Cubic Equations of State for Transport Properties

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A method is presented for the prediction of the background contribution of residual thermal conductivities and residual viscosities of nonpolar or slightly polar substances. The method is based on the concept of transport equations of state describing the transport properties in terms of pressure and temperature by pressure explicit equations similar to thermal equations of state. The transport equation of state is derived from a generalized cubic thermal equation of state and a universal function for the density dependence of the residual part of the transport properties. A comparison of calculated and recommended values of the thermal conductivity of 35 and the viscosity of 23 substances yields an absolute average deviation of 6% for the thermal conductivity and of 5% for the viscosity. The Maxwell condition is applied to the generalized transport equation of state to predict consistently the transport properties along the vapor–liquid coexistence curve.

1. INTRODUCTION

Most of the prediction methods for the transport properties, i.e., thermal conductivity and viscosity, of pure fluids are limited to the temperature dependence of either the dilute gases or liquids at atmospheric pressure [1]. A pressure dependence is considered, if at all, only by correction terms, e.g., Ref. 2. Few attempts were made to describe the transport properties over a wide fluid range with one consistent equation, e.g., Refs. 3–9. None of these methods can predict the vapor–liquid phase equilibrium. In these equations temperature and density are used as independent variables. For given values of temperature and pressure, in addition, a

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thermal equation of state is needed for the evaluation of the density. Errors in the density thus affect the accuracy of the transport property [10, 11].

The concept of transport equations of state [12–15] aims at describing the transport properties directly in terms of pressure and temperature by means of pressure explicit equations similar to thermal equations of state.

As is well known from thermal equations of state, virial equations can describe the thermal properties very accurately over a wide range of pressure and temperature, provided that sufficient experimental data exist to fit the parameters properly. When experimental data are scarce or completely lacking, cubic equations of state are more appropriate, because of the smaller numbers of adjustable parameters needed. They mostly permit a better extrapolation and prediction.

Transport equations of state might be classified in the same way: equations of the virial type for an accurate representation of the transport properties and cubic equations for extrapolation and prediction.

As shown in a recent study [16], the thermal conductivity of oxygen represented by a virial transport equation of state [13] may as well be presented by a cubic transport equation of state with only a little loss of accuracy. The number of parameters in the cubic transport equation is, however, much lower than that in the virial transport equation.

In this paper, a generalized cubic transport equation of state is presented for the thermal conductivity and viscosity of nonpolar or slightly polar substances. Also, the transport properties along the vapor–liquid coexistence curve can be described by this equation.

2. BACKGROUND

Previous studies [12–14] revealed that the p, TP^2, T surfaces of the transport properties are similar to the p, ρ, T surfaces of the thermal properties. This holds also in the critical region provided that the critical enhancements of the transport properties are neglected. According to Sengers [17] one can separate the transport properties into a background contribution and an additive singular contribution which accounts for the critical enhancement. In this paper only the background contribution is dealt with.

The phenomenological similarity suggests that the transport properties can be represented, analogously to thermal equations of state, by means of pressure-explicit transport equations of state. Laesecke [13] proposed to describe transport properties by virial-type equations of state, where the density should be replaced by the transport property. In these equations

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[2] TP stands for "transport property."

the temperature functions of the parameters need to be modified to represent transport properties within their experimental accuracy. More effective equations of this type are obtained by evolutionary optimization methods [15].

Recent phenomenological investigations [11, 16] revealed that the surface of the residual transport property ΔTP in a p, ΔTP, T representation corresponds much better to the p, ρ, T surface. Thus it was proposed to formulate transport equations of state in terms of the residual transport property

$$p = p(\Delta\mathrm{TP}, T) \tag{1}$$

the residual transport property being defined as

$$\Delta\mathrm{TP} = \mathrm{TP}(\rho, T) - \mathrm{TP}_0(T) \tag{2}$$

where TP_0 is the transport property of the dilute gas. As is well known the residual transport property is a strictly monotonic increasing function of the density and depends only slightly on temperature for high densities, so that it can be assumed to be temperature independent for densities $\rho/\rho_\mathrm{c} \leqslant 2.5$:

$$\Delta\mathrm{TP} = f(\rho) \tag{3}$$

When the density is replaced in a thermal equation of state by the univalent inverse function of Eq. (3),

$$\rho = f^{-1}(\Delta\mathrm{TP}) \tag{4}$$

one obtains a transport equation of state, Eq. (1), where the temperature functions of the parameters of the initial thermal equation of state need not to be modified, because the inverse function, Eq. (4), does not introduce an additional temperature dependence.

As yet, the transport properties along the vapor–liquid coexistence curve can be evaluated only by means of a transport equation of state, when a consistent pair of saturation temperature and vapor pressure is available. If only the temperature is given, an additional vapor pressure equation is needed.

If the transport properties are considered as intensive variables of state, it should be possible, according to the Gibbs phase rule, to evaluate for a particular fluid in vapor–liquid equilibrium at a given temperature T_s, the three unknown variables vapor pressure p_s, residual transport property of the saturated liquid $\Delta\mathrm{TP}'$, and residual transport property of the

saturated vapor $\Delta\mathrm{TP}''$ from the transport equation of state. This requires three conditions. The transport equation yields for each phase,

$$p_\mathrm{s} = F(\Delta\mathrm{TP}', T_\mathrm{s}) \tag{5}$$

$$p_\mathrm{s} = F(\Delta\mathrm{TP}'', T_\mathrm{s}) \tag{6}$$

The third condition is derived subsequently.

   To evaluate the thermal properties in equilibrium the Maxwell condition [18] is applied. It reads

$$\int_{v'}^{v''} p(v)\, dv = p_\mathrm{s}(v'' - v') \tag{7}$$

Equation (7) can be rewritten in terms of the density

$$-\int_{\rho'}^{\rho''} p(\rho)\frac{1}{\rho^2}\, d\rho = p_\mathrm{s}\left(\frac{1}{\rho''} - \frac{1}{\rho'}\right) \tag{8}$$

Eliminating the density from Eqs. (4) and (8) yields the third condition sought after:

$$-\int_{\Delta\mathrm{TP}'}^{\Delta\mathrm{TP}''} p[f^{-1}(\Delta\mathrm{TP})]\,\frac{1}{[f^{-1}(\Delta\mathrm{TP})]^2}\,\frac{\partial\rho}{\partial\Delta\mathrm{TP}}\bigg|_T\, d\Delta\mathrm{TP}$$

$$= p_\mathrm{s}\left(\frac{1}{f^{-1}(\Delta\mathrm{TP}'')} - \frac{1}{f^{-1}(\Delta\mathrm{TP}')}\right) \tag{9}$$

Since Eqs. (5), (6), and (9) contain the unknown variables implicitly the solution requires iteration. It is self-evident that the transport properties in vapor–liquid equilibrium can be evaluated for given variables other than the temperature as well.

3. FORMULATION OF THE TRANSPORT EQUATION OF STATE

   The choice of a suitable correlation $p(\Delta\mathrm{TP}, T)$ depends mainly on the objectives. A generalized transport equation covering a wide fluid range should be based on a generalized thermal equation of state also valid in a wide pressure and temperature range. Such an equation was proposed by Schreiner [19]. It describes the thermal properties over a wide fluid range of p and T with good accuracy. Only the critical temperature T_c, critical pressure p_c, and the acentric factor ω are needed as characteristic parameters for a particular substance. These are listed in Table I. In

Table I. Characteristic Parameters for Selected Substances

Substance	M (kg · kmol^{-1})	P_c (MPa)	T_c (K)	ω	Ref. No.
Neon	20.179	27.6	44.4	−0.029	1
Argon	39.948	48.65	150.69	−0.003	19
Krypton	83.8	55.022	209.4	−0.001	19
Xenon	131.3	58.4	289.7	0.008	1
Nitrogen	28.013	33.991	126.26	0.035	19
Oxygen	31.999	50.43	154.58	0.022	19
Fluorine	37.997	52.2	144.3	0.054	1
Carbon monoxide	28.01	34.987	132.91	0.048	19
Carbon dioxide	44.01	73.861	304.21	0.224	19
Sulfur hexafluoride	146.05	37.6	318.7	0.286	1
Methane	16.043	45.988	190.56	0.011	19
Ethane	30.069	48.714	305.33	0.097	19
Propane	44.096	42.46	369.85	0.156	19
n-Butane	58.123	37.838	425.14	0.198	19
i-Butane	58.123	36.4	407.85	0.185	19
n-Pentane	72.15	33.638	469.69	0.251	19
i-Pentane	72.15	33.696	460.39	0.227	19
n-Hexane	86.177	30.63	507.85	0.304	19
n-Heptane	100.203	27.17	540.16	0.33	19
n-Octane	114.23	25.17	569.35	0.398	19
n-Nonane	128.257	22.9	594.6	0.445	1
n-Decane	142.284	21.2	617.7	0.489	1
n-Undecane	156.311	19.7	638.8	0.535	1
n-Dodecane	170.337	18.2	658.2	0.575	1
n-Tridecane	184.364	17.2	676	0.619	1
n-Tetradecane	198.391	14.4	693	0.581	1
n-Pentadecane	212.418	15.2	707	0.706	1
n-Hexadecane	226.445	14.1	722	0.742	1
n-Octadecane	254.498	12	748	0.79	1
Ethene	28.034	50.404	282.34	0.087	19
Propene	42.05	46	364.9	0.144	1
Refrigerant 11	137.368	44.1	471.2	0.189	1
Refrigerant 12	120.914	41.29	384.95	0.179	19
Refrigerant 13B1	148.91	39.7	340.2	0.171	1
Refrigerant 22	86.469	49.9	369.33	0.22	19
Refrigerant 113	187.376	34.1	487.25	0.254	19
Refrigerant 114	170.922	33	418.6	0.263	1
Refrigerant 218	188.02	26.8	345.1	0.325	1
Refrigerant C318	200.031	27.8	388.5	0.356	1

contrast to the other generalized cubic equations of state, not only phase equilibria but also the entire liquid and gaseous regions are well described.

The equation of Schreiner reads

$$p_r = \frac{T_r}{v^* - a^*} + \frac{B^*}{v^* - b^*} - \frac{B^*}{v^* - c^*} \tag{10}$$

where $p_r = p/p_c$ is the reduced pressure and $T_r = T/T_c$ the reduced temperature. The volume is reduced according to

$$v^* = v p_c / (T_c R) \tag{11}$$

where R is the universal gas constant.

The universal temperature functions of the parameters read

$$a^* = a_k^* [1 + F_{a,1} \ln T_r + F_{a,2} (\ln T_r)^2] \tag{12}$$

$$b^* = a^* - [a_k^* - b_k^*][1 + F_{ab,1} \ln T_r + F_{ab,2} (\ln T_r)^2] \tag{13}$$

$$c^* = b^* - [b_k^* - c_k^*][1 + F_{bc,1} \ln T_r + F_{bc,2} (\ln T_r)^2] \tag{14}$$

$$B^* = B_k^* [1 + F_{B,1} \ln T_r + F_{B,2} (\ln T_r)^2] \tag{15}$$

$$a_k^* = g_1 + g_2 \omega + g_3 \omega^2 \tag{16}$$

$$b_k^* = \frac{3 Z_{c,cal} - (a_k^* + 1) + \sqrt{arg}}{2} \tag{17}$$

with

$$arg = -4 Z_{c,cal}^3 + 3 Z_{c,cal}^2 (4a_k^* + 3) - 6 Z_{c,cal} (a_k^* + 1)(2a_k^* + 1)$$
$$+ (a_k^* + 1)^2 (4a_k^* + 1)$$

$$Z_{c,cal} = g_4 + g_5 \omega + g_6 \omega^2 \tag{18}$$

$$c_k^* = 3 Z_{c,cal} - (a_k^* + 1) - b_k^* \tag{19}$$

$$B_k^* = \frac{Z_{c,cal}^3 - (a_k^* + 1) b_k^* c_k^*}{(c_k^* - b_k^*) a_k^*} \tag{20}$$

For $T_r \leqslant 1$,

$$F_{a,1} = g_7 + g_8 \omega$$

$$F_{a,2} = g_9 + g_{10} \omega$$

$$F_{ab,1} = g_{11} + g_{12} \omega$$

$$F_{ab,2} = g_{13} + g_{14} \omega$$

$$F_{bc,1} = g_{15} + g_{16}\omega$$

$$F_{bc,2} = g_{17} + g_{18}\omega$$

$$F_{B,1} = g_{19} + g_{20}\omega$$

$$F_{B,2} = g_{21} + g_{22}\omega$$

For $T_r \geqslant 1$,

$$F_{a,1} = g_{23} + g_{24}\omega$$

$$F_{a,2} = 0$$

$$F_{ab,1} = 0$$

$$F_{ab,2} = 0$$

$$F_{bc,1} = g_{25} + g_{26}\omega$$
$$F_{bc,2} = g_{27} + g_{28}\omega$$

$$F_{B,1} = g_{29} + g_{30}\omega$$

$$F_{B,2} = 0$$

The coefficients g_1 are given in Table II.

According to Schreiner [19] the universal functions are applicable to reduced pressures up to 20.

A wealth of empirical correlations was found in the literature for the residual transport property as a function of density, because many evaluations take advantage of the empirical fact that the residual transport property depends not or only slightly on temperature; see, for example, Refs. 12–15 and 20–22. Most of these correlation functions have such a complex structure that they cannot easily be inverted. In an earlier paper

Table II. Coefficients for the Thermal Equation of State [19]

i	g_i	i	g_i	i	g_i
1	0.09151	11	0.08406	21	−0.10437
2	−0.00782	12	−0.25843	22	−0.25021
3	0.04200	13	1.50084	23	0.18409
4	0.31128	14	6.06085	24	0.58237
5	−0.14363	15	0.57059	25	−0.33559
6	0.10896	16	1.30280	26	−6.14272
7	−0.14978	17	1.08132	27	−0.02383
8	1.27687	18	5.11775	28	6.46291
9	−0.36241	19	−0.58914	29	−0.10343
10	0.78579	20	−0.63664	30	1.39773

[16] we proposed an empirical inverse function $\rho = f^{-1}(\varDelta TP)$ for oxygen. The proposed equation turns out to represent the density as a function of residual transport property of other substances also well. It reads

$$\rho^* = \frac{\varDelta TP^*}{E^* + F^* \varDelta TP^{*m}} \tag{21}$$

where E^*, F^*, and m are adjustable parameters and ρ^* is the reduced density; see Eq. (11). The residual transport property $\varDelta TP$ is reduced by a group consisting of critical pressure p_c, critical temperature T_c, molar mass M, universal gas constant R, and Avogadro constant N_A according to a dimensional analysis [6, 9]. For the reduced residual thermal conductivity, one obtains

$$\varDelta\lambda^* = \varDelta\lambda(M^3 p_c^{-4} T_c R^{-5} N_A^2)^{1/6} \tag{22}$$

and for the reduced residual viscosity,

$$\varDelta\eta^* = \varDelta\eta(M^{-3} p_c^{-4} T_c R N_A^2)^{1/6} \tag{23}$$

As already mentioned the temperature dependence of the residual transport property can be neglected for densities $\rho/\rho_c \leqslant 2.5$. This means that it is negligible for $\rho^* = \rho/(Z_c\rho_c) \leqslant 10$, where Z_c is the critical compressibility factor, because most of the substances have critical compressibility factors between 0.25 and 0.3.

From Eqs. (10) and (21) one obtains the transport equation of state:

$$p_r = \frac{T_r \varDelta TP^*}{W^* - a^* \varDelta TP^*} + \frac{B^* \varDelta TP^*}{W^* - b^* \varDelta TP^*} - \frac{B^* \varDelta TP^*}{W^* - c^* \varDelta TP^*} \tag{24}$$

where

$$W^* = E^* + F^* \varDelta TP^{*m} \tag{25}$$

In principle, the temperature function of the transport properties of the dilute gases can be derived from kinetic theory. However, the length- and energy-scaling parameters of the intermolecular potential and the temperature function of the collision integral are not available for all substances considered here. Therefore an equation is used which was previously found to represent the reduced transport properties in the dilute gas state TP_0^* as a function of reduced temperature well [10]. It reads

$$TP_0^* = K_1 T_r^{1/5} + K_2 T_r^{1/3} + K_3 T_r + K_4 \tag{26}$$

where K_1 to K_4 are adjustable coefficients. The reduction constants for the respective transport property, λ_0^* and η_0^*, are the same as in Eqs. (22) and (23).

4. EVALUATION OF PARAMETERS

Three parameters in Eq. (25), namely, E^*, F^*, and m, and four coefficients in Eq. (26), namely, K_1 to K_4, remain to be evaluated from experimental data. They were fitted by means of the least-squares method to recommended values of the transport properties, compiled in our

Table III. Recommended Data Sets for the Thermal Conductivity and Coefficients for the Temperature Dependence of the Dilute Gas, Eq. (26)

	Data points	P range (MPa)	T range (K)	K_1	K_2	K_3	K_4
Neon	1834	0.1–100	26–1300	−22.774	18.995	0.19620	5.7780
Argon	1688	0.1–100	90–1300	−39.506	30.272	−0.09858	11.570
Krypton	1758	0.1–100	120–1300	−44.541	33.673	−0.22241	13.333
Xenon	1758	0.1 100	170–1300	−46.568	35.051	−0.27018	14.034
Nitrogen	1584	0.1–100	70–1100	34.786	−16.760	1.6829	−16.771
Oxygen	1236	0.1–100	70–1400	−14.606	14.033	1.0696	2.4436
CO_2	608	0.1–250	220–1300	−278.19	192.96	−3.8101	92.553
SF_6	252	0.1–50	230–400	134.16	−105.18	22.163	−42.540
Methane	586	0.1–110	100–700	285.50	−210.38	16.362	−88.212
Ethane	571	0.1–115	190–800	489.99	−369.06	34.571	−150.47
Propane	325	0.1–50	220–475	3132.6	−2320.3	160.78	−965.02
n-Butane	328	0.1–50	280–675	2204.6	−1720.9	157.40	−628.70
i-Butane	416	0.1–50	195–410	3912.7	−2949.7	223.53	−1174.8
n-Pentane	193	0.1–230	300–475	−25.749	20.492	24.399	−2.8020
n-Hexane	378	0.1–230	300–640	1421.4	−1119.1	125.72	−407.27
n-Heptane	300	0.1–230	300–700	−2727.6	1843.7	−20.846	930.44
n-Octane	153	0.1–50	280–640	1836.9	−1453.5	171.36	−524.87
n-Nonane	282	0.1–220	280–700	1498.0	−1177.5	156.13	−441.76
n-Decane	231	0.1–50	280–680	2499.9	−1972.5	230.07	−718.20
n-$C_{11}H_{24}$	218	0.1–50	300–680	4660.5	−3681.9	381.95	−1316.1
n-$C_{12}H_{26}$	270	0.1–200	300–680	8295.0	−6560.6	630.92	−2315.1
n-$C_{13}H_{28}$	211	0.1–49	310–670	7937.4	−6288.7	621.41	−2215.2
n-$C_{14}H_{30}$	209	0.1–49	310–670	22032	−17466	1580.8	−6080.2
n-$C_{15}H_{32}$	195	0.1 49	310–670	35006	−27754	2443.6	−9626.3
n-$C_{16}H_{34}$	213	0.1–49	320–690	86358	−68368	5849.6	−23755
n-$C_{18}H_{38}$	215	0.1–49	320–690	10627	−84144	7233.2	−29252
Ethene	378	0.1–60	180–520	300.94	−244.71	27.874	−80.175
Propene	378	0.1–60	180–520	219.37	−209.63	39.446	−41.937
R 11	191	0.1–5	320–500	374.59	−277.52	26.681	−116.61
R 12	427	0.1–60	200–600	0.15380	−0.10920	10.353	−2.9026
R 22	236	0.1–60	230–480	−174.31	127.07	1.5798	51.603
R 113	483	0.1–30	240–500	7.6540	−5.5626	18.071	−6.4209
R 114	334	0.1–20	280–500	−0.30281	0.22058	16.803	−4.3972
R 218	456	0.1–60	130–430	−460.40	330.31	3.0544	141.49
R C318	385	0.1–60	240–450	−0.89963	0.65816	24.207	−7.4134

MIDAS data base. The evaluation of these recommended values was based on a critical comparison of experimental data sets from different literature sources, so that their accuracy could be assessed. In a final step reliable values were selected and interpolated on convenient round numbers of pressure and temperature. More detailed descriptions of the evaluation procedure and the MIDAS data base system are given in Refs. 10, 12, 14, 20, and 23. At present, MIDAS contains recommended values for about 50 pure substances. Recommended values of the viscosity were already published in a monograph [24], whereas the recommended values of the thermal conductivity were compiled in a report [25]. Meanwhile some of the substances were reworked such as oxygen [13], nitrogen [14], and refrigerants [20].

Tables III and IV list the substances used for the evaluation of the aforementioned parameters, the number of data points stored in MIDAS, the pressure and temperature range, and the coefficients K_1 to K_4 of the

Table IV. Recommended Data Sets for the Viscosity and Coefficients for the Temperature Dependence of the Dilute Gas, Eq. (26)

	Data points	P range (MPa)	T range (K)	K_1	K_2	K_3	K_4
Neon	1836	0.1–100	6–1300	−6.0592	5.0559	0.05246	1.5365
Argon	1743	0.1–100	90–1300	−10.560	8.0880	−0.02700	3.0959
Krypton	1758	0.1–100	120–1300	−11.970	9.0397	−0.06147	3.5889
Xenon	1760	0.1–100	170–1300	−12.513	9.4117	−0.07495	3.7753
Nitrogen	1517	0.1–100	80–1100	−3.8128	3.9087	0.06210	0.44292
Oxygen	1270	0.1–150	60–1500	−4.7310	4.4644	0.04992	0.83324
Fluorine	476	0.1–20	90–300	−20.100	14.841	−0.39074	6.2054
CO	238	0.1–80	220–510	47.291	−28.435	0.98898	−19.334
CO_2	600	0.1–100	310–900	−36.502	26.600	−0.79075	11.532
Methane	850	0.1–70	100–520	−20.616	14.264	−0.14185	7.1128
Ethane	900	0.1–70	300–750	−41.859	29.503	−0.92350	13.879
Propane	648	0.1–35	175–750	−31.968	23.293	−0.84389	10.105
n-Butane	620	0.1–70	300–850	−181.53	125.58	−5.2005	61.771
i-Butane	685	0.1–50	310–850	0.43504	1.2273	0.07036	−1.1648
n-Pentane	486	0.1–50	320–900	1.1431	0.58418	0.13539	−1.2646
i-Pentane	572	0.1–60	280–750	0.83571	−0.57733	0.63337	−0.2819
n-Hexane	459	0.1–50	380–1000	−9.0140	7.7188	−0.17791	2.0745
n-Heptane	408	0.1–50	300–620	−41.821	30.988	−1.4167	12.838
n-Octane	432	0.1–50	320–670	48.848	−35.595	2.6452	−15.324
Ethene	378	0.1–60	180–520	−5.4423	4.3445	0.19407	1.5167
Propene	378	0.1–60	180–520	−16.453	12.280	−0.22430	4.9965
R 12	384	0.1–60	250–575	12.847	−9.8817	1.2213	−3.6235
R 13B1	638	0.1–60	290–435	−15.995	11.233	−0.00708	5.3238

dilute gas function, Eq. (26). Maximum deviations between calculated and recommended values of the dilute gases did not exceed 1.8%.

The parameter fit of E^*, F^*, and m revealed that the parameters E^* and m were only slightly different for different substances and a particular transport property. Therefore mean values could be used, namely, $E^* = 0.7$ and $m = 0.8$ for the thermal conductivity and $E^* = 0.14$ and $m = 0.95$ for the viscosity. A second fit of parameter F^* led then to a slight change in F^* but revealed no significant loss of accuracy in the respective transport property.

Parameter F^* was then analyzed in view of a correlation with a characteristic property of the substances. As Figs. 1 and 2 show, the parameter F^* can be well expressed as a function of the acentric factor [27, 28]. The following correlation function was found for the thermal conductivity:

$$F^* = 0.1682 + 0.0434\,\omega + 0.1305\,\omega^2 \tag{27}$$

and for the viscosity,

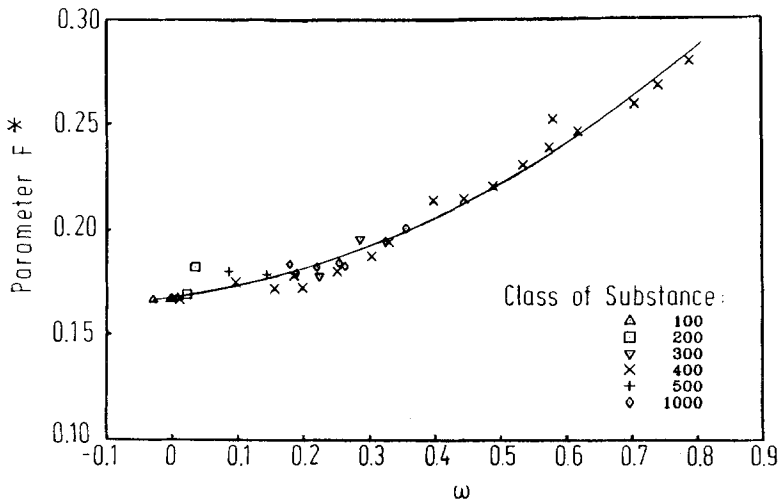$$F^* = 0.093 + \frac{1}{55.2 + 301\,\omega} \tag{28}$$

Fig. 1. Parameter F^* for the thermal conductivity as a function of the acentric factor ω for different substances. 100, noble gases; 200, 2-atomic gases; 300, 3-atomic gases; 400, alkanes; 500, alkenes; 1000, refrigerants.
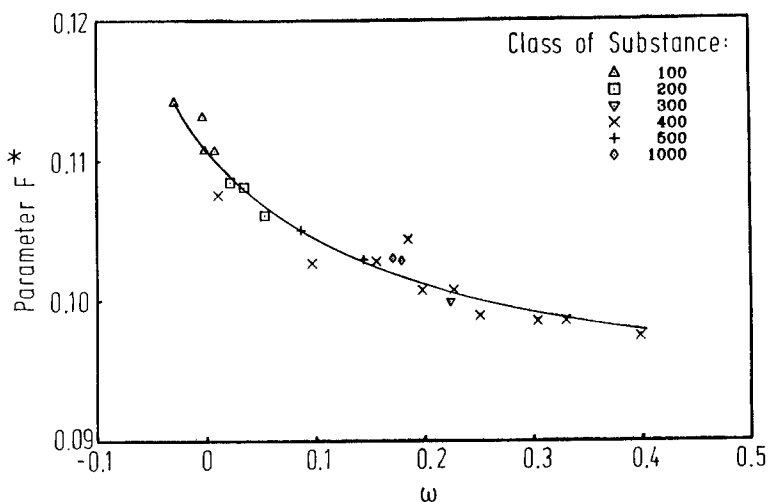
Fig. 2. Parameter F^* for the viscosity as a function of the acentric factor ω for different substances. 100, noble gases; 200, 2-atomic gases; 300, 3-atomic gases; 400, alkanes; 500, alkenes; 1000, refrigerants.

5. RESULTS

5.1. One-Phase Region

The thermal conductivity of oxygen has been represented by a recently derived cubic [16] and a virial [13] transport equation of state. In Fig. 3 the pressure, calculated by means of the generalized cubic transport equation of state represented by solid lines, versus the residual thermal conductivity of oxygen is shown for different temperatures. The symbols refer to the recommended values. The analogy to a p, ρ diagram is obvious. The departure plot (Fig. 4) reveals fairly good agreement, with a maximum deviation of 5% for residual thermal conductivities above values of $10 \, mW \cdot m^{-1} \cdot K^{-1}$. For lower residual thermal conductivities the deviation increases up to 36%, because in this region the dilute gas function in Eq. (2) approaches the value of the thermal conductivity, so that experimental uncertainties strongly influence the residual part.

The property of interest is the transport property itself (Fig. 5), rather than its residual part. This figure clearly demonstrates that the errors become low for low values of the thermal conductivity.

In Table V the results obtained with the virial [13], cubic [16], and generalized cubic transport equation of state are compared.
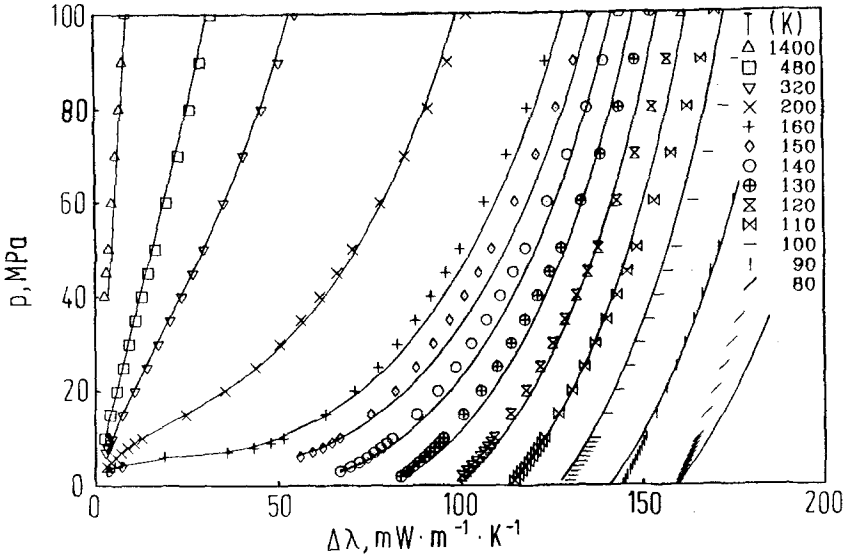
Fig. 3. Pressure as a function of residual thermal conductivity of oxygen for different temperatures. Symbols, recommended values [13]; lines, calculated from Eq. (24).
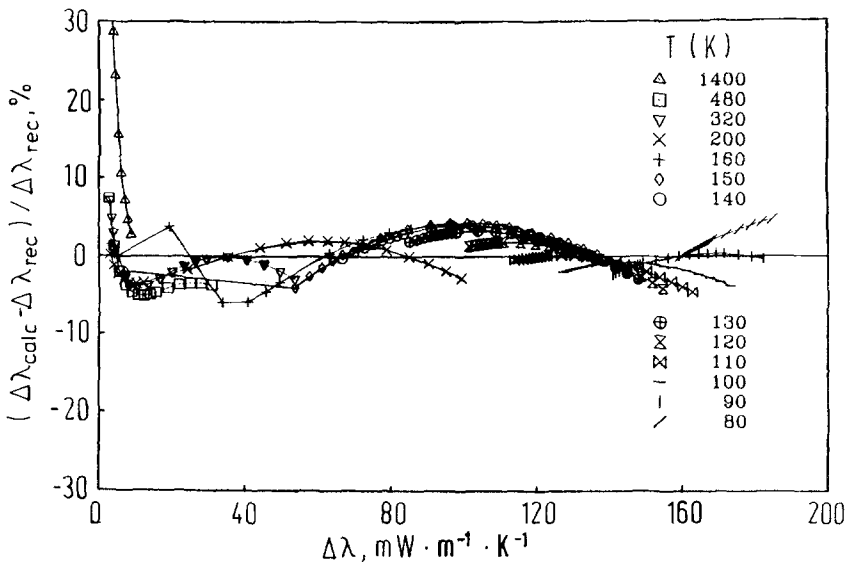

Fig. 4. Departures of calculated and recommended residual thermal conductivities of oxygen for different temperatures.
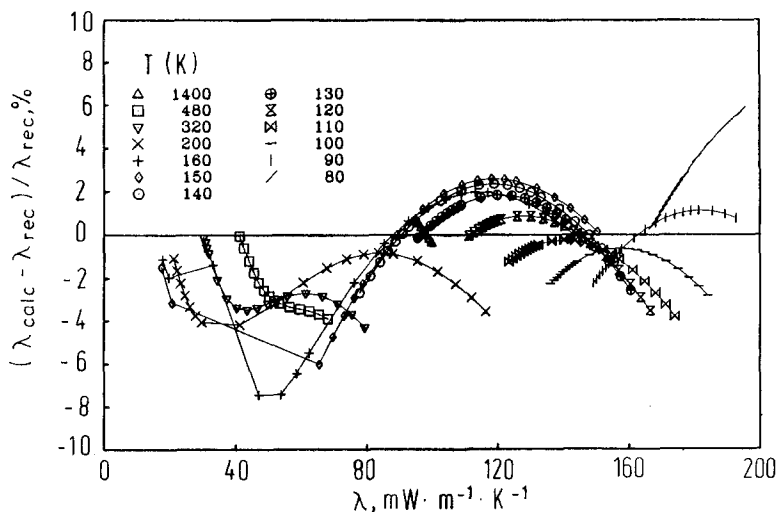
Fig. 5. Departures of calculated and recommended thermal conductivities of oxygen for different temperatures.

From the absolute average deviation, one can conclude that the simpler but more general representation with the generalized cubic transport equation, Eq. (24), leads to an increase in error by a factor of about two.

The results obtained with the generalized cubic transport equation of state, Eq. (24), for substances other than oxygen are presented in Tables VI and VII. The absolute average deviation over all substances for the thermal conductivity is 6.2%, and that for the viscosity 4.7%. In view of the experimental uncertainties these deviations seem to be tolerable. Some substances show larger maximum deviations up to 53% of the thermal con-

Table V. Comparison of Three Different Transport Equations of State (TEOS) for the Thermal Conductivity of Oxygen[a]

	MRE (%)	AAD (%)
Virial TEOS [13]	<0.1	0.6
Cubic TEOS [16]	0.4	0.9
This work	−1.6	2.0

[a] MRE, mean relative error; AAD, absolute average deviation.

Table VI. Comparison of Calculated and Recommended Thermal Conductivity for Selected Substances[a]

	MRE (%)	AAD (%)	MAXE (%)
Neon	−2.01	3.19	12.5
Argon	−0.75	2.50	8.05
Krypton	−0.38	2.54	8.41
Xenon	0.07	2.59	7.39
Nitrogen	−4.34	4.34	16.93
Oxygen	−1.62	2.02	7.45
Carbon dioxide	0.02	5.43	29.92
Sulfur hexafluoride	−9.16	12.48	52.92
Methane	−0.01	2.27	21.01
Ethane	−1.64	2.78	21.32
Propane	3.99	7.21	15.61
n-Butane	8.72	9.52	14.45
i-Butane	4.20	5.91	15.55
n-Pentane	6.14	6.65	9.05
n-Hexane	5.32	5.77	7.14
n-Heptane	2.02	2.34	4.36
n-Octane	−8.49	8.99	16.59
n-Nonane	−2.96	7.02	17.36
n-Decane	−1.97	5.64	20.11
n-Undecane	−3.10	7.09	17.45
n-Dodecane	−3.86	8.54	21.16
n-Tridecane	−2.46	7.71	17.50
n-Tetradecane	−13.6	13.60	22.54
n-Pentadecane	4.43	10.04	29.65
n-Hexadecane	3.44	10.01	36.96
n-Octadecane	4.46	10.58	30.45
Ethene	−7.45	7.45	17.40
Propene	−4.37	4.39	16.49
Refrigerant 11	−2.02	5.13	27.71
Refrigerant 12	−5.05	5.05	17.41
Refrigerant 22	−4.53	8.12	24.90
Refrigerant 113	2.25	3.01	5.37
Refrigerant 114	3.75	5.19	9.94
Refrigerant 218	−3.55	8.28	26.56
Refrigerant C318	−1.88	4.17	9.73
Mean	−1.04	6.22	18.21

[a] MRE, mean relative error; AAD, absolute average deviation; MAXE, maximum error.

ductivity, particularly in the critical region, because some of the data included a critical enhancement. When omitting these data the maximum error reduces to about 10%. The larger errors for the viscosity in the liquid region up to 33% are caused by the sharp increase of the viscosity with density at lower reduced temperatures of about 0.6.

As a test for the quality of the generalized transport equation of state, the viscosity of *n*-decane shall be determined. Because of the lack of data for the dilute gas, *n*-decane data could not be used for the development of the generalized transport equation. According to the corresponding-states principle proposed by Ely and Hanley [5], the dilute gas viscosities can be evaluated. When added to the residual part from the transport equation of state, Eq. (24), a mean relative error of 0.3%, an absolute average devia-

Table VII. Comparison of Calculated and Recommended Viscosity for Selected Substances[a]

	MRE (%)	AAD (%)	MAXE (%)
Neon	−1.17	3.61	9.85
Argon	−0.57	3.90	24.2
Krypton	0.35	3.16	15.44
Xenon	−1.49	3.07	13.16
Nitrogen	2.80	3.25	7.08
Oxygen	5.37	5.97	17.69
Fluorine	1.87	3.21	10.79
Carbon monoxide	6.99	6.99	8.48
Carbon dioxide	3.83	4.17	9.92
Methane	10.26	10.26	25.51
Ethane	1.77	2.66	11.88
Propane	0.44	2.36	9.01
n-Butane	4.73	6.06	32.90
i-Butane	−6.12	7.94	26.92
n-Pentane	0.84	4.13	8.17
i-Pentane	−4.20	5.94	25.14
n-Hexane	−1.28	5.30	19.09
n-Heptane	−1.21	5.13	19.60
n-Octane	1.72	5.81	13.45
Ethene	0.62	3.81	10.53
Propene	−2.70	3.38	15.45
Refrigerant 12	−3.15	3.71	14.12
Refrigerant 13B1	−2.95	3.29	13.02
Mean	0.73	4.66	15.71

[a] MRE, mean relativ error; AAD, absolute average deviation; MAXE, maximum error.

tion of 4%, and a maximum error of 13% are obtained. These deviations are of the same order as for the substances which were used for the development of the equation.

5.2. Vapor–Liquid Equilibrium

The transport properties along the vapor–liquid coexistence curve are difficult to be measured. The data base contains such values of the thermal conductivity of 27 and of the viscosity of 10 substances.

The thermal conductivity of oxygen along the saturation line calculated with the aid of Eqs. (5), (6), and (9) is shown in Fig. 6. The symbols refer to the recommended values [13]. As the departure plot (Fig. 7) reveals, the errors are below 5% except two points near the critical temperature of 154.58 K, where the error increases up to about 10%. This is still acceptable compared to an accuracy of 18% stated for the recommended values in this region [13]. Results for substances other than oxygen are given in Tables VIII and IX. The good representation of the vapor pressure is an indication for the quality of the thermal equation of state. The prediction of the transport properties along the vapor liquid coexistence curve yielded absolute average deviations up to 15%, with a
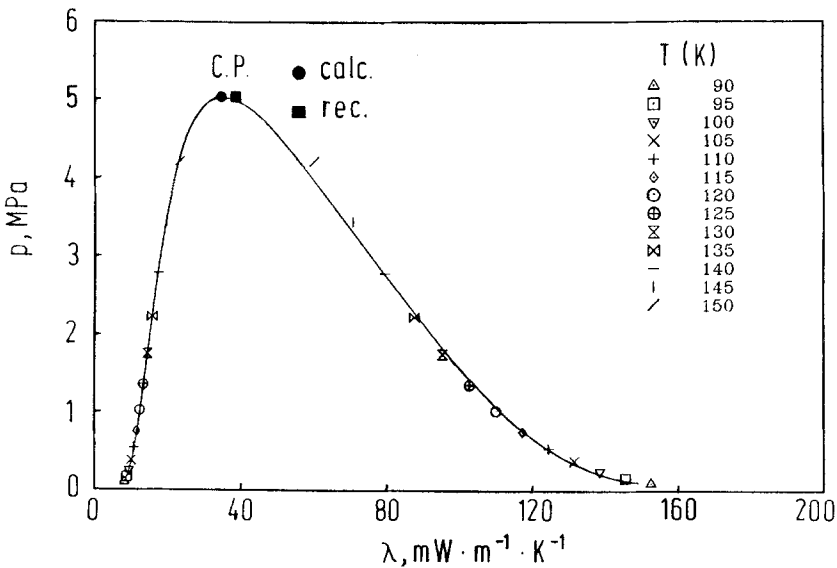

Fig. 6. Saturation line of the thermal conductivity of oxygen. Symbols, recommended values [13]; lines, calculated from Eq. (24).
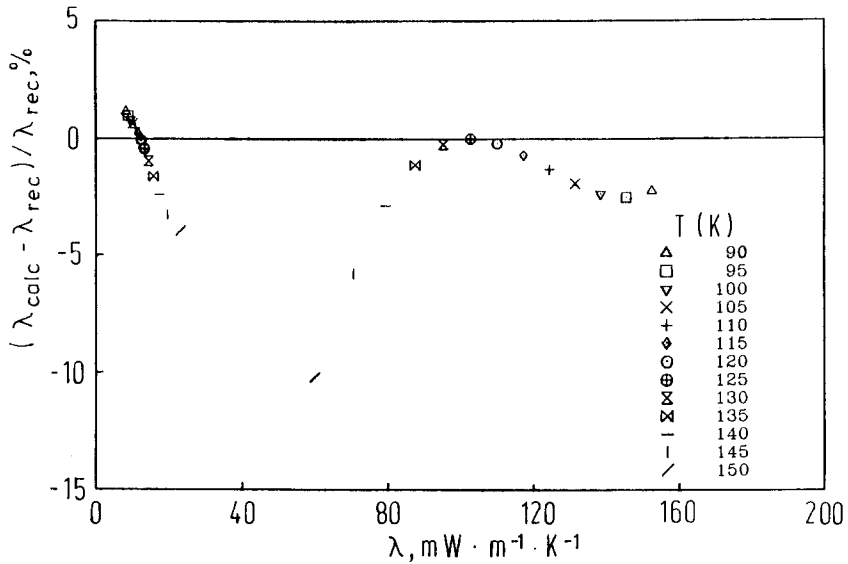
Fig. 7. Departures of calculated and recommended thermal conductivities along the saturation line.

mean deviation of about 5.5%, which comes close to the deviations in the one-phase region. These results are all the more satisfactory as equilibrium data were not used for the development of the transport equation.

5.3. Critical Region

Transport equations of state describe only the background contribution of the transport properties in the critical region. In principle, the Maxwell condition permits the calculation of the background contribution at the critical point. However, the numerical solution of Eqs. (5), (6), and (9) is difficult, because in the limit of critical temperatures both sides of Eq. (9) vanish. Thus the coexistence curve can be calculated only up to 0.5 K from the critical temperature.

According to Lucas [29] the Riedel number [30], defined as

$$Ri = \frac{\partial p_r}{\partial T_r}\bigg|_{\text{Sat,C.P.}} = \frac{\partial p_r}{\partial T_r}\bigg|_{v_c,\text{C.P.}} \tag{29}$$

can be used to evaluate consistency between transport equations of state and thermal properties.

Table VIII. Comparison Between Predicted and Recommended Thermal Conductivity Along the Saturation Line for Selected Substances[a]

	Points DL/BL	P_r range	T_r range	DL (%)			BL (%)			Vap. press (%)		
				MRE	AAD	MAXE	MRE	AAD	MAXE	MRE	AAD	MAXE
Neon	6/6	0.026–0.81	0.58–0.97	−0.8	0.9	3.3	1.4	4.2	6.5	2.3	2.5	4.0
Argon	7/7	0.027–0.80	0.59–0.97	−1.2	1.5	2.5	3.2	3.7	6.7	0.1	0.3	0.9
Krypton	10/10	0.018–0.89	0.57–0.98	−0.4	1.0	1.8	0.9	3.5	7.9	−0.2	0.3	0.6
Xenon	13/13	0.022–0.91	0.58–0.99	−1.1	1.3	5.5	1.0	3.8	11.0	−0.7	0.8	1.3
Nitrogen	12/12	0.011–0.95	0.55–0.99	−6.5	6.5	14.0	−13.6	13.6	18.0	−0.2	0.3	0.6
Oxygen	13/13	0.019–0.84	0.58–0.97	−0.7	1.3	4.0	−2.4	2.4	10.2	−0.0	0.2	0.3
CO_2	16/16	0.081–0.95	0.72–0.99	−14.6	14.6	29.8	0.4	10.8	27.9	−0.7	0.7	1.1
SF_6	10/10	0.082–0.93	0.72–0.99	−10.8	10.8	32.5	−8.0	13.6	36.2	−6.7	6.7	14.3
Methane	18/18	0.007–0.87	0.52–0.98	−3.0	3.3	14.8	0.1	2.7	9.2	−1.0	1.0	2.3
Ethane	22/22	0.025–0.93	0.61–0.99	−6.9	7.1	16.8	3.1	6.3	13.8	0.6	0.7	1.7
Propane	14/14	0.023–0.95	0.62–0.99	−5.9	6.4	16.6	0.8	7.2	12.3	−0.1	0.2	0.9
n-Butane	18/18	0.035–0.93	0.65–0.99	−5.9	6.3	17.5	4.5	7.7	12.4	0.2	0.3	0.6
i-Butane	11/11	0.027–0.88	0.64–0.98	−11.4	11.4	26.0	−3.3	6.7	20.4	0.3	0.3	0.4
n-Pentane	—/13	0.021–0.90	0.63–0.99	—	—	—	1.3	7.7	8.8	−0.1	0.4	0.6
n-Hexane	15/15	0.042–0.89	0.68–0.99	−2.2	2.2	6.6	2.6	5.3	8.0	−0.2	0.2	0.8
n-Heptane	10/10	0.047–0.94	0.70–0.99	−5.0	5.0	10.9	−5.3	7.0	16.4	1.4	1.7	4.8
n-Nonane	2/8	0.065–0.82	0.74–0.98	−0.6	0.6	1.2	3.9	7.8	13.4	1.6	1.6	3.4
n-Decane	—/7	0.098–0.77	0.77–0.97	—	—	—	0.9	8.0	16.6	3.7	3.7	6.4
Ethene	11/11	0.036–0.95	0.63–0.99	−5.8	5.8	13.8	−9.6	9.6	24.1	0.0	0.2	0.5
Propene	13/13	0.040–0.92	0.65–0.99	−4.2	4.2	10.5	−5.4	5.4	19.7	−0.2	0.2	0.4
R 11	17/17	0.025–0.86	0.63–0.98	1.4	2.3	7.0	2.8	4.8	8.8	−0.4	0.4	1.0
R 12	16/16	0.013–0.92	0.59–0.99	−0.9	2.0	10.2	−6.2	6.2	19.8	0.3	0.3	0.5
R 22	14/14	0.021–0.89	0.63–0.98	−7.0	7.1	18.7	−2.0	7.9	27.3	−0.0	0.3	0.4
R 113	15/15	0.029–0.67	0.65–0.95	−1.3	1.3	2.4	2.2	2.2	3.9	0.1	0.3	0.6
R 114	—/13	0.034–0.72	0.66–0.96	—	—	—	4.0	5.4	8.3	0.3	0.4	1.0
R 218	9/9	0.098–0.89	0.75–0.99	−5.7	5.7	17.9	1.8	9.2	18.6	−0.7	0.9	1.6
R C318	9/9	0.060–0.57	0.72–0.93	−1.8	1.8	3.2	2.4	3.2	5.7	−0.9	0.9	1.5
Mean				−4.3	4.6	12.0	−0.7	6.5	14.5	−0.0	1.0	1.9

[a] DL, dew line; BL, bubble line; MRE, mean relative error; AAD, absolute average deviation; MAXE, maximum error; —, no data available.

Table IX. Comparison Between Predicted and Recommended Viscosity Along the Saturation Line for Selected Substances[a]

	Points DL/BL	P_r range	T_r range	DL (%)			BL (%)			Vap. press. (%)		
				MRE	AAD	MAXE	MRE	AAD	MAXE	MRE	AAD	MAXE
Neon	6/6	0.026–0.73	0.58–0.96	2.9	3.9	5.6	−0.9	2.3	4.8	2.3	2.5	4.0
Argon	7/7	0.027–0.80	0.59–0.97	5.7	11.8	−7.0	7.5	15.2	0.1	0.3	0.9	0.9
Krypton	10/10	0.018–0.89	0.57–0.98	4.8	4.8	8.3	−4.9	4.9	8.6	−0.2	0.3	0.6
Xenon	13/13	0.022–0.91	0.58–0.99	4.2	4.2	9.1	−9.4	9.4	15.1	−0.7	0.8	1.3
Nitrogen	11/11	0.022–0.94	0.59–0.99	3.6	4.3	9.7	−1.3	4.0	7.9	−0.3	0.3	0.6
Oxygen	16/16	0.003–0.84	0.48–0.97	3.4	3.7	10.4	5.1	6.1	11.2	0.1	0.2	0.4
Methane	10/10	0.140–0.85	0.73–0.97	11.5	11.5	19.3	7.2	10.2	16.3	−0.7	0.7	1.0
Propane	7/7	0.167–0.84	0.77–0.97	12.9	12.9	16.0	−1.6	4.3	11.5	−0.9	0.9	1.2
Ethene	11/11	0.036–0.95	0.63–0.99	3.2	3.2	4.8	−0.5	5.2	17.1	0.0	0.2	0.5
Propene	14/14	0.027–0.92	0.63–0.99	−1.7	2.1	4.4	−4.4	4.5	18.2	−0.3	0.3	0.4
Mean				5.1	5.6	9.9	−1.8	5.9	12.6	0.1	0.7	1.1

[a] DL, dew line; BL, bubble line; MRE, mean relative error; AAD, absolute average deviation; MAXE, maximum error;—, no data available.

Table X. Comparison of Riedel Numbers[a]

	Ri_{TEOS}	Ri_{vp}	Ri_{Est}	ΔRi_{vp} (%)	ΔRi_{Est} (%)
Neon	5.575	5.660	5.665	−1.5	−1.6
Argon	5.706	5.760	5.793	−0.9	−1.5
Krypton	5.717	5.940	5.803	−3.8	−1.5
Xenon	5.763	5.830	5.847	−1.2	−1.4
Nitrogen	5.905	5.980	5.980	−1.3	−1.3
Oxygen	5.836	6.044[b]	5.916	−1.4	−1.4
Fluorine	6.007	6.330	6.074	−5.1	−1.1
CO	5.974	6.040	6.044	−1.1	−1.2
CO_2	6.993	6.920	6.911	1.1	1.2
SF_6	7.379	7.210	7.217	2.3	2.2
Methane	5.779	5.860	5.862	−1.4	−1.4
Ethane	6.244	6.280	6.286	−0.6	−0.7
Propane	6.584	6.540	6.576	0.7	0.1
n-Butane	6.835	6.770	6.783	1.0	0.8
i-Butane	6.757	6.710	6.719	0.7	0.6
n-Pentane	7.160	7.030	7.044	1.9	1.6
i-Pentane	7.012	6.870	6.926	2.1	1.2
n-Hexane	7.492	7.270	7.305	3.1	2.6
n-Heptane	7.657	7.270	7.433	5.3	3.0
n-Octane	8.092	7.760	7.768	4.3	4.2
n-Nonane	8.393	7.940	8.000	5.7	4.9
n-Decane	8.673	8.180	8.217	6.0	5.6
n-Undecane	8.961	8.370	8.443	7.1	6.1
n-Dodecane	9.207	8.540	8.640	7.8	6.6
n-Tridecane	9.469	8.810	8.857	7.5	6.9
n-Tetradecane	9.243	8.310	8.670	11.2	6.6
n-Pentadecane	9.954	9.140	9.286	8.9	7.2
n-Hexadecane	10.139	9.790	9.463	3.6	7.1
n-Octadecane	10.369	9.410	9.700	10.2	6.9
Ethene	6.188	6.180	6.236	0.1	−0.8
Propene	6.514	6.400	6.517	1.8	0.1
Refrigerant 11	6.781	6.740	6.739	0.6	0.6
Refrigerant 12	6.721	6.660	6.690	0.9	0.5
Refrigerant 13B	6.673	—	6.650	—	0.3
Refrigerant 221	6.969	7.140	6.892	−2.4	1.1
Refrigerant 113	7.179	10.380	7.059	−30.8	1.7
Refrigerant 114	7.235	7.600	7.103	−4.8	1.8
Refrigerant 218	7.626	—	7.409	—	2.9
Refrigerant C318	7.823	—	7.562	—	3.5
Absolute average deviation				4.2	2.6

[a] Ri_{TEOS}, Riedel number from generalized transport equation of state; Ri_{vp}, Riedel number from generalized vapor pressure equation [30]; Ri_{Est}, Riedel number estimated from Eq. (2–34) in Ref. 31 (p. 31).
[b] Recommended Riedel number of oxygen from Ref. 13.

Equation (29) can be rewritten for the transport property, in terms of the residual part, as

$$Ri = \frac{\partial p_r}{\partial T_r}\bigg|_{\varDelta TP_c, C.P.} \tag{30}$$

The Riedel number obtained from the transport equation of state, Eq. (24), thus can be compared to those from other sources, e.g., from a vapor pressure equation or a thermal equation of state. This comparison may serve as an indication for the accuracy of the transport equation of state. For this purpose one has to define a value of the critical background contribution of the transport property $\varDelta TP_c$. This can be done by the conditions of the critical point

$$\frac{\partial p}{\partial \varDelta TP}\bigg|_{T_c} = 0 \tag{31}$$

and

$$\frac{\partial^2 p}{\partial \varDelta TP^2}\bigg|_{T_c} = 0 \tag{32}$$

when applied to the transport equation of state, Eq. (24). Table X lists the Riedel number calculated from the transport equation of state together with values obtained by a generalized vapor pressure equation [30] and estimated values, both tabulated in Ref. 31. The agreement is satisfactory.

The recommended value of the Riedel number for oxygen is 6.04 [13]. From the accurate virial transport equation of state for the thermal conductivity of oxygen [13], one obtains a Riedel number of 6.43, and from the equation for the viscosity, 6.67, whereas the generalized transport equation of state yields the slightly better value of 5.84.

Hence the background contribution obtained from the generalized transport equation of state is consistent with the thermal properties as far as the slope of the vapor pressure curve at the critical point is concerned.

To evaluate the true values of the transport properties in the vicinity of the critical point, the singular contribution has to be added to account for the critical enhancement.

6. CONCLUSION

The concept of transport equations of state previously used for the description of the transport properties of well-investigated substances in terms of pressure and temperature can also be used to predict the residual

transport properties in a broad fluid range, when experimental data are lacking. The method makes use of a generalized cubic transport equation of state, wherein the density is substituted by a universal temperature-independent function of the residual transport property, so that the temperature functions in the initial thermal equation of state can be retained. The method presented requires critical temperature, critical pressure, and the acentric factor as species-dependant constants. It describes the background contribution of the residual thermal conductivity with a mean deviation of 6% and that of the viscosity with a mean deviation of 5%. The substances covered are noble gases, two- and three-atomic gases, alkanes up to C_{18}, alkenes, and refrigerants.

Viscosity data for n-decane, which were not used for the development of the equation, were predicted with a mean deviation of 4%, which may serve as an indication of the predictive capacity of the equation.

It is shown that the Maxwell condition for vapor–liquid equilibrium can be applied to transport equations of state to predict consistently the transport properties along the vapor–liquid coexistence curve without an additional vapor pressure equation. The prediction yielded mean deviations of the transport properties along the saturation line of less than 6.4%.

It is felt that the results meet demands for a simple estimation method for transport properties in terms of pressure and temperature in a broad fluid range.

ACKNOWLEDGMENT

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