# METHODS CORRELATING DATA ON THE HEAT CONDUCTIVITY OF DISSOCIATING GASES

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This article describes three methods of correlating experimental data on the heat conductivity of dissociating systems with a single chemical reaction. Criterial equations for the coefficients of thermal conductivity are given.

In studies on dissociating gases, the problem of determining the physical constants of the transport phenomena and, in particular, the coefficient of thermal conductivity is of special interest. In such investigations, however, experimental methods in the high-temperature range are complicated and need further development, while in the case of polyatomic mixtures in which chemical reactions are taking place the practical computations are cumbersome and inaccurate. Therefore, the development of general methods of correlating the available experimental data on the heat conductivity of chemically reacting gases is of definite importance. In this article three methods of evaluating experimental data are discussed in relation to dissociating gases.

## 1. Method Using the Lewis Number and Equilibrium Constants.

The differential equations describing heat transfer with chemical reactions taken into account have been given in their most general form by Ya. M. Braines [1].

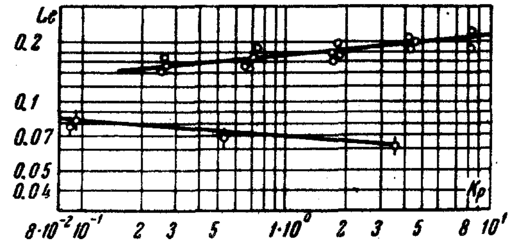

Fig. 1

Given local chemical equilibrium and assuming that the process is stationary and quasi-static and that free convection and external forces are absent, the criterial equation of heat and mass transfer process has the form

$$\Phi(P, P_D, K_p) = 0, \qquad (1.1)$$

where P denotes the Prandtl number, $P_D$ the diffusion Prandtl number, and $K_p$ the partial pressure equilibrium constant. The criteria P and $P_D$ can be expressed in terms of the Lewis number

$$L = P / P_D = c_p \rho D / \lambda,$$

where $c_p$ denotes the specific heat at constant pressure (joule/kg°K), $\rho$ the density (kg/m$^3$), D the diffusion coefficient for the mixture of all the reactants (m$^2$/sec), and $\lambda$ the heat conductivity (joule/m · °K · sec).

Finally, the criterial equation assumes the form

$$L = f(K_p). \qquad (1.2)$$

Figure 1 shows the results of correlation based on (1.2) for the dissociating systems $N_2O_4 \rightleftharpoons 2NO_2$ (circles) and $(HF)_6 \rightleftharpoons 6HF$ (barred circles) in logarithmic coordinates. The data on the specific heat $c_p$ for HF were taken from [2]; the data for $N_2O_4$ were calculated from the formula given in [3].

The density (kg/m$^3$) as a function of the degree of dissociation $\alpha$ was calculated from the formulas

$$\rho = \frac{Mp}{gRT(1+\alpha)} \quad \text{for } N_2O_4 \rightleftarrows 2NO_2, \quad \rho = \frac{Mp}{gRT(1+5\alpha)} \quad \text{for } (HF)_6 \rightleftarrows 6HF,$$

The diffusion coefficient was determined by Hirschfelder's method [4]. The constants $\varepsilon/k$ and $\sigma$ for both gas systems were taken [5] as 337°K and 4.48 Å for HF and as 284.5°K and 4.17 Å for $N_2O_4$, respectively.

Using experimental data on the heat conductivity for the system $N_2O_4 \rightleftharpoons 2NO_2$, we obtain the relation for the diffusion coefficient in the form

$$D = 0.85 \cdot 10^{-6}\, T^{2} / p \ [\text{m}^2/\text{sec}].$$

A similar relation for the same system was obtained in [6].

Data on the heat conductivity $\lambda$ and the equilibrium constants $K_p$ for $N_2O_4$ were taken from the work of Srivastava and Barua [7], where the values of $\lambda$ for this same system determined by Coffin and O'Neill are also indicated; for HF values of $\lambda$ were taken from [8] and values of $K_p$ from [9]. The results for $N_2O_4$ can be represented by the formula

$$L = 0.156 K_p^{0.1}. \qquad (1.3)$$

Formula 1. 3 can be refined by the introduction of a correction term for the pressure; then

$$L = 0.156\, K_p^{0.10} \left(\frac{p}{p_0}\right)^{-0.12}. \qquad (1.4)$$

Here p denotes the variable pressure, and $p_0$ the normal pressure. For hydrogen fluoride

$$L = 0.0725 K_p^{-0.06}. \qquad (1.5)$$

Because of the lack of experimental data relation (1. 5) needs refining. The error in calculating the heat conductivity from formulas (1. 4) and (1. 5) did not exceed 4% with respect to the experimental values.

## 2. The Entropy Method.

The method in which the quantity $(S_1 - S)/R$ is taken as a criterion was suggested by A. G. Usmanov and coworkers. However, it was not possible to use this method in the form in which the authors used it [10].

The actual correlation formula includes the degree of dissociation $\alpha$ and may be written in the form

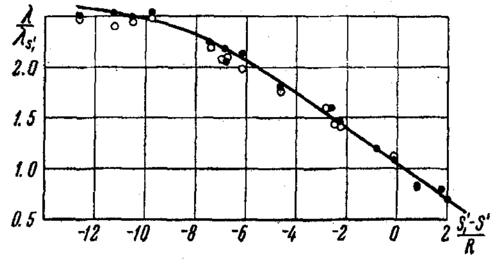

Fig. 2

$$\frac{\lambda}{\lambda_{S_1}} = \frac{S_1(1-\alpha_1) - S(1-\alpha)}{R}$$

or

$$\frac{\lambda}{\lambda_{S_1}'} = \frac{S_1' - S'}{R}. \qquad (2.1)$$

Here $\lambda$ denotes the variable heat conductivity; $\lambda_{S_1'}$ is the heat conductivity corresponding to the origin of the entropy scale for $\alpha_1 = \text{const}$; S denotes the variable entropy corresponding to the degree of dissociation $\alpha$; $S_1$ is the entropy value corresponding to the origin of the $\alpha_1$-scale; $S_1'$ denotes the reduced origin of the entropy scale; and $S'$ the reduced variable entropy.

Experimental data on the heat conductivity of the system $N_2O_4 \rightleftharpoons 2NO_2$ were correlated by this method. The results are given in Fig. 2. The origin of the entropy scale was chosen at $\alpha_1 = 0.898$; the black circles are points obtained by Srivastava and Barua, the open circles are points obtained by Coffin and O'Neill.

The choice of entropy origin corresponding to $\alpha_1 = 0.898$ was conditioned by the fact that in the region of large values of $\alpha$ (of the order of $\alpha = 0.85$ and higher) the heat conductivity depends only slightly on the pressure for $\alpha = \text{const}$. This enabled us to choose the heat conductivity $\lambda_{S_1'} = 6.6 \cdot 10^{-2}$ joule/m · deg · sec corresponding to the selected $S_1'$ and to use the same coefficient for all pressures. Figure 3 shows the variation of $\lambda$ as a function of $\alpha$ for the system $N_2O_4 \rightleftharpoons 2NO_2$ at different constant pressures. The points 1, 2, 3, 4, and 5 correspond to the values p = 100, 200, 300, 400, and 500 mm Hg, respectively.

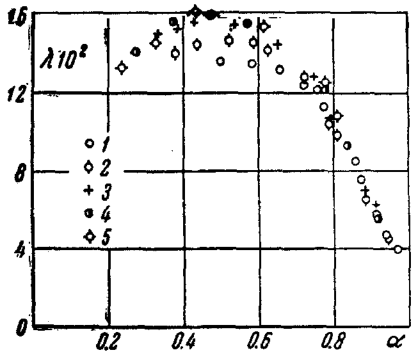

Fig. 3

Note that this choice of the origin of the entropy scale is not only correct for a degree of dissociation $\alpha \geq 0.5$, but can also be used in the range $\alpha < 0.5$ if the reduced variable entropy is taken as $S' = \alpha S$. The available experimental data on the heat conductivity in the region $\alpha < 0.5$ confirm the above. The scatter of the points obtained by this method does not exceed 9% with respect to the experimental points.

## 3. Method using Critical Parameters.

This method employs the relation

$$\lambda = \frac{g^{1/2} P_k^{2/3} R_\mu^{5/6}}{M^{1/2} T_k^{1/6}} f\left(\pi, \tau, \frac{c_{p\mu_0}}{R_\mu}\right) \qquad (3.1)$$

for thermodynamically similar substances.

When a dissociation reaction takes places, the gas constant and molecular weight of the mixture change. For the system $N_2O_4 \rightleftharpoons 2NO_2$ the gas constant and the molecular weight as functions of the degree of dissociation can be written thus:

$$R = \frac{8314.4}{92}(1+\alpha), \qquad M = \frac{92}{1+\alpha}.$$

Here M denotes the 92-molecular weight of $N_2O_4$; 8314.4 is the universal gas constant (joule/kmole · °K). Then (3.1) assumes the form

$$\lambda = g^{1/2} P_k^{2/3} \left[\frac{8314.4}{92}(1+\alpha)\right]^{5/6} \left(\frac{92}{1+\alpha}\right)^{-1/2} T_k^{-1/6} f\left(\pi, \tau, \frac{c_{p\mu_0}}{R_\mu}\right). \tag{3.2}$$

In writing Eq. (3.2) one has to take into account the fact that $\alpha$ depends both on the type of the reaction and on the external conditions, i.e., $\alpha = f(\pi, \tau)$.

Using (3.2) with constant values for ($\tau$, $c_{p\mu_0}/R_\mu$ or $\pi$, $c_{p\mu_0}/R_\mu$ and introducing the degree of dissociation, we can calculate the relative change in heat conductivity. Analytically, this can be written in the form

$$\frac{\lambda}{\lambda_1} = \left(\frac{1+\alpha}{1+\alpha_1}\right)^{4/3} \left(\frac{1-\alpha}{1-\alpha_1}\right)^n \quad \text{for } \alpha \geqslant 0.5 \tag{3.3}$$

or

$$\frac{\lambda}{\lambda_1} = \left(\frac{1+\alpha}{1+\alpha_1}\right)^{4/3} \left(\frac{\alpha}{\alpha_1}\right)^n \quad \text{for } \alpha \leqslant 0.5.$$

The exponent n is taken as equal to 3/4 for $0.9 > \alpha > 0.1$ and 1/4 for $0.9 < \alpha < 0.1$.

The factors $[(1-\alpha)/(1-\alpha_1)]^n$ and $(\alpha/\alpha_1)^n$ describe the experimentally determined change in heat conductivity sufficiently well.

Any available experimental value of $\lambda_1$ may be used to define its scale.

The error of this method did not exceed the experimentally obtained values by more than 11%. The error of the analytical computations of the heat conductivity in [7], however, is in some cases 17%.

Thus, the coefficients of thermal conductivity of dissociating gases can apparently be described quite well by means of Eqs. (1.2), (2.2), and (3.3). Each of these enables one to obtain data on the heat conductivity of dissociating mixtures with a single chemical reaction with an error of 4-11%. Using the generalized relations, it is possible to obtain $\lambda$-values for these reactions in regions not covered by experiments. Relation (1.2) provides a possibility of indirectly determining the diffusion coefficients for various external conditions.

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