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Thermophysical Properties of Natural Gases for On-Line Metering[1]

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The evaluation of the background transport properties of natural gas multicomponent mixtures over a moderate temperature and pressure range around ambient is considered in the context of the development of certifiable sensors for the measurement of mass and energy fluxes. The best available, theoretically based procedures to predict the properties are compared with experimental information to test the internal consistency, accuracy, and range of validity of the prediction. This is of primary concern to the demonstration of the viability of such sensors. It is shown that for low to moderate pressures, it is possible to achieve an internal consistency of the order of a few parts in a thousand and an accuracy of better than $\pm 1\%$. At very high pressures the predictive scheme is also satisfactory, with errors of the order of a few percent. However, the procedure employed here systematically underestimates the thermal conductivity of the gas mixtures studied for intermediate pressures owing to the neglect of the critical enhancement even for temperatures quite far removed from the critical. The range of conditions for which the critical enhancement of the thermal conductivity is significant in mixtures is explored with data for binary mixtures of methane and ethane.

KEY WORDS: ethane; gas metering; methane; natural gas; prediction; thermal conductivity; viscosity.

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1. INTRODUCTION

The continued trend to deregulate the gas industry in the United States and to privatize the industry in Europe has led to increased competition among gas suppliers. In turn, this has increased the demand for precision in the monitoring of gas supplies, with a greater emphasis upon energy rather than mass or volume flux [1-5]. These trends are further compounded by the increased variability in the composition and thus heating value of natural gas. Considerable efforts are therefore being devoted to the development of sensors for the measurement of mass and energy fluxes for residential, industrial, and compressed natural gas mixtures which satisfy the following conditions: (a) the dynamic flow range should be as much as 3000:1; (b) the meters should have a low power consumption and be rugged (particularly for automotive operation), durable, and of a low cost; and (c) the sensors should yield accurate measurements of mass or energy flux independently of temperature, pressure, or gas composition.

A sensor design which fulfills most of the requirements is based upon the principles of thin-film anemometry [6–10]. The sensor design of interest makes use of the simultaneous measurement of flow velocity and the thermophysical properties of a gas mixture to derive its heat content [6, 7]. It is therefore important to demonstrate that, following a calibration of the device with a range of pure gases with known thermophysical properties, the sensor returns reliable values of the thermophysical properties for gas mixtures of an arbitrary composition. For this purpose, it is necessary to have these properties available and the present paper examines our ability to predict them in a fashion consistent with the properties of pure components. The examination is conducted with respect to one example, the methane–ethane system, which is relevant to natural gases and for which experimental data exist.

2. METHODOLOGY

An internally consistent procedure for the evaluation of the transport properties of dense gas mixtures is based upon the application of the Thorne–Enskog equations for rigid sphere systems to real gases. The development of the procedure and an assessment of its accuracy for some systems and some regions of the thermodynamic surface have been given elsewhere [11-13]. Here it is sufficient to state the essential features of the procedure before considering its application to the conditions of interest for gas flow monitoring.

The Thorne–Enskog equations relate the transport properties of a dense gas mixture to those of the constituent pure species and to characteristics of binary pairs of components in the limit of zero density. The effect of density upon the properties is included through a set of radial distribution functions for rigid spheres at contact, one for each pair of species, and by a mean free-path shortening parameter for each interaction (equivalent to a covolume). In the present application of this theory the radial distribution functions for rigid spheres at contact are replaced by functions deduced from experimental data on the transport properties for pure gases, which data are also the source of the mean free-path shortening parameter. The pseudo-radial distribution functions deduced in this manner, and the corresponding volume parameters are a consistent pair automatically chosen to reproduce the pure-gas property [14]. These functions are then used to evaluate appropriate pseudo-radial distribution functions for each binary interaction in the multicomponent mixture through combination rules based upon those for rigid spheres. A similar technique is also employed to evaluate the binary mean free-path shortening parameter. The procedure therefore provides a theoretically based interpolation scheme between the transport properties of all pure components, which are themselves exactly reproduced.

It should be emphasized that the Thorne–Enskog theory takes no account of correlations in velocity space, such as are known to occur in real systems [14]. However, they are necessarily present in the experimental data employed for the pure gases so that some account, albeit an heuristic one, is taken of these effects in mixtures. However, no account at all is taken of the contributions from critical enhancements of the thermal conductivity [15].

We define the background transport property X_{bkg} as the sum of a zero-density contribution, $X_0(T)$, and an excess contribution, $\Delta X(\rho, T)$, so that

$$X_{\mathrm{bkg}}(\rho, T) = X_0(T) + \Delta X(\rho, T) \tag{1}$$

and recognize that the total transport property consists of the background plus a critical enhancement term

$$X(\rho, T) = X_{\mathrm{bkg}}(\rho, T) + \Delta X_c(\rho, T) \tag{2}$$

where T denotes the absolute temperature and ρ the fluid density.

3. APPLICATION

In this study we have applied the methodology set out above to the prediction of the background viscosity and thermal conductivity of methane–ethane gas mixtures for which significant amounts of experimental data are available and for which the pure components occur in natural gas mixtures.

For each of the pure components, accurate representations of the properties are available. For methane Friend et al. [16] have provided a representation of both the viscosity and the thermal conductivity. For ethane Friend et al. [17] and Vesovic et al. [18, 19] have provided representations of the transport properties. Here we employ the representation of Vesovic et al. [18, 19]. In all cases we employ for our predictions only the background component X_{bkg} of the pure gas properties.

For each pure fluid, we have employed consistently in the calculations the equations of state recommended for the particular correlation employed for the transport properties [16–19]. For the mixtures, the calculations are performed entirely in terms of the mixture density so that no equation of state is required [11–13]. Naturally, the calculations always then refer to the density of the mixture reported by experimenters. The interaction quantities for the binary system in the limit of zero density have been taken from the correlations of the extended law of corresponding states [20] in which the scaling parameters of the methane–ethane interaction were derived from the dilute gas viscosity measurements of Abe et al. [21].

4. COMPARISONS

4.1. Viscosity

Figure 1 displays the deviations of the experimental viscosity data of Abe et al. [21] for the methane–ethane mixture (claimed uncertainty, ±0.3%) at a pressure of 0.1 MPa as a function of temperature from the present predictions for several different compositions. It can be seen that the experimental data do not depart from the prediction by more than ±0.5%, which is almost consistent with the experimental uncertainty and with the fact that the data were used to establish the corresponding states parameters [20, 21].

Measurements of the viscosity of methane–ethane mixtures over a wide range of conditions have been reported by Diller [22]. We have compared our predictions with these results in Fig. 2 for temperatures very close to those employed by Abe et al. [21]. The magnitude of the deviations shown, which is typical of that under other conditions, is about 2 or 3%, although values of 8% are attained in the extreme cases. This agreement can be considered reasonable since Diller claims an uncertainty of about ±2%. However, it is important to note that at low densities the deviations rise to 5%. This implies that at least under these conditions the data are inconsistent with those of Abe et al. [21]. It would seem therefore that the error in the data in the vapor phase must be rather larger than originally estimated, a view confirmed by an examination of data for other

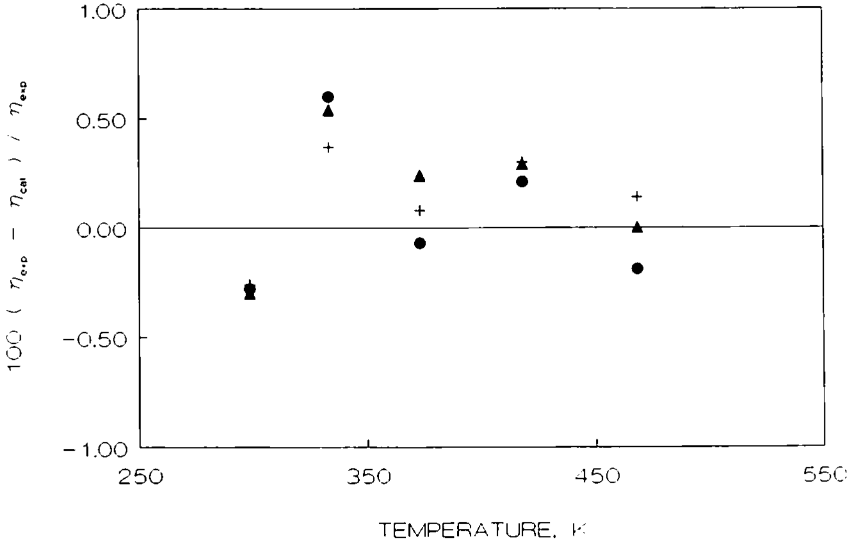

Fig. 1. Deviations of the experimental viscosity data of Abe et al. [21] from the predictions at zero density. x_{CH_4}: (+) 0.26; (▲) 0.49; (●) 0.75.

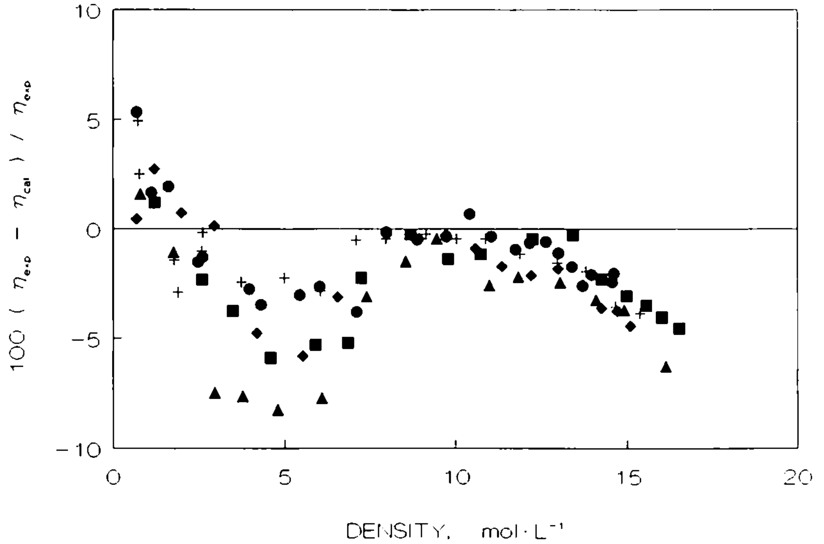

Fig. 2. Deviations of the experimental viscosity data of Diller [22] from the predictions. (+) $x_{CH_4} = 0.5$, $T = 300$ K; (▲) $x_{CH_4} = 0.5$, $T = 280$ K; (●) $x_{CH_4} = 0.69$, $T = 300$ K; (■) $x_{CH_4} = 0.69$, $T = 270$ K; (◆) $x_{CH_4} = 0.35$, $T = 300$ K.

systems from the same source. It is estimated that the accuracy of the viscosity data derived from the present correlation is approximately ±2% over the entire range of density and it is believed that this is better than that associated with the direct measurements available. Certainly, because the composition dependence of the viscosity is obtained from theory, the results as a function of composition have a greater internal consistency than those from experiment.

4.2. Thermal Conductivity

The thermal conductivity of methane–ethane mixtures has been measured over a wide range of temperature and pressure in a transient hot-wire instrument by Roder and Friend [23]. Their results have an estimated uncertainty of ±1.5% except in the critical region, where it may be poorer. The same authors have also provided an empirical correlation for the thermal conductivity surface of methane–ethane mixtures [24]. Figure 3 contains a comparison between the experimental results for the subcritical vapor region and the present calculations for three compositions. It can be seen that the deviations are of the order of ±2% and therefore consistent with the experimental error. This is substantial confirmation of the validity of the procedure employed for prediction and is comparable with the performance of the procedure for other systems [11–13].

Figures 4 and 5 display similar results for supercritical temperatures for two mixtures. In each figure we identify the temperature of the measurements and the ratio of the temperature to the critical temperature for the mixture. It can be seen that at very low densities and very high densities the agreement between calculation and experiment is comparable with that for the subcritical vapor, except under some conditions at the highest densities, where it has been necessary to extrapolate the representation of one of the pure components. However, at intermediate densities a large positive peak in the deviations occurs which grows with approach to the critical temperature. Quite obviously, this peak is associated with the enhancement of the thermal conductivity, with which the theory employed is unable to deal since it is confined to the background property. The extent in temperature and density of the enhancement as deduced from the present evaluation of the background thermal conductivity is very large (from 1 to 15 $\mathrm{mol\,L^{-1}}$ even 70 K above the critical temperature of the mixture). Figures 4 and 5 also include plots of the thermal conductivity enhancement deduced from the correlation of Roder and Friend. The fact that the correlated critical enhancement does not represent well the experimental data in Figs. 4 and 5 reflects the fact that the critical enhancement term was originally deduced from experimental data with the aid of a plausible but arbitrary background term. The use of a more soundly based

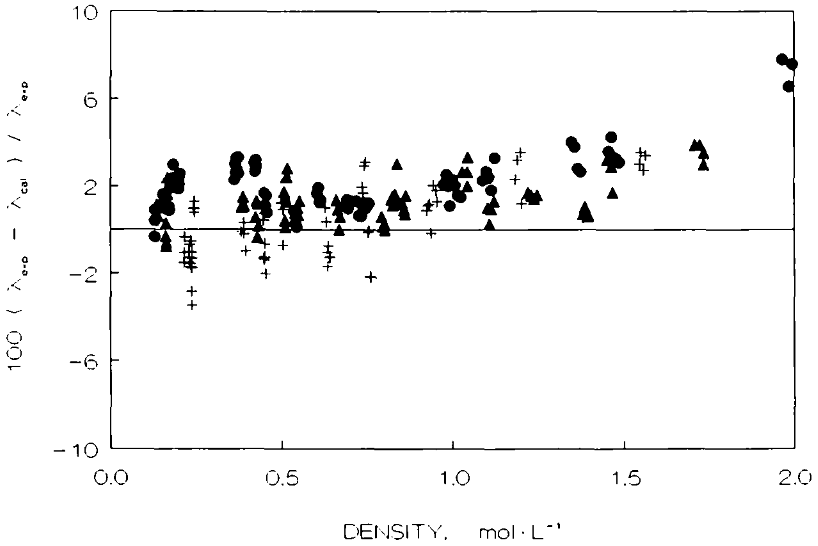

Fig. 3. Deviations of the experimental thermal conductivity data of Roder and Friend [23] from the predictions in the vapor. (+) $x_{CH_4} = 0.69$, $194 < T < 234$ K; (▲) $x_{CH_4} = 0.5$, $231 < T < 260$ K; (●) $x_{CH_4} = 0.35$, $227 < T < 278$ K.

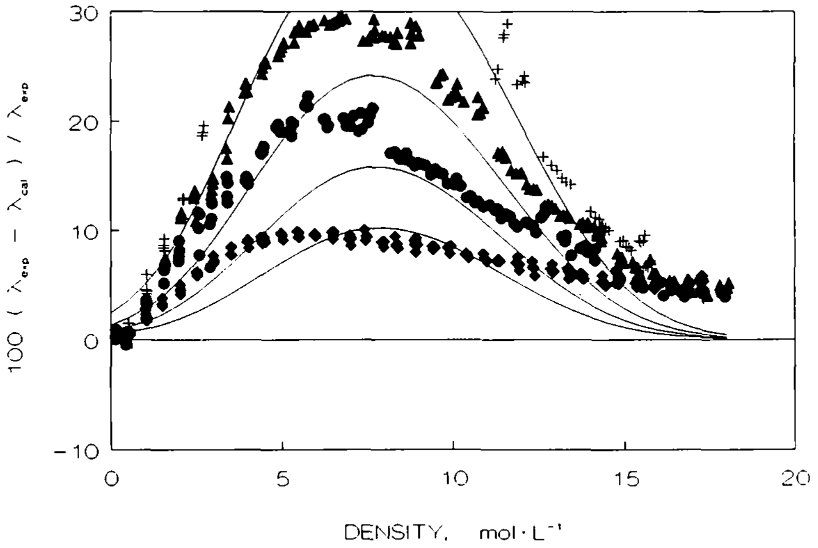

Fig. 4. Deviations of the experimental thermal conductivity data of Roder and Friend [23] from the predictions in the supercritical region for $x_{CH_4} = 0.69$: (+) $T = 239$ K, $T/T_c = 1.01$; (▲) $T = 254$ K, $T/T_c = 1.06$; (●) $T = 274$ K, $T/T_c = 1.15$; (◆) $T = 296$ K, $T/T_c = 1.25$. The solid lines correspond to the critical enhancement deduced from the correlation of Roder and Friend [24].

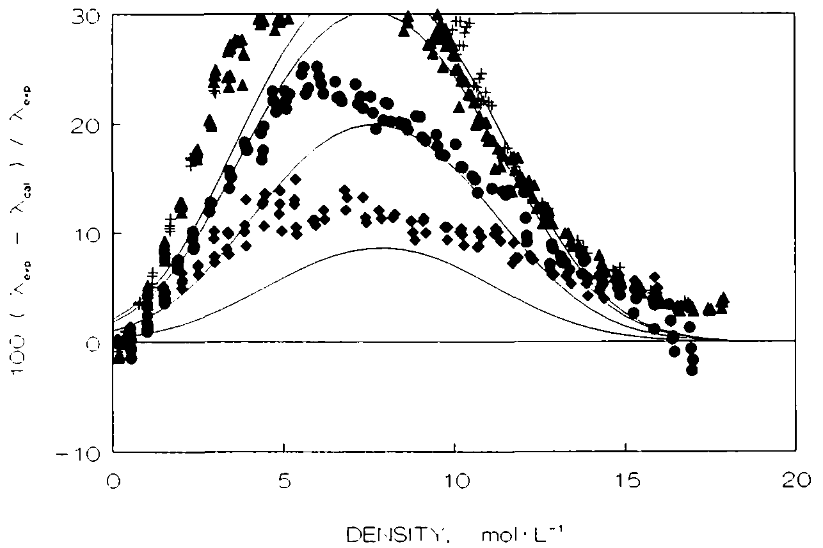

Fig. 5. Deviations of the experimental thermal conductivity data of Roder and Friend [23] from the predictions in the supercritical region for $x_{CH_4} = 0.50$: (+) $T = 265$ K, $T/T_c = 1.01$; (▲) $T = 269$ K, $T/T_c = 1.02$; (●) $T = 290$ K, $T/T_c = 1.10$; (◆) $T = 330$ K, $T/T_c = 1.26$. The solid lines correspond to the critical enhancement deduced from the correlation of Roder and Friend [24].

background term naturally would require a new evaluation of the "experimental" critical enhancement.

It is interesting to note from Figs. 4 and 5 that the magnitude of the relative deviation of the thermal conductivity for each composition is almost exactly the same at the same reduced temperature, (T/T_c). A similar observation in the case of refrigerants and refrigerant mixtures has been exploited by Huber et al. [25] to develop a corresponding-states procedure for the representation of the critical enhancement of the thermal conductivity.

5. CONCLUSIONS

The scheme proposed by Vesovic and Wakeham [11–13] for the evaluation of the background transport properties of gas mixtures seems to be almost as accurate as the available experimental data for the viscosity and thermal conductivity of a binary mixture occurring in natural gas. In regions where the critical enhancement of the transport properties is not important, the accuracy of the predictions is estimated to be ±2%. Since the procedure automatically reproduces the properties of the pure components, does not rely upon information on the properties of mixtures at high pressures, and is internally consistent, it can provide a valuable means of predicting the properties required for natural gas flow sensors as long as conditions are not within a region around the critical point of the mixture.

The region in which the critical enhancement is significant has been shown to be very large, extending to at least 30% above the critical temperature of the mixture at the same composition and for pressures from 2 to 20 MPa. For the characterization of flux sensors with compressed natural gas in this region the present scheme will have to be supplemented by the accurate evaluation of the critical enhancement of the thermal conductivity. Fortunately, this will now be possible because formal theoretical results for the enhancement of the thermal conductivity of mixtures in the critical region have recently been derived [26]. At present, these theoretical results have been applied only to the mixtures of ethane and carbon dioxide. However, their application to other systems, in combination with the results of this work, encourage the view that it will be possible to predict the transport properties of gas mixtures representative of natural gases over the complete range of relevant thermodynamic states. In turn, this will permit validation of the proposed metering sensors in that larger range of states.

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