are positive.
2. $$\frac{\mathrm{d}F(\lambda)}{\mathrm{d}\lambda} = \sum_{j=1}^{n}\left[C_j\Delta_j + \sum_{i=0}^{N}\Delta^i_j\left(C^i_j + \ln\frac{y^i_j + \lambda\Delta^i_j}{y + \lambda\Delta}\right)\right] + \Delta_e\left(C_e + \ln\frac{y_e + \lambda\Delta_e}{y + \lambda\Delta}\right) \leqslant 0$$

where

$$\Delta = \Delta_e + \sum_{j=1}^{n}\sum_{i=0}^{N}\Delta^i_j.$$

To find the rate of change of the moles with respect to the temperature we differentiate equations (2, 3, 7–9). It is easy to show that equations (8, 9, 11) also hold for the derivatives, $\mathrm{d}u/\mathrm{d}T$, $\mathrm{d}\pi_k/\mathrm{d}T$, $\mathrm{d}\theta/\mathrm{d}T$, $\mathrm{d}x_j/\mathrm{d}T$, $\mathrm{d}x^i_j/\mathrm{d}T$ and $\mathrm{d}X_e/\mathrm{d}T$ provided that

$$f^i_j(X) = -x^i_j\left(\frac{H}{RT^2}\right)^i_j \text{ and } f_e(X) = -x_e\left(\frac{H}{RT^2}\right)_e.$$

The method described above has been successfully used to calculate the equilibrium composition of carbon–nitrogen mixtures to temperatures of 15000 K [3]. It was found to be particularly suited for use with a high-speed electronic computer.

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