Correlation for Gas Thermal Conductivity of Halogenated Methanes

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A knowledge of the thermal conductivity of gases is of great importance in engineering as well as in science. Well-established measured values are scarce and estimation techniques (*8*) are relatively imprecise for this property.

We found the following empirical correlation for the gas thermal conductivity of halogenated methanes

$$10^5 k V_c^{2/3} M^{-1/2} T_c^{-1/2} = -0.70 + 3.125\, T_r \qquad (1)$$

One should note that Equation (1) is dimensional. This correlation was found while attempting to establish values for the gas thermal conductivity of mixtures of these compounds (*7*). Equation (1) fits experimental gas thermal conductivity data at normal pressure for carbon tetrachloride, chloroform, and for six fluorinated derivatives thereof with a standard deviation of 2.6%. These eight fluids are listed in Table 1 together with the required properties.

The constants in Equation (1) were computed from the experimental fluid properties given in Table 1. The molecular weight, critical temperature, and critical molecular volume used are literature values (*2* to *4*). Two standard references (*5, 10*) were used as sources for the gas thermal conductivity of these fluids with the exception of carbon tetrafluoride. The tabulated values in these two standard references are those recommended by the editors from the various results of several investigators. The stated accuracy for these gas thermal conductivity data varies between 1 and 10%. The gas thermal conductivity values for carbon tetrafluoride which were taken from (*1*) were stated to have an accuracy of 2%. Table 1 summarizes the gas thermal conductivity in the reduced temperature range $0.5 < T_r < 2$ of the fluids used in this investigation. Values are reported only at temperatures at which the accuracy is believed to be better than 5%. The data were rounded to the nearest 0.0005 W./(m.)(°K.).

Using the information given in Table 1, values of the expression $k V_c^{2/3} M^{-1/2} T_c^{-1/2}$ in Equation (1) were calculated at different temperatures and the results are plotted in Figure 1 as a function of the reduced temperature. These data were fitted to a linear function by least squares. The result, given by Equation (1), is valid for the reduced temperature range $0.5 < T_r < 2$.

During the study it was found that the recommended gas thermal conductivities of monofluorodichloromethane (*5, 10*) show a rather large disagreement in their temperature coefficients. See slope of the curves *A* and *B* in Figure 2. This is due to the fact that the recommended values were specifically based upon measurements of two different investigations (*6, 9*). Taking M, T_c, and V_c as listed in Table 1, Equation (1) was used to calculate the gas thermal conductivity of monofluorodichloromethane. The result is

$$10^3 k[\text{W./(m.)(°K.)}] = -4.46 + 0.04405\, T\ (\text{°K.}) \qquad (2)$$

With Equation (2) one can determine which of the two recommended gas thermal conductivities is more probable. Equation (2), represented in Figure 2 by curve *C*, gives good agreement with the thermal conductivity recommended by (*10*) in the temperature range from 250° to 400°K.

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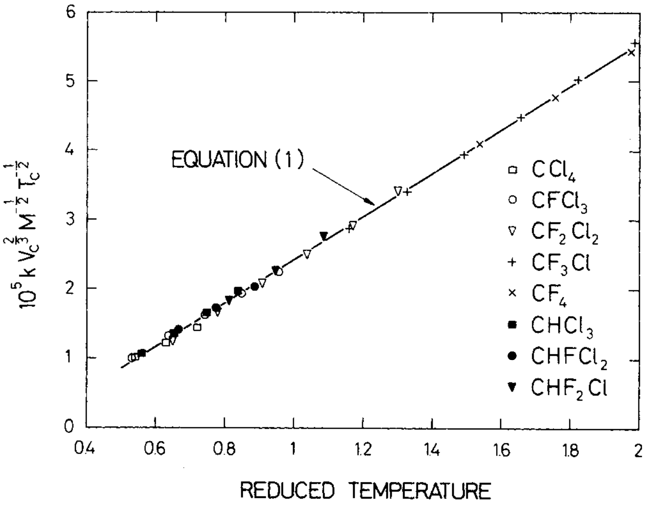

Fig. 1. Empirical correlation for the gas thermal conductivity of eight halogenated methanes. Ordinate is dimensional: k, W/(m.)(°K.); V_c, cu.m./kmole; T_c, °K.

Table 1. Molecular Weight M, Critical Temperature T_c, Critical Molecular Volume V_c, and Smoothed Experimental Gas Thermal Conductivity k of Halogenated Methanes

Fluid	M (*2* to *4*)	T_c, °K. (*2* to *4*)	V_c, cu. m./kmole (*2* to *4*)	k, w./(m.)(°K.) (*1, 5, 10*) 250°K.	300°K.	350°K.	400°K.	450°K.	500°K.	550°K.	600°K.
CCl_4	153.83	556.4	0.276		0.0070	0.0085	0.0100				
$CFCl_3$	137.37	471.2	0.248	0.0065	0.0085	0.0105	0.0125	0.0145			
CF_2Cl_2	120.92	384.9	0.217	0.0075	0.0100	0.0125	0.0150	0.0175	0.0205		
CF_3Cl	104.47	302.0	0.180			0.0160	0.0190	0.0220	0.0250	0.0280	0.0310
CF_4	88.01	227.6	0.140			0.0215	0.0250	0.0285			
$CHCl_3$	119.39	536.5	0.239		0.0070	0.0090	0.0110	0.0130			
$CHFCl_2$	102.93	451.7	0.197		0.0090	0.0110	0.0130				
CHF_2Cl	86.48	369.3	0.165		0.0110	0.0135	0.0165				

NOTATION

k = thermal conductivity, W./(m.) (°K.)
M = molecular weight
T = temperature, °K.
T_c = critical temperature, °K.
T_r = T/T_c, reduced temperature
V_c = critical molecular volume, cu.m./k.mole

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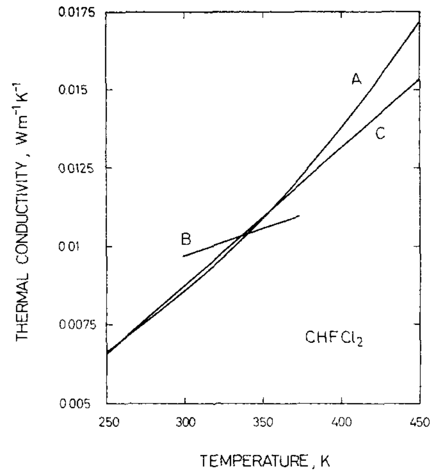

Fig. 2. Gas thermal conductivity of monofluorodichloromethane, CHFCl$_2$: (A) Touloukian et al. *(10)*, (B) Landolt-Börnstein *(5)*, (C) Equation (2).

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Die Swell Behavior of Two-Phase Polymer Melts

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It has long been believed that the increase in diameter that extrudate undergoes after leaving the die (hereafter called die swell) is characteristic of the elastic properties of visco-elastic fluids. In particular, there is abundant literature (*1* to *6*) concerning studies made on polymer melt die swell. This is because polymer melt die swell is closely associated with determining the most desirable operating conditions of various processing devices. Die swell measurements have often been used for designing dies for plastic extrusion and spinneretts for fiber spinning, etc.

However, most of the literature published to date has dealt with melt die swell behavior of homopolymer systems, but very little has dealt with incompatible two-phase systems. With respect to two-phase systems, it would be most desirable for practical purposes today to establish some kind of correlation between the die swell ratio and the composition ratio of individual components. Commercially important two-phase systems, for example, high-impact polystyrene and ABS resin, have different grades of the materials based on the amount of the rubbery component contained in each resin.

The purpose of this paper is to present some new experimental data on the polymer melt die swell behavior of two-phase systems. The two-phase systems chosen for study are blends of polystyrene and high density polyethylene.

EXPERIMENT

Materials

Blends were prepared from two polymers. These were: high density polyethylene (Union Carbide DMDJ 5140) which has a polydispersity ($\overline{Mw}/\overline{Mn}$) of about 8.4, and melt index of about 0.8, and general purpose polystyrene (Dow Chemicals STYRON® 686). The blending ratios and sample codes are given in Table 1.

Polymer blends were prepared by mixing the two polymers, in the form of pellets, in a tumbling operation. Fortunately, the pellet sizes of both polymers were almost identical (about 1/8 in.) and hence no particle segregation was observed when the blends were fed to an extruder.

Apparatus and Experimental Procedure

The description of the apparatus used in the present study has been given in a previous paper (*7*), and the detailed layout of the die design has been given in another recent paper by the authors (*8*) in which it was stated that the capillary diameter was 0.125 in. In the present study die swell measurements were taken with an L/D ratio of 4 at 200°C. The experimental procedure for the measurement of die swell is as follows:

1. Polymer melt flows vertically through a capillary device and into a chamber, about 15 in. long, maintained at a temperature the same as the capillary. The chamber is equipped with

TABLE 1. BLENDING RATIOS AND SAMPLE CODE OF TWO-PHASE SYSTEM

Sample code	Blending ratio
PS	100% polystyrene
PS/PE = 20/80	20% polystyrene and 80% polyethylene
PS/PE = 50/50	50% polystyrene and 50% polyethylene
PS/PE = 80/20	80% polystyrene and 20% polyethylene
PE	100% polyethylene