

Viscosity of the Dry Combustion Products of Carbon in Air

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The paper presents tabulated values of the viscosity of the dry combustion products of pure carbon in air. The data provided refer to atmospheric pressure and extend over the temperature range 0 to 1000°C, and over air contents from the stoichiometric limit for complete combustion to five times this value. The data have been generated with the aid of the kinetic theory of multicomponent gas mixtures supported by the extended law of corresponding states formulated by Kestin, Ro, and Wakeham. The tabulated data have an estimated accuracy of $\pm 0.3\%$. The relations used for the generation of the tables are provided to allow their extrapolation, whereas simplified, empirical correlations enable their interpolation.

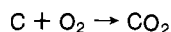
An accurate knowledge of the thermophysical properties of fluids is a prerequisite to the optimum design of process plant and power generation equipment. However, the large number of fluids and fluid mixtures encountered in practice renders the direct measurement of the physical properties of all systems over a wide range of states impossible. Consequently, it is desirable to develop a scheme which will allow the generation of a large body of data from a limited amount of experimental information.

In a series of papers (1, 2, 5-10) such a scheme has been established for the correlation and prediction of the viscosity and diffusion coefficient of arbitrary dilute, gaseous multicomponent mixtures containing the monatomic gases and several, nonpolar polyatomic species. The scheme is based upon the classical kinetic theory and the single additional hypothesis that the intermolecular potential for all the pure species and their unlike, binary interactions can be rendered almost conformal by means of two scaling parameters, a length parameter σ_{ij} and an energy parameter ϵ_{ij} . This hypothesis has been subjected to rigorous tests for multicomponent mixtures of gases of increasing complexity, using information obtained from studies of binary mixtures alone, and has been shown to allow reliable prediction of viscosity judged against direct measurements (2, 6, 8).

In this paper we use this predictive scheme to provide tables for the viscosity of the products of the combustion of carbon in dry air. The tables cover the temperature range 0-1000°C, at atmospheric pressure and excess air factors from 0 to 4. The tabulated data are estimated to have an uncertainty of $\pm 0.3\%$. The predictive scheme, which is also detailed, allows extrapolation of the tables with a similar confidence level, and simplified expressions allow convenient interpolation.

The Combustion Products

For the purposes of this paper we consider dry air to be composed of N_2 , O_2 , and Ar, in the mole fractions of 0.7808, 0.2095, and 0.0097, respectively. The stoichiometric combustion of pure carbon in this air is given by



so that in an excess of air the combustion product is a four-component gaseous mixture of N_2 , O_2 , Ar, and CO_2 .

In practice, the equilibrium combustion products will contain finite amounts of CO as well. However, in the absence of excess carbon the amount of CO present in the equilibrium products will remain negligibly small in the temperature range 0-1000°C as

illustrated by the Boudouard diagram contained in Figure 1 for the dissociation reaction (4)



The stoichiometric air to fuel mass ratio for the combustion system, r_s , is 11.5118. We can therefore define an excess air factor, α , by the relation

$$r = r_s(1 + \alpha)$$

where r is the air to fuel ratio for nonstoichiometric combustion.

In this case the mole fractions of the product gases can easily be shown to be

$$\left. \begin{aligned} x_{CO_2} &= 0.2095/(1 + \alpha) \\ x_{O_2} &= 0.2095\alpha/(1 + \alpha) \\ x_{N_2} &= 0.7808 \\ x_{Ar} &= 0.0097 \end{aligned} \right\} \quad (1)$$

Accordingly, in the next section we present a scheme for the evaluation of viscosity of a mixture of these gases for various values of excess air factor.

The Calculations

The basis of the calculation scheme is the Curtiss-Hirschfelder (3) expression for the viscosity of multicomponent gas mixtures, which, using usual notation may be written

$$\mu = -1 \times \frac{\begin{vmatrix} H_1 & \dots & H_{1n} & x_1 \\ & \dots & & \\ H_{n1} & \dots & H_{nn} & x_n \\ x_1 & \dots & x_n & 0 \end{vmatrix}}{\begin{vmatrix} H_1 & \dots & H_{1n} \\ & \dots & \\ H_{n1} & \dots & H_{nn} \end{vmatrix}} \quad (2)$$

where

$$H_{ii} = \frac{x_i^2}{\mu_i} + \sum_{\substack{k=1 \\ k \neq i}}^n \frac{2x_i x_k}{\mu_{ik}} \frac{M_i M_k}{(M_i + M_k)^2} \left\{ \frac{5}{3A_{ik}^*} + \frac{M_k}{M_i} \right\} \quad (2a)$$

and

$$H_{ij} = - \frac{2x_i x_j}{\mu_{ij}} \frac{M_i M_j}{(M_i + M_j)^2} \left\{ \frac{5}{3A_{ij}^*} - 1 \right\} \quad (2b)$$

$i \neq j$

with

$$\mu_{ij} = \left(\frac{5}{16} \right) [2kM_i M_j T / \pi N (M_i + M_j)]^{1/2} (1/\sigma_{ij}^2 \Omega_{22}) \quad (2c)$$

Although these equations are attained by solution of the Boltzmann equation for monatomic species, it has been shown (11) that their formal structure remains unaltered in the case of nonpolar, polyatomic gases. The quantities Ω_{22} and A_{ij}^* which enter these expressions are functionals of the intermolecular potential (3) for the species i and j . The postulate of the extended law of corresponding states asserts that the intermolecular

Table I. Scaling Parameters

	Ar	N ₂	O ₂	CO ₂
		$\epsilon_{ij}/k, K$		
Ar	153.6 ₁	130.3 ₂	145.4 ₇	169.8 ₆
		N ₂	119.5 ₈	164.0 ₂
		O ₂	137.0 ₀	168.9 ₆
			CO ₂	266.1 ₃
		σ_{ij}, nm		
Ar	0.3291	0.3419	0.3304	0.3540
		N ₂	0.3454	0.3640
		O ₂	0.3323	0.3536
			CO ₂	0.3703

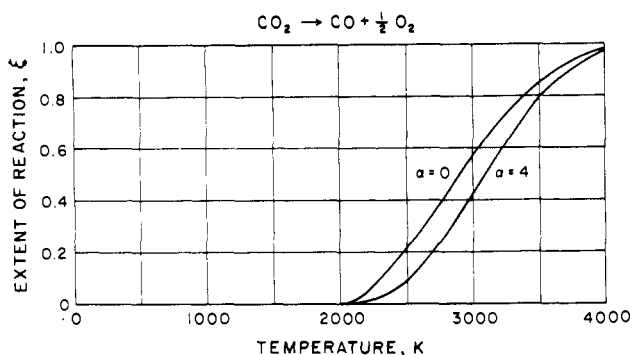


Figure 1. Boudouard diagram for the reaction $CO_2 \rightarrow CO + \frac{1}{2}O_2$.

potentials of all the monatomic species may be made conformal by a suitable choice of two scaling parameters (σ_{ij} for and ϵ_{ij} for energy) and leads to the result that the functionals Ω_{22} and A^* are universal functions of the reduced temperature $T^* = (kT/\epsilon_{ij})$ among these species. This result is well supported by the available experimental data, and empirical correlations of the relation between the functionals and the reduced temperature have been established (7, 10). These are

$$\Omega_{22} = \exp\{0.45667 - 0.53955(\ln T^*) + 0.18265(\ln T^*)^2 - 0.3629(\ln T^*)^3 + 0.00241(\ln T^*)^4\} \quad (3)$$

and

$$A^* = \exp\{0.10967 - 0.09555(\ln T^*) + 0.08965(\ln T^*)^2 - 0.02629(\ln T^*)^3 + 0.00241(\ln T^*)^4\} \quad (4)$$

$$1 < T^* < 25$$

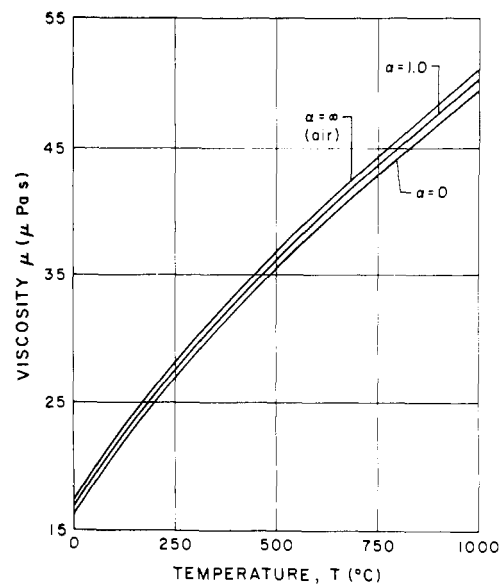


Figure 2. Viscosity of the dry combustion products of carbon in air at constant excess air factor.

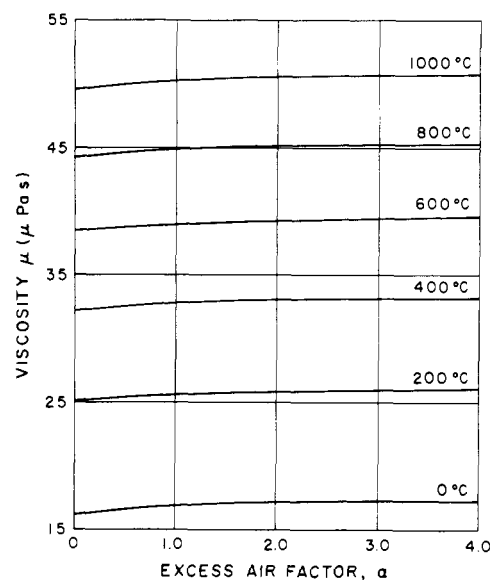


Figure 3. Isotherms for the viscosity of the dry combustion products of carbon in air.

Table II. Viscosity of the Dry Products of the Combustion of Carbon

T, °C	Excess air factor α										
	0.0	0.1	0.3	0.5	0.8	1.0	1.4	2.0	3.0	4.0	∞
0	16.20	16.29	16.44	16.55	16.67	16.73	16.82	16.90	16.99	17.04	17.24
100	20.84	20.94	21.10	21.22	21.34	21.40	21.49	21.59	21.68	21.73	21.95
200	24.95	25.06	25.22	25.34	25.47	25.53	25.63	25.73	25.82	25.88	26.10
300	28.68	28.79	28.96	29.09	29.22	29.29	29.39	29.49	29.59	29.64	29.88
400	32.13	32.25	32.42	32.55	32.69	32.76	32.87	32.97	33.07	33.13	33.38
500	35.37	35.49	35.67	35.80	35.95	36.02	36.13	36.23	36.34	36.41	36.66
600	38.43	38.55	38.74	38.88	39.03	39.11	39.22	39.33	39.44	39.51	39.77
700	41.35	41.48	41.67	41.82	41.97	42.05	42.17	42.28	42.40	42.47	42.74
800	44.15	44.28	44.49	44.64	44.80	44.88	45.00	45.12	45.24	45.31	45.60
900	46.85	46.99	47.20	47.35	47.52	47.60	47.73	47.86	47.98	48.06	48.36
1000	49.46	49.61	49.82	49.98	50.16	50.25	50.38	50.51	50.64	50.72	51.03

In later work it has been demonstrated that these same functionals are also universal among some nonpolar, polyatomic gases, their mixtures with each other and with the monatomic species (1, 5, 7, 8). In particular, the scaling parameters σ_{ij} and ϵ_{ij} for each binary interaction in the system N_2 , O_2 , Ar, CO_2 have been found which ensure the best representation of their functionals by eq 3. The values of these parameters are listed in Table I. Thus eq 2-4 together with the parameters of Table I immediately allow prediction of the viscosity of any mixtures of these gases over the large temperature range indicated by the limits on eq 3 and 4.

Results

The calculation scheme described in the previous section was utilized to predict the viscosity of the combustion products of carbon in dry air. The results are given in Table II for the temperature range 0-1000 °C and for air-to-fuel ratios extending from the stoichiometric value ($\alpha = 0$) to infinity (pure air). The results are also shown graphically in Figures 2 and 3. Basing our estimate of the possible uncertainty in the calculated values upon the previous success of the prediction scheme for other mixtures of complex gases (5, 6, 8) we estimate the accuracy of the data to be within $\pm 0.3\%$. Figure 2 shows that the temperature dependence of the viscosity of the combustion products differs very little from that of air. The maximum difference between the viscosity of the combustion products and that of air does not exceed 5%.

The equations (1) to (4), given earlier, allow accurate interpolation and extrapolation in the temperature-composition space subject only to the limitations imposed by eq 3 and 4 and by the onset of molecular dissociation. However, the complexity of the

equations necessitates the use of a digital computer. For the purpose of performing quick calculations of the viscosity of the combustion products as a function of temperature and excess air factors, $\mu(T, \alpha)$, we propose the much simpler formula

$$\mu(T, \alpha) = \mu(T, 0) + \alpha / [(1 + \alpha)(0.9313 - (0.3167 \times 10^{-3})T)] \quad (5)$$

where

$$\mu(T, 0) = T^{1/2} \{0.627 + 128.38(1/T) - 5818.8(1/T)^2\}^{-1} \quad (6)$$

with T in K and μ in $\mu Pa \cdot s$. Equations 5 and 6 reproduce the data of Table II to within $\pm 0.4\%$ for $100 \leq T \leq 1000$ °C and $0 \leq \alpha \leq \infty$. The difference increases to 0.9% at $T = 0$ °C as $\alpha \rightarrow \infty$.

Literature Cited

- (1) Hellemans, J., Kestin, J., Ro, S. T., *Physica (Utrecht)*, **65**, 362 (1973).
- (2) Hellemans, J., Kestin, J., Ro, S. T., *Physica (Utrecht)*, **71**, 1 (1974).
- (3) Hirschfelder, J. O., Curtiss, C. F., Bird, R. B., "The Molecular Theory of Gases and Liquids", Wiley, New York, N.Y., 1964.
- (4) Kestin, J., "A Course in Thermodynamics", Vol. II, Blaisdell, Waltham, Mass., 1968.
- (5) Kestin, J., Khalifa, H. E., Ro, S. T., Wakeham, W. A., *Physica (Utrecht)*, in press.
- (6) Kestin, J., Khalifa, H. E., Wakeham, W. A., *J. Chem. Phys.*, **65**, 5186 (1977).
- (7) Kestin, J., Mason, E. A., *AIP Conf. Proc.*, No. 11, 137 (1973).
- (8) Kestin, J., Ro, S. T., *Ber. Bunsenges. Phys. Chem.*, **78**, 20 (1974).
- (9) Kestin, J., Ro, S. T., Wakeham, W. A., *Physica (Utrecht)*, **58**, 165 (1972).
- (10) Kestin, J., Ro, S. T., Wakeham, W. A., *J. Chem. Phys.*, **56**, 4119 (1972).
- (11) Monchick, L., Yun, K. W., Mason, E. A., *J. Chem. Phys.*, **39**, 696 (1963).

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A Critical Review of Equations for Predicting Saturated Liquid Density

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An extensive evaluation of recently published generalized methods for predicting the saturated liquid density of pure compounds has been made with a large set of critically evaluated experimental density data. Results of these evaluations are given. The Spencer-Danner version of the Rackett equation with one adjustable constant, Z_{RA} , determined from the experimental data is shown to be slightly more accurate on an overall basis than the other equations. This equation also compares favorably to the other equations in terms of availability of input parameters, range of application, and ease of use. Updated values of Z_{RA} are given for 75 hydrocarbons, 71 other organic compounds, and 19 inorganics. With these values one can predict accurately the variation of the saturated liquid density over the entire temperature range from the triple point to the critical point. It is also shown that for highly associated compounds the Joffe-Zudkevitch equation is superior.

An important input parameter to most process design calculations is the liquid density and in particular the saturated liquid density of the pure component or mixture at hand. For example, accurate liquid densities are required in calculating the capacity of storage tanks, tower heights, pressure corrections to liquid

fugacities, and compressor loads, for custody transfers, and in some cases, to estimate other physical properties such as surface tension (107, 123).

The prediction of orthobaric liquid density has been the subject of numerous studies over the last 100 years. Therefore, unlike many other physical properties where both data and correlations which do not have important limitations are relatively scarce, both correlations and data are plentiful. In 1972, Spencer and Danner (102) made an extensive evaluation of the available methods for predicting saturated liquid density of pure compounds as a function of temperature. They concluded that the simplest and most accurate means of prediction was a slightly modified version of the Rackett equation (87). In addition, they developed values of Z_{RA} , the single adjustable input parameter required for this equation, for 64 hydrocarbons, 36 organics, and 11 inorganics. The work described herein has a threefold purpose: to review and evaluate liquid density correlations that have been published since 1972, to update the recommended values of Z_{RA} , to expand compound coverage based on recently published data.

Only pure component saturated liquid density correlations are considered in this work. Extension of the final recommended equation to mixtures at both saturated and subcooled conditions is considered elsewhere (107).