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TRANSPORT PROPERTIES OF DENSE GASES (ARGON AND OXYGEN)

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ABSTRACT: In this work transport properties of dense gases are calculated using the empirical equations of the Modified Enskog Theory. A two parameter equation of state is used for the fluids here studied. With it the necessary specific heat functions can be obtained. Also, a reasonable knowledge of the PVT behavior of the fluids in the dense region can be obtained from it. The transport properties of the dilute gas are calculated using Chapman-Enskog's equations. Finally, the above method is applied to Argon and Oxygen comparing the results obtained with those of other of other authors.

INTRODUCTION

Many attempts have recently been made to develope a theory capable of predicting transport properties of dense gases and liquids. In the low density limit the transport properties of a gas (viscosity, thermal conductivity and difusivity) can be obtained from the Chapman-Enskog equations. These latter are based on Boltzmann's equation and their validity is limited to mono-

atomic gases. They have to be modified when the molecules of interest have internal structure, and several such modifications have been proposed, particularly in connection to thermal conductivity.

A first step towards the extension of the theory to higher densities was made by Enskog himself, who in order to extend the dilute gas theory, restricted himself to hard spheres. More recently, Hanley McCarthy and Cohen have put forward an empirical modification to Enskog's theory. Both the theories of Hanley and Enskog allow corrections to be made to the transport properties of a gas obtained at atmospheric pressure to extend their validity to higher pressures.

In this work transport properties of Argon and Oxygen are calculated using the empirical equations of HMC's theory. For a proper application of such theory it is necessary to know the PVT behaviour of the fluid under consideration as well as the specifi heat function and the transport properties of the dilute gas. A universal two parameter equation of state is used for the fluids studied here. With it the necessary, specific heat functions can be obtained, as well as a reasonable knowledge of the PVT behaviour of the fluids in the dense region. Previous to this work this modified theory of Enskog was applied using a different equation of state for each fluid considered, furthermore these equations involved many more parameters.

The transport properties of the dilute gas are calculated using Chapman-Enskog's equations. The general method of calculating the transport properties as well as the PVT behaviour and specific heat functions of dense gases is then given. Finally, results are shown for Argon and Oxygen and are compared with those of the modified Enskog's theory[1]

MODIFIED ENSKOG'S THEORY

The modified Enskog's theory (MET) is an extension to the real gases of Enskog's results for the transport properties of a hard sphere model[1]. The basic assumptions are:

a) There are no fundamental differences between the mechanism of momentum and energy transfer in a real fluid and that of a hard-sphere gas.

b) The existing differences may be assumed to be contained in the functional relationship between the collision frequency and the temperature. For real fluids this can be expressed in terms of PVT data.

The expressions given by MET are:

Thermal Conductivity. For a dense gas or a liquid there exist two contributions to the thermal conductivity: one due to the translational degrees of freedom and the other due to the internal motion.

$$\lambda = \lambda_0' \beta\rho \left[\frac{1}{\beta\rho\chi} + \frac{6}{5} + 0.755\,\beta\rho\chi \right] + \frac{\lambda_0''}{\chi} \quad . \tag{1}$$

Viscosity. The expression obtained is the same as Enskog's:

$$\eta = \eta_0 \beta\rho \left[\frac{1}{\beta\rho\chi} + \frac{4}{5} + 0.761\,\beta\rho\chi \right] . \tag{2}$$

In the above equations $\beta\rho\chi$ is Enskog's modulus, defined in the case of hard spheres by the equation of state:

$$\frac{PV}{RT} = 1 + \beta\rho\chi \tag{3}$$

Nevertheless, in MET the pressure is replaced by the thermal pressure $T(\partial P/\partial T)_V$, transforming equation (3) into

$$\frac{1}{R}\left(\frac{\partial PV}{\partial T}\right)_V = 1 + \beta\rho\chi$$

or

$$\frac{V}{R}\left(\frac{\partial P}{\partial T}\right)_V = 1 + \beta\rho\chi \quad .$$

On the other hand, Mason and Monchick [1] have shown that the thermal conductivity dilute polyatomic gas can be splitted in two parts: one part describing the thermal energy transfer due to the translational motion of the molecules, and the other one depicting the energy transfer produced by the internal energy changes of the molecules. That is:

$$\lambda_0 = \lambda_0' + \lambda_0'' \quad .$$

Moreover, it is known that the specific heat at constant volume can be separated into a translational part and into an internal one[2]:

$$C_V = C_V' + C_V'' \ .$$

Then, according to Mason and Monchick:

$$\lambda_0 = \frac{5}{2}\eta_0 \frac{C_V'}{m} + \rho D_0 \frac{C_V''}{m} \quad , \tag{4}$$

where λ_0', η_0 and D_0 are, respectively, the thermal conductivity, the viscosity and the autodiffusivity of the dilute gas.

In MET it is assumed that the thermal conductivity for a dense gas or liquid can also be splitted into a translational and an internal part. Hence,

$$\lambda = \lambda' + \lambda''$$

where:

$$\lambda' = \lambda_0' \beta\rho \left[\frac{1}{\beta\rho\chi} + \frac{6}{5} + 0.755\,\beta\rho\chi \right] , \tag{5}$$

and:

$$\lambda'' = \rho \frac{D C_V''}{m} \ . \tag{6}$$

If the autodiffusion coefficient is written in the following way:

$$D = \frac{D_0}{\chi} \ ,$$

the contribution to the thermal conductivity due to the internal motion can be explicitly written as follows:

$$\frac{\lambda_0''}{\chi} = \rho \frac{D_0 C_V''}{\chi} \quad , \tag{7}$$

since the internal energy transfer is due to the molecular diffusion.

In this case, according to Eucken[2], C_V'' can be expressed by the equation:

$$C_V'' = \frac{(N-3)}{2} R \quad , \tag{8}$$

where R is the Rydberg constant, and similarly:

$$N = 2/\left(\frac{C_P}{C_V} - 1\right) \quad , \tag{9}$$

where C_P is the specific heat at constant pressure and C_V is the specific heat at constant volume[2].

CHAPMAN-ENSKOG'S RESULTS

In MET, values of the transport properties at low densities are required. These can be either experimentally obtained or calculated[3] from the Chapman-Enskog's results. The final expressions[4] being:

Thermal Conductivity

$$\lambda_0' = 1.9891 \times 10^{-4} \frac{\sqrt{T/M}}{\sigma^2 \Omega^{(2,2)^*}} \tag{10}$$

Viscosity

$$\eta_0 = 2.6693 \times 10^{-5} \frac{\sqrt{MT}}{\sigma^2 \Omega^{(1,2)^*}} \tag{11}$$

Autodiffusivity

$$D_0 = 3.2027 \times 10^{-5} \frac{\sqrt{T/M}}{\sigma^2 \Omega^{(1,1)^*}} \frac{1}{C} \tag{12}$$

where $\Omega^{(1,s)^*}$ are the reduced collision integrals calculated with a Lennard-Jones (12-6) potential. The different constants that appear in these expressions are necessary to obtain the data in cgs unit system, when σ (collision diameter) is in Å, T in K and M in g/gmo.

DATA PREDICTED WITH MET

To apply MET it is necessary to have a description of the PVT behaviour of the fluid studied. In the present work use is made, up to the third coefficient, of an equation of state applicable only to gases and with a precision not yet determined, but good enough for practical purposes. Due to these restrictions, only calculations for dense gases are made.

From the equation of state

$$P = \rho RT(1 + \beta\rho + C\rho^2 \tag{13}$$

it is possible to obtain the expression

$$\beta\rho\chi \equiv \beta\rho + \gamma\rho^2 \tag{14}$$

where, in equation (13), B stands for the second virial coefficient and C for the third virial coefficient. In equation (14), $\beta\rho\chi$ is commonly known as Enskog's modulus; $\beta = B + TB'$, $\gamma = C + TC'$ and B', C' are the temperature derivatives of B and C.

Pitzer and Curl[5] have shown that B is a function of the reduced temperature and the acentric factor, w, while Chueh[6] has shown that C is a function of the reduced temperature and a parameter d that takes into account the value of C at $T_r = 1$.

The conductivity correction term in MET takes into account the internal contribution at constant volume to the heat capacity. Eucken[2] writes this contribution as given in equations (8) and (9).

The Chapman-Enskog results are used to predict the viscosity, conductivity and autodiffusivity requiring a correction due to the non dilution of the gas. These corrections can be made either using Enskog's results or using the modified theory here analyzed.

MET's correction to Enskog's theory for the conductivity is given here by equation (7). In Fig. (1) the value of this corrective factor for A_r, has been plotted as a function of pressure for a given value of the absolute temper-

ature. It is worth stressing that this correction takes negative values since C_V'' is a negative for the temperatures considered (298K). This fact arises from $N < 3$ or $C_P/C_V > 5/3$, (the value at which $C_V'' = 0$ is $C_P/C_V = 5/3$, corresponding to the ideal gas).

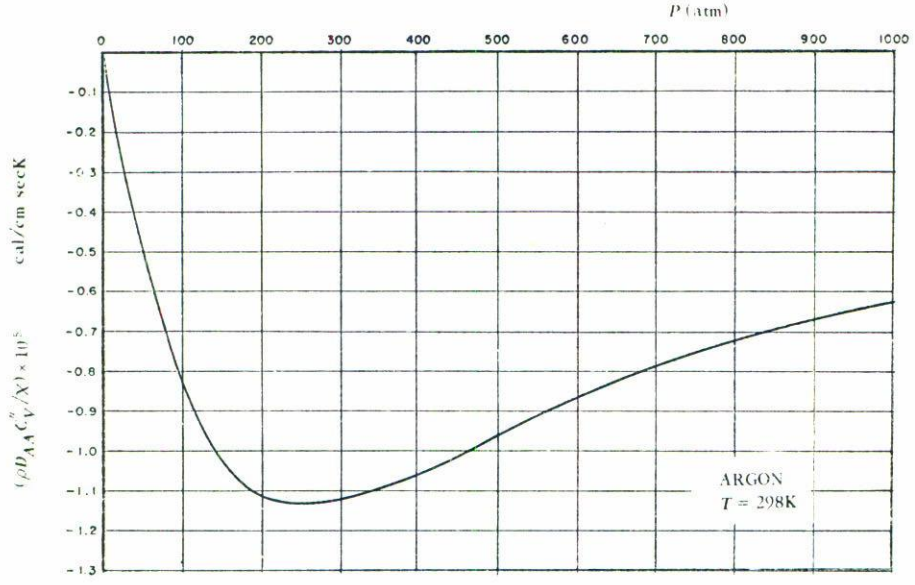

Fig. 1. Thermal conductivity correction factor according to Enskog's modified theory.

To use equation (8) the C_P and C_V values at the P and T conditions of the problem are needed. These values can be obtained using an empirical correlation between C_P^0, (the heat capacity at atmospheric pressure), and the usual thermodynamic relations for heat capacities, together with the equation of state (13). The functions used in this work are given in the Appendix[7].

RESULTS AND CONCLUSION

MET adds to Enskog's conductivity one correction term λ_0'', while leaving the viscosity unchanged. Therefore, in checking MET, particular attention has to be given to the conductivity.

The gases under consideration are Argon and Oxygen. No significant differences were found between the values obtained and those reported by Hanley et al[1] for the same gases at similar conditions. The results here obtained and also those of Hanley are presented in Figs. (2-3), where the MET's excess functions, $\Delta\eta$ and $\Delta\lambda$, and those computed in this paper have been compared graphically. These functions are defined in[1] as follows:

$$\Delta\eta(\rho, T) = \eta(\rho, T) - \eta_0(T)$$

$$\Delta\lambda(\rho, T) = \lambda(\rho, T) - \lambda_0(T)$$

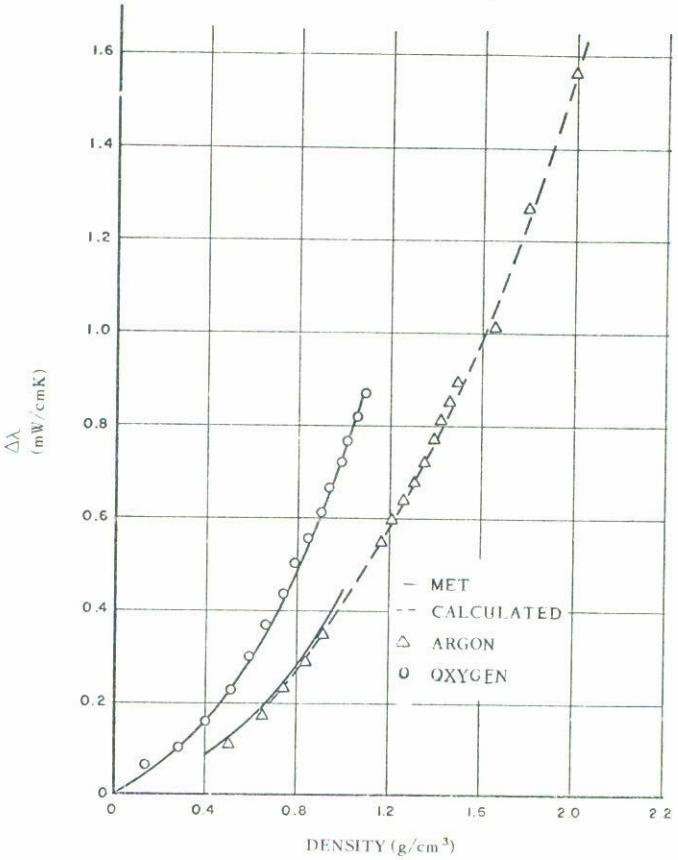

Fig. 2. Excess conductivity

In the graphs no experimental data is included since the graphs purpose was to compare a particular equation of state with the multiparameter one used by the said authors.

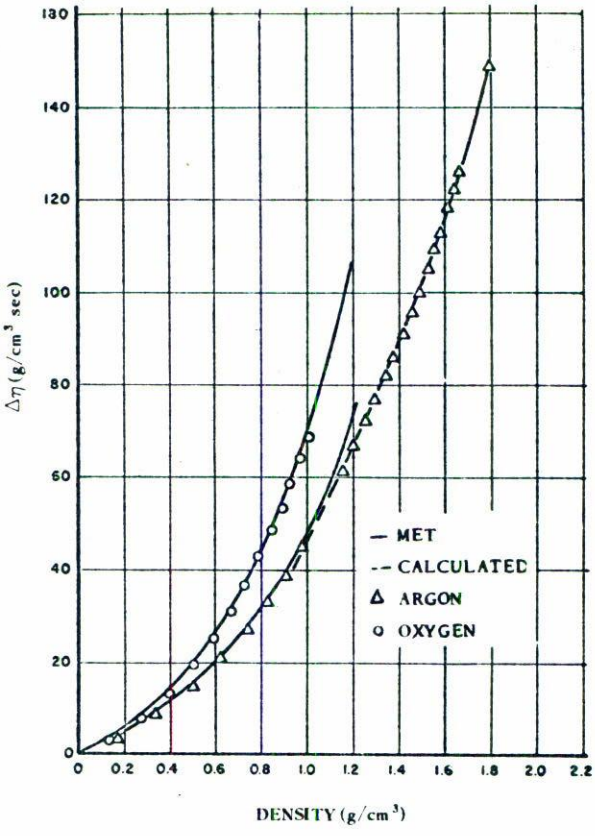

Fig. 3. Excess viscosity

The results that have been obtained here are valid in the pressure range that goes from the atmospheric pressure to 4,000 atmospheres.

Fig. (4) shows the results for Argon using MET and the experimental values reported by Bailey and Kellner[8] for 298K. Also included are the expected results using Enskog's expressions. In this graph it can be seen that Enskog's values fit better the experimental data than those obtained with MET.

Such result should not be considered applicable to other real gases. Rather, it suggests the necessity of a deeper study of the modifying term λ''_0, particularly in connection with the internal part of the specific heat (C''_V). Besides, for a proper comparison more experimental data not yet available is needed.

The most important result here reported is the possibility of using em-

pirical correlations of virial coefficients to predict transport properties at high densities.

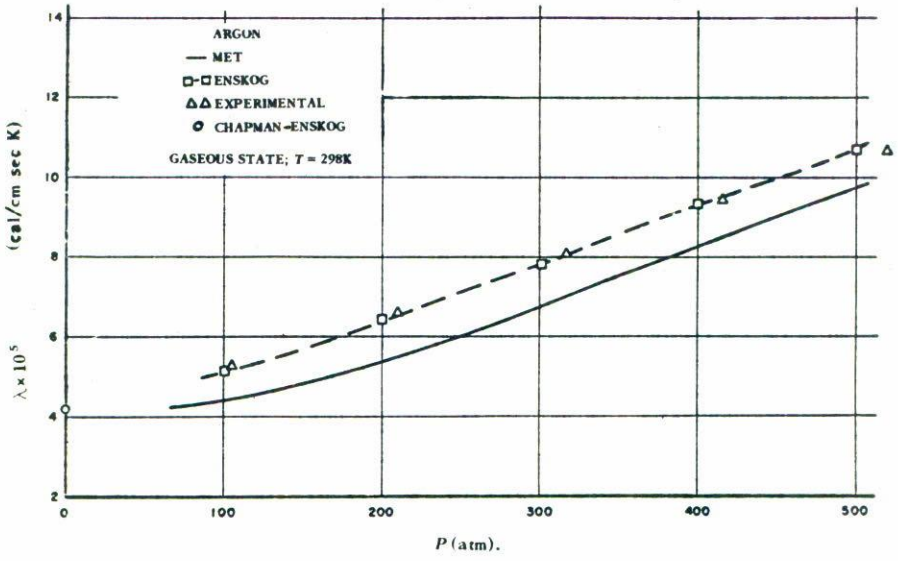

Fig. 4. Thermal conductivity

APPENDIX

1. Virial Coefficients Correlation

A power expansion in terms of the reciprocal of the reduced temperature, T_r, will be used for the second virial coefficient. Hence, according to Pitzer and Curl:

$$B_r = \frac{BP_0}{RT_0} = f_0 + wf_1 \tag{A.1}$$

where

$$f_0 = -\frac{0.33}{T_r} - \frac{0.1385}{T_r^2} - \frac{0.0121}{T_r^2} + 0.1445 \tag{A.2}$$

$$f_1 = \frac{0.46}{T_r} - \frac{0.5}{T_r^2} - \frac{0.097}{T_r^3} - \frac{0.0073}{T_r^8} + 0.073 \tag{A.3}$$

In (A.1), B_r is the second reduced coefficient and the acentric factor. In (A.2), (A.3), the constants were adjusted to fit both volumetric and thermal data for many real gases. From the three expressions B' and B'' can be obtained.

For the third virial coefficient Chue's correlation is

$$C_r = \frac{C}{v_c^2} = f_1 f_2 + df_3 \tag{A.4}$$

where

$$f_1 = \frac{0.232}{T_r^{0.25}} + \frac{0.468}{T_r^5} \tag{A.5}$$

$$f_2 = 1 - \exp\left[1 - 1.89\,T_r^2\right] \tag{A.6}$$

$$f_3 = \exp\left[-(2.49 - 2.3\,T_r + 2.7\,T_r^2)\right] \tag{A.7}$$

Here the derivatives C' and C'' can also be found.

In (A.1) the correlation factor is w, the acentric factor, while in (A.4) it is d. Values of these parameters can be found in the usual literature[5], for example.

2. Heat Capacity Functions

When the equation of state is the virial equation one can obtain the following expressions using known thermodynamical relations.

$$\frac{C_V - C_V^0}{R} = -\rho T(2B' + B''T) - \rho^3 T\left(C' + \frac{C''}{2}T\right) \qquad (A.8)$$

and

$$\frac{C_P - C_V}{R} = \frac{[1 + (B + TB')\rho + (C + TC')\rho^2]^2}{1 + 2B\rho + 3C\rho^2} \qquad (A.9)$$

that together with

$$\frac{C_P - C_P^0}{R} = \frac{C_V - C_V^0}{R} + \frac{C_P - C_V}{R} - 1 \qquad (A.10)$$

define C_P and C_V completely for any P, T condition.

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RESUMEN

Se calculan propiedades de transporte para gases en la región densa, usando las ecuaciones empíricas de la teoría modificada de Enskog. Se usa una ecuación de estado con sólo dos parámetros para los fluidos aquí estudiados. Con ella es posible calcular las funciones de capacidad calorífica requeridas, así como también tener un conocimiento bastante adecuado para nuestros propósitos, del comportamiento PVT de los fluidos en la región densa. Las propiedades de transporte para el gas diluido, se calculan usando las ecuaciones de Chapman-Enskog. Finalmente, todo lo anterior se aplica al Argón y al Oxígeno, comparándose los resultados obtenidos con los reportados por otros autores.