Transport Properties of Fluids

Their Correlation, Prediction and Estimation

Edited by

Jürgen Millat
NORDUM Institut für Umwelt und Analytik GmbH, Kessin/Rostock, Germany

J. H. Dymond
The University, Glasgow, UK

C. A. Nieto de Castro
University of Lisbon, Portugal

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Reacting Mixtures at Low Density – Alkali Metal Vapors

P. S. FIALHO
University of Azores, Portugal

M. L. V. RAMIRES and C. A. NIETO DE CASTRO
University of Lisbon, Portugal

J. M. N. A. FARELEIRA
Technical University of Lisbon, Portugal

16.1 Introduction[a]

Previous chapters of this volume dealt with the transport properties of nonreacting mixtures. However, there are several systems of scientific and industrial interest that involve chemical reactions between some of the atoms or molecules present. This fact modifies the values of the transport properties of these systems because there are additional processes of heat and mass transfer caused by the existence of the chemical reaction.

The simplest kind of system where chemical reaction is present is an alkali metal vapor, where dimerization of atoms takes place, with a temperature– and pressure–dependent composition. This fact, allied to the high–temperature domain of the application of these vapors, makes the determination of the transport properties of these systems very challenging from a theoretical point of view.

The thermophysical properties of alkali–metal vapors are very important for several technological processes, namely as working fluids for Rankine cycles, solar power plants and magnetic hydrodynamic generation (Ohse 1985). Their measurement is, however, very difficult to achieve with accuracies similar to those obtainable for other fluids, because of the high temperatures and low pressures, and therefore low densities involved (Wakeham *et al.* 1991). The prediction of these properties is the recommended alternative to the deficient quality and scarcity of the experimental data. In addition to the difficulties associated with the formation of dimers, the alkali metal atoms interact via either one of two intermolecular pair potential energy functions, namely, the ground singlet [$^1U(R)$] and the triplet [$^3U(R)$] potential energy curves, belonging respectively to the $^1\Sigma_g^+$ and $^3\Sigma_u^+$ diatomic molecular states.

The calculation of the transport properties of alkali metal vapors involves the use of the kinetic theory of binary reacting mixtures and its application to a mixture of monomers and dimers. The use of the theory requires the evaluation of the monomer properties, the establishment of some approximations to calculate the viscosity and the

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[a] This chapter is dedicated to the memory of Professor V. B. Vargaftik (1904–1994) for his outstanding contributions in the field of thermophysical properties of alkali metal vapors.

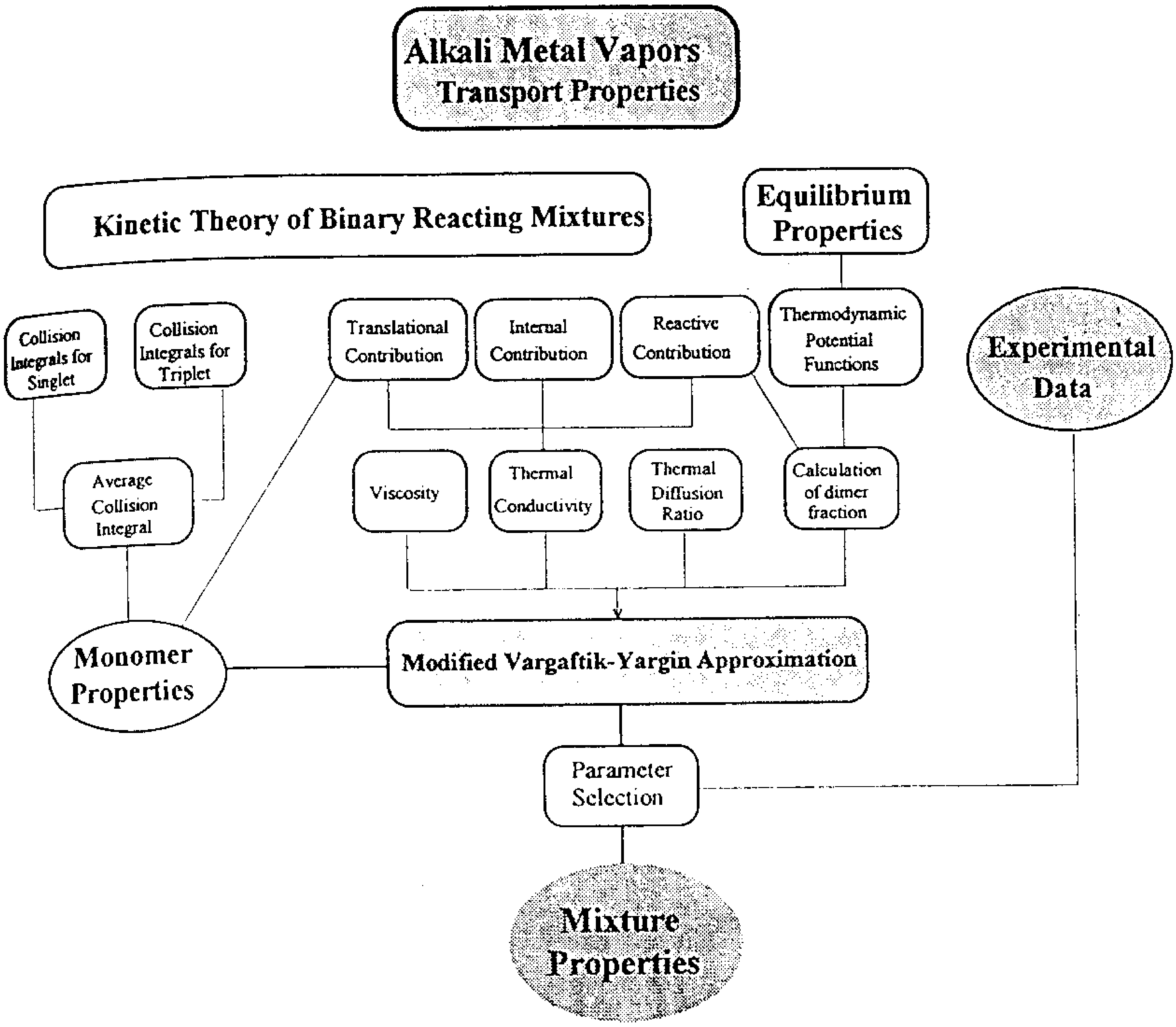

Fig. 16.1. Diagram for the calculation of the transport properties of alkali metal vapors.

contributions for the thermal conductivity and thermal diffusion ratio of dimers and of the mixture, and the evaluation through thermodynamic calculations of the dimer fraction at each temperature and pressure. This procedure is exemplified in Figure 16.1 and will be described in the following sections, with reference to the possible types of approaches.

16.2 Monatomic Systems

A fundamental requirement for the theoretical calculation of the transport properties of a system composed of alkali atoms is the knowledge of sound reliable pair potential energy functions along which any two atoms interact. According to previous works (Davies *et al.* 1965), if the atoms are assumed as neutral, in their ground electronic state, the problem reduces to that of obtaining the ground singlet $[{}^1U(R)]$ and triplet $[{}^3U(R)]$ potential energy curves. Most of the previous calculations of the equilibrium (second virial coefficients) and transport properties of these systems used the Lennard-Jones

(LJ), Morse or Rydberg functions to represent $[^1U(R)]$ (Davies *et al.* 1965; Polishchuk *et al.* 1980; Sannigrahi *et al.* 1976; Sinanoglu & Pitzer 1959; Vargaftik & Yargin 1985). These functions have been shown to overestimate the attraction at large separations. The $^3\Sigma_u^+$ state is repulsive except for the long–range van der Waals attraction, and the available information about it was very limited until recently. In their pioneer works Sinanoglu & Pitzer (1959) used an LJ (9-6) potential, while Davies *et al.* (1965) adopted an (exp-6) form calibrated from their own semiempirical calculation of $[^3U(R)]$.

With the development of computational techniques, more accurate approaches have been used. Quantum–mechanical partition function evaluation of the second virial coefficient $B_{\mathrm{MM}}(T)$ has been performed by Mies & Julienne (1982) for lithium and sodium, using the singlet and triplet potentials of Konowalow and Olsen. Holland *et al.* (1986, 1987) calculated $B_{\mathrm{MM}}(T)$, η_{M}, λ_{M} and D_{M} for lithium and sodium by accurately representing quantum mechanically potential energy curves with the Hulburt-Hirschfelder (HH) potential. These authors used *ab initio* quantum–mechanical results to provide information about the long–range part of the singlet potential to overcome the less accurate representation of the attractive tail provided by that potential. The triplet state was described by using a fitting of the HH potential to *ab initio* results.

In a recent paper, Nieto de Castro *et al.* (1990) used a hybrid extension of the Murrell-Sorbie (MS) analytic potential, which has the correct long–range behavior at large internuclear distances, r, is continuous and has a continuous first derivative at the boundary for the ground singlet state (Varandas 1980). For the triplet state, those authors have used a model which expresses the interaction potential in terms of the Hartree-Fock interaction energy, and the interatomic correlation energy as approximated semiempirically from the second–order dispersion energy calculated, including the effect of charge overlap between the electron clouds of the two interacting species (Varandas & Brandão 1982). The viscosity, thermal conductivity, self–diffusion coefficients and second virial coefficients of lithium, sodium, potassium, rubidium and cesium monatomic vapors, have been calculated between 600 and 5000 K, and the results were compared with previous work (Holland *et al.* 1986, 1987; Mies & Julienne 1982; Polishchuk *et al.* 1980; Stefanov 1980; Vargaftik & Yargin 1985). The results have shown that, in general, there was a significant improvement in the quality of the predictions.

Recently, Varandas & Dias da Silva (1992) have developed a new model potential for the ground molecular state of diatomic molecules, which is a development of the so–called Extended Hartree-Fock Approximate Correlation Energy (EHFACE) potential (Varandas & Dias da Silva 1986). These authors have pointed out the need to include in the latter model '*... a more realistic description of the potential energy curve at the highly repulsive regions near the united-atom limit which results from the collapsed diatomic for a vanishing internuclear separation* ($r \rightarrow 0$).' To accomplish this, Varandas & Dias da Silva (1992) have developed a new model potential (whose acronym is EHFACE2U) for the ground molecular state of diatomic molecules, including the alkali metals, which gives the correct description of the potential energy as $r \to 0$ (Varandas & Dias da Silva 1992). This is based on the addition of an extended Hartree-Fock-type energy to the dynamical correlation.

When analyzing the experimental data with the former models some inconsistencies were found, namely for cesium, where the amount of dimers present at high temperatures is very small; therefore, a higher accuracy is required for the monatomic systems.

As the transport properties are particularly sensitive to the repulsive part of the intermolecular potential, especially at high temperatures, Fialho *et al.* (1993) have repeated their previous calculations of the transport properties of the atomic alkali metal vapors, using for comparison the EHFACE2U model for the ground singlet intermolecular potential interaction. The calculations presented earlier (Nieto de Castro *et al.* 1990) were repeated using the new potential functions for the ground singlet states of the alkali metals, lithium, sodium, potassium, rubidium and cesium. The excited state triplet potential functions were the same as before. The precision of the calculations has been improved, by the use of more sophisticated numerical procedures. Furthermore, because of the utilization of the monomeric systems results for the purposes of comparison with experimental data at the temperatures at which they have been obtained, a new interpolation scheme for the collision integrals has been developed. Details of the potentials can be found in the work of Varandas & Brandão (1982) and Varandas & Dias da Silva (1992).

The first–order Chapman-Enskog solution of the Boltzmann equation for the viscosity and thermal conductivity of monatomic species are given by the expressions in terms of effective collision cross sections outlined in Chapter 4. However, in order to be consistent with the original papers, here the equivalent expressions in terms of collision integrals are adopted.

$$[\eta]_1 = \frac{5}{16}(\pi m k_B T)^{1/2} \frac{1}{\bar{\Omega}^{(2,2)}(T)} \tag{16.1}$$

$$[\lambda]_1 = \frac{25}{32}\left(\frac{\pi k_B T}{m}\right)^{1/2} \frac{c_V}{\bar{\Omega}^{(2,2)}(T)} \tag{16.2}$$

$$[D]_1 = \frac{3}{8P}\left(\frac{\pi k_B^3 T^3}{m}\right)^{1/2} \frac{1}{\bar{\Omega}^{(1,1)}(T)} \tag{16.3}$$

where m is the molecular mass, $\bar{\Omega}^{(l,s)}(T)$ are weighted average collision integrals defined as (Sinanoglu & Pitzer 1959)

$$\bar{\Omega}^{(l,s)}(T) = \frac{1}{4}\pi\sigma_1^2\bar{\Omega}_1^{(l,s)*}(T_1^*) + \frac{3}{4}\pi\sigma_3^2\bar{\Omega}_3^{(l,s)*}(T_3^*) \tag{16.4}$$

$\bar{\Omega}_1^{(l,s)*}(T_1^*)$ and $\bar{\Omega}_3^{(l,s)*}(T_3^*)$ are reduced collision integrals for the singlet (subscript 1) and for the triplet (subscript 3) interactions, and T_i^* are the corresponding reduced temperatures, such that $T_i^* = k_B T/\epsilon_i$. The second–order Kihara correction factors to these solutions are given by Maitland *et al.* (1987) and Hirschfelder *et al.* (1954). The collision integrals $\bar{\Omega}_1^{(l,s)*}(T_1^*)$ and $\bar{\Omega}_3^{(l,s)*}(T_3^*)$ are related to the interatomic potential functions through the usual expressions (Maitland *et al.* 1987).

Fialho *et al.* (1993) calculated the viscosity and thermal conductivity of the monatomic alkali systems using the above mentioned pair potentials. A description of the calculation of the collision integrals can be found therein. The calculation of the transport properties of the monatomic alkali metal vapors at temperature T requires the determination of two reduced collision integrals at the corresponding reduced temperatures T_1^* and T_3^*. This is conveniently carried out using adequate interpolation procedures between tabulated values of the collision integrals for both the singlet and the triplet potentials. For this purpose, polynomials of the form

$$\ln\left[\bar{\Omega}_i^{(l,s)*}(T_i^*)\right] = \sum_{j=0}^{4} C_j T_i^{*(j-2)} \tag{16.5}$$

were fitted to the results obtained for $\bar{\Omega}_i^{(l,s)*}(T_i^*)$, where $i = 1$ or $i = 3$. The results obtained for $\bar{\Omega}_i^{(l,s)*}(T_i^*)$, $l = 1, 2$ and $s = 1, 2, 3$, for the singlet ($i = 1$) and for the triplet ($i = 3$) states in the range $500 < T < 2000$ K are summarized in Tables 16.1 and 16.2 where the fitting parameters of equation (16.5), obtained for each of the alkali metals, are presented together with the rms deviation, σ, of the fittings. The precision with which the values of the collision integrals can be estimated within that temperature interval is better than ±0.6% and ±0.03% for the singlet and triplet states, respectively, at a 95% confidence level. The overall precision of the estimates of the average collision integrals of the monatomic alkali metals using expression (16.5) with the values of Table 16.1 is estimated to be of the order of ±0.6%.

The average collision integrals $\bar{\Omega}^{(l,s)}(T)$ given by equation (16.4) and the fitting polynomials (16.5) for each of the metals were compared with the results obtained by Nieto de Castro *et al.* (1990). The agreement is very good for lithium, sodium and cesium, where the maximum deviation is less than ±1% in the temperature range $700 \leq T \leq 2000$ K, and also for rubidium where it amounts to ±1.5%. Therefore, the comparisons made by Nieto de Castro *et al.* (1990), in their previous paper for lithium and sodium, with those published by other authors remain essentially unchanged. For potassium, a systematic negative deviation of the previous calculations from this work was found, which amounts to −3.5% at 700 K decreasing with increasing temperature to less than −0.5% at 2000 K, probably due to the fact that the new singlet potential function is slightly less steeply repulsive than the previous one.

The calculated viscosity, thermal conductivity and self-diffusion coefficients (the latter at 0.10 MPa) of nonionized monatomic lithium, sodium, potassium, rubidium and cesium vapors can be consulted for temperatures between 700 and 2000 K in Tables VIII to XII of the work of Fialho *et al.* (1993).

Table 16.1. *Singlet potential parameters for equation (16.5) (Fialho et al. 1993).*

	$10^4 \cdot C_0$	$10^3 \cdot C_1$	C_2	C_3	C_4	$\frac{\sigma}{\%}$
			a) $\Omega_1^{(1,1)*}(T_1^*)$			
Li	-0.5516051	7.729600	2.558459	-2.008881	-1.770730	0.11
Na	0.3513133	3.852063	2.331874	-2.374357	0.1364867	0.16
K	5.985651	-7.206078	2.089676	-2.450936	0.8512206	0.11
Ru	3.931187	-5.047879	2.149760	-2.590676	1.011096	0.12
Cs	5.293546	-7.041881	1.930501	-2.196644	0.6830733	0.12
			b) $\Omega_1^{(1,2)*}(T_1^*)$			
Li	0.2042988	2.577080	2.611257	-3.092686	-2.339541	0.18
Na	2.518076	-7.700390	2.473208	-3.938448	1.272143	0.23
K	12.23200	-30.29785	2.309786	-4.086829	2.311473	0.13
Ru	7.494228	-21.40654	2.327975	-4.158040	2.371899	0.15
Cs	10.09811	-25.26335	2.109774	-3.601405	1.846914	0.17
			c) $\Omega_1^{(1,3)*}(T_1^*)$			
Li	1.828337	-9.054357	2.840996	-5.701037	0.8521955	0.22
Na	5.224332	-23.14067	2.725702	-6.367950	4.284772	0.27
K	9.513925	-31.21800	2.391396	-5.477656	3.871515	0.14
Ru	3.654676	-19.00137	2.389106	-5.550351	3.921720	0.18
Cs	7.474690	-25.70764	2.187178	-4.889873	3.234587	0.22
			d) $\Omega_1^{(2,2)*}(T_1^*)$			
Li	-2.650538	23.80728	2.100460	0.4879992	-3.929917	0.20
Na	-3.454700	26.63395	1.850960	0.2934780	-3.124283	0.13
K	0.6798244	15.25509	1.744732	-0.7737833	-0.7625710	0.15
Ru	13.55447	-17.31024	2.048434	-1.495705	-0.1425657	0.28
Cs	2.427715	8.738779	1.681272	-0.8506149	-0.5733677	0.18
			e) $\Omega_1^{(2,3)*}(T_1^*)$			
Li	-3.088718	27.79483	1.910291	2.093833	-10.01412	0.19
Na	-0.9001423	15.53608	1.919113	-0.0193895	-4.046381	0.21
K	20.16255	-40.61396	2.202697	-2.561157	0.0673081	0.20
Ru	33.41984	-74.01689	2.520579	-3.347017	1.317932	0.30
Cs	20.20223	-41.97838	2.094257	-2.443705	0.6469965	0.25

16.3 The vapor mixture

To a first approximation, the vapor phase of an alkali metal may be considered as a binary mixture of monomer and dimer species, whose molar fractions are dependent on both temperature and pressure. The viscosity of such a binary mixture with mole fractions y_M and y_D (subscripts M and D refer to monomer and dimer respectively) is well described by the first-order Chapman–Enskog theory (Hirschfelder *et al.* 1954;

Table 16.2. *Triplet potential parameters for equation (16.5) (Fialho et al. 1993).*

	$10 \cdot C_0$	C_1	$10 \cdot C_2$	$10^2 \cdot C_3$	$10^3 \cdot C_4$	$\frac{\sigma}{\%}$
a) $\Omega_3^{(1,1)*}(T_3^*)$						
Li	-2.590547	1.212185	-4.138669	-6.654710	2.191451	0.05
Na	-2.615505	1.153324	-4.081251	-4.666220	1.135139	0.12
K	-2.304266	1.080582	-3.733486	-4.534369	1.313487	0.03
Ru	-2.350945	1.084547	-3.758147	-4.233029	1.151050	0.02
Cs	-2.551676	1.120338	-3.980115	-3.541296	0.7348892	0.04
b) $\Omega_3^{(1,2)*}(T_3^*)$						
Li	-1.080536	0.8241279	-4.579437	-7.685941	2.444255	0.02
Na	-1.081520	0.7723458	-4.296703	-5.777638	1.521760	0.10
K	-0.8940780	0.7206854	-3.970009	-5.405562	1.574559	0.03
Ru	-0.8876363	0.7148743	-3.914575	-5.234619	1.515485	0.03
Cs	-0.8959670	0.7137547	-3.913260	-4.954174	1.404486	0.02
c) $\Omega_3^{(1,3)*}(T_3^*)$						
Li	-0.5811200	0.6083763	-4.603172	-9.596871	3.576178	0.003
Na	-0.7662706	0.6038852	-4.492843	-6.839778	1.977117	0.012
K	-0.5344234	0.5437907	-4.052455	-6.574065	2.169167	0.006
Ru	-0.5201589	0.5370695	-3.978914	-6.404623	2.119163	0.005
Cs	-0.5047070	0.5310475	-3.937206	-6.159051	2.045112	0.005
d) $\Omega_3^{(2,2)*}(T_3^*)$						
Li	-2.796898	1.269097	-3.320011	-3.717834	0.3520759	0.004
Na	-2.426747	1.146071	-2.949714	-3.053893	0.3819975	0.031
K	-2.385169	1.123730	-2.939140	-2.428154	0.1376324	0.015
Ru	-2.341062	1.111948	-2.884526	-2.360277	0.1359558	0.014
Cs	-2.281250	1.100439	-2.855358	-2.288036	0.1495502	0.011
e) $\Omega_3^{(2,3)*}(T_3^*)$						
Li	-1.199342	0.8934929	-3.101604	-5.165962	0.9138658	0.018
Na	-0.9349136	0.7934329	-2.684982	-4.358730	0.9132173	0.024
K	-0.8964713	0.7722816	-2.624224	-3.735935	0.7181930	0.026
Ru	-0.8768487	0.7648212	-2.579292	-3.621804	0.6904539	0.026
Cs	-0.8500697	0.7582051	-2.567246	-3.477965	0.6626365	0.025

Maitland *et al.* 1987; Chapter 4 of this volume)

$$[\eta_{\mathrm{mix}}]_1 = \frac{1 + Z_\eta}{X_\eta + Y_\eta} \tag{16.6}$$

with

$$X_\eta = \frac{y_{\mathrm{M}}^2}{[\eta_{\mathrm{M}}]_1} + \frac{2 y_{\mathrm{M}} y_{\mathrm{D}}}{[\eta_{\mathrm{MD}}]_1} + \frac{y_{\mathrm{D}}^2}{[\eta_D]_1} \tag{16.7}$$

$$Y_\eta = \frac{3}{5}A^*_{\mathrm{MD}}\left\{\frac{y_{\mathrm{M}}^2}{2[\eta_{\mathrm{M}}]_1} + \frac{9y_{\mathrm{M}}y_{\mathrm{D}}[\eta_{\mathrm{MD}}]_1}{4[\eta_{\mathrm{M}}]_1[\eta_{\mathrm{D}}]_1} + \frac{2y_{\mathrm{D}}^2}{[\eta_D]_1}\right\} \tag{16.8}$$

$$Z_\eta = \frac{3}{5}A^*_{\mathrm{MD}}\left\{\frac{y_{\mathrm{M}}^2}{2} + 2y_{\mathrm{M}}y_{\mathrm{D}}\left[\frac{9}{8}\left(\frac{[\eta_{\mathrm{MD}}]_1}{[\eta_{\mathrm{M}}]_1} + \frac{[\eta_{\mathrm{MD}}]_1}{[\eta_{\mathrm{D}}]_1}\right) - 1\right] + 2y_{\mathrm{D}}^2\right\} \tag{16.9}$$

where

$$A^*_{\mathrm{MD}} = \frac{\left\langle\Omega^{(2,2)}_{\mathrm{MD}}(T)\right\rangle}{\left\langle\Omega^{(1,1)}_{\mathrm{MD}}(T)\right\rangle} \tag{16.10}$$

and $[\eta_{\mathrm{M}}]_1$, $[\eta_{\mathrm{D}}]_1$ and $[\eta_{\mathrm{MD}}]_1$ are the first–order solutions for the viscosity coefficients of the monomer, the dimer and monomer-dimer interaction, given by the expressions

$$[\eta_{\mathrm{M}}]_1 = \frac{5}{16}(\pi m_{\mathrm{M}}k_{\mathrm{B}}T)^{1/2}\frac{1}{\bar{\Omega}^{(2,2)}_{\mathrm{M}}(T)} \tag{16.11}$$

$$[\eta_{\mathrm{D}}]_1 = \frac{5}{16}(\pi m_{\mathrm{D}}k_{\mathrm{B}}T)^{1/2}\frac{1}{\left\langle\Omega^{(2,2)}_{\mathrm{D}}(T)\right\rangle} \tag{16.12}$$

$$[\eta_{\mathrm{MD}}]_1 = \frac{5}{16}\left(\frac{2\pi m_{\mathrm{M}}m_{\mathrm{D}}k_{\mathrm{B}}T}{m_{\mathrm{M}} + m_{\mathrm{D}}}\right)^{1/2}\frac{1}{\left\langle\Omega^{(2,2)}_{\mathrm{MD}}(T)\right\rangle} \tag{16.13}$$

The quantity $\bar{\Omega}^{(2,2)}_{\mathrm{M}}(T)$ is the average collision integral for the monomer systems (equation (16.4)). The quantities $\left\langle\Omega^{(2,2)}_{\mathrm{D}}(T)\right\rangle$ and $\left\langle\Omega^{(2,2)}_{\mathrm{MD}}(T)\right\rangle$ appearing in equations (16.12) and (16.13) are angle–averaged collision integrals for the polyatomic interactions between monomer–dimer and dimer–dimer, respectively (Maitland *et al.* 1987). According to an approximate scheme originally proposed by Stogryn & Hirschfelder (1959), the thermal conductivity of a mixture of this kind can be assumed to be the sum of two contributions: a 'frozen' (nonreacting) coefficient, λ_{f}, and a chemical reaction coefficient, λ_{r}, associated with the transport of the energy involved in the formation of the dimers. The 'frozen' thermal conductivity is itself composed of a translational part, λ_{tr}, and an internal part, λ_{int}, due to the contribution of the internal degrees of freedom of the dimers. Therefore,

$$\lambda_{\mathrm{mix}} = \lambda_{\mathrm{tr}} + \lambda_{\mathrm{int}} + \lambda_{\mathrm{r}} \tag{16.14}$$

The translational contribution is assumed to be the same as that for a monatomic gas and thus can be obtained from the Chapman-Enskog theory of binary mixtures of monatomic species (Chapter 4)

$$[\lambda_{\mathrm{tr}}]_1 = \frac{1 + Z_\lambda}{X_\lambda + Y_\lambda} \tag{16.15}$$

with

$$X_\lambda = \frac{y_{\mathrm{M}}^2}{[\lambda_{\mathrm{M}}]_{1,\mathrm{tr}}} + \frac{2y_{\mathrm{M}}y_{\mathrm{D}}}{[\lambda_{\mathrm{MD}}]_{1,\mathrm{tr}}} + \frac{y_{\mathrm{D}}^2}{[\lambda_{\mathrm{D}}]_{1,\mathrm{tr}}} \tag{16.16}$$

$$Y_\lambda = \frac{y_{\mathrm{M}}^2}{[\lambda_{\mathrm{M}}]_{1,\mathrm{tr}}}U^{(1)} + \frac{2y_{\mathrm{M}}y_{\mathrm{D}}}{[\lambda_{\mathrm{MD}}]_{1,\mathrm{tr}}}U^{(y)} + \frac{y_{\mathrm{D}}^2}{[\lambda_{\mathrm{D}}]_{1,\mathrm{tr}}}U^{(2)} \tag{16.17}$$

$$Z_\lambda = y_{\mathrm{M}}^2 U^{(1)} + 2y_{\mathrm{M}}y_D U^{(z)} + y_{\mathrm{D}}^2 U^{(2)} \tag{16.18}$$

$$U^{(1)} = \frac{4}{15}A_{\mathrm{MD}}^* - \frac{1}{24}\left(\frac{12}{5}B_{\mathrm{MD}}^* + 1\right) + \frac{1}{4} \tag{16.19}$$

$$U^{(2)} = \frac{4}{15}A_{\mathrm{MD}}^* - \frac{1}{6}\left(\frac{12}{5}B_{\mathrm{MD}}^* + 1\right) + \frac{1}{4} \tag{16.20}$$

$$\begin{aligned} U^{(y)} = {} & \frac{3}{10}A_{\mathrm{MD}}^* \frac{[\lambda_{\mathrm{MD}}]_{1,\mathrm{tr}}^2}{[\lambda_{\mathrm{M}}]_{1,\mathrm{tr}}[\lambda_{\mathrm{D}}]_{1,\mathrm{tr}}} - \frac{1}{12}\left(\frac{12}{5}B_{\mathrm{MD}}^* + 1\right) \\ & - \frac{5}{64A_{\mathrm{MD}}^*}\left(\frac{12}{5}B_{\mathrm{MD}}^* - 5\right) \end{aligned} \tag{16.21}$$

$$U^{(z)} = \frac{4}{15}A_{\mathrm{MD}}^*\left[\frac{9}{8}\left(\frac{[\lambda_{\mathrm{MD}}]_{1,\mathrm{tr}}}{[\lambda_{\mathrm{M}}]_{1,\mathrm{tr}}} + \frac{[\lambda_{\mathrm{MD}}]_{1,\mathrm{tr}}}{[\lambda_{\mathrm{D}}]_{1,\mathrm{tr}}}\right) - 1\right] - \frac{1}{12}\left(\frac{12}{5}B_{\mathrm{MD}}^* + 1\right) \tag{16.22}$$

where

$$B_{\mathrm{MD}}^* = \frac{5\left\langle\Omega_{\mathrm{MD}}^{(1,2)}(T)\right\rangle - 4\left\langle\Omega_{\mathrm{MD}}^{(1,3)}(T)\right\rangle}{\left\langle\Omega_{\mathrm{MD}}^{(1,1)}(T)\right\rangle} \tag{16.23}$$

and $[\lambda_{\mathrm{M}}]_1$, $[\lambda_{\mathrm{D}}]_1$ and $[\lambda_{\mathrm{MD}}]_1$ are the first order solutions of the Chapman-Enskog theory for the monomer, dimer and monomer-dimer interaction thermal conductivity coefficients respectively

$$[\lambda_{\mathrm{M}}]_{1,\mathrm{tr}} = \frac{25}{32}\left(\frac{\pi k_{\mathrm{B}}T}{m_{\mathrm{M}}}\right)^{1/2}\frac{c_{V,\mathrm{tr}}}{\bar{\Omega}_{\mathrm{M}}^{(2,2)}(T)} \tag{16.24}$$

$$[\lambda_{\mathrm{D}}]_{1,\mathrm{tr}} = \frac{25}{32}\left(\frac{\pi k_{\mathrm{B}}T}{m_{\mathrm{D}}}\right)^{1/2}\frac{c_{V,\mathrm{tr}}}{\left\langle\Omega_{\mathrm{D}}^{(2,2)}(T)\right\rangle} \tag{16.25}$$

$$[\lambda_{\mathrm{MD}}]_{1,\mathrm{tr}} = \frac{25}{32}\left(\frac{\pi k_{\mathrm{B}}T\,(m_{\mathrm{M}} + m_{\mathrm{D}})}{2m_{\mathrm{M}}m_{\mathrm{D}}}\right)^{1/2}\frac{c_{V,\mathrm{tr}}}{\left\langle\Omega_{\mathrm{MD}}^{(2,2)}(T)\right\rangle} \tag{16.26}$$

where $c_{V,\mathrm{tr}} = 3k_{\mathrm{B}}/2$ is the translational contribution to the molecular heat capacity.

The dimer is a diatomic molecule and therefore has internal degrees of freedom that contribute to energy transfer, as explained in Chapter 4. In addition, it creates anisotropy in the intermolecular interaction with the monomer. Lacking information on the details of the internal molecular energy transfer in the dimers in order to employ more accurate theoretical expressions, one may use the approximate Eucken expression for λ_{int} (Stogryn & Hirschfelder 1959), which, for simple molecules, does not overestimate the value of this contribution by more than 3%

$$\lambda_{\text{int}} = \rho D_2 y_{\text{D}} C^{\text{id}}_{V,\text{D,int}} \tag{16.27}$$

with

$$D_2 = \left(\frac{y_{\text{D}}}{[D_{\text{D}}]_1} + \frac{y_{\text{M}}}{[D_{\text{MD}}]_1} \right)^{-1} \tag{16.28}$$

D_{D} and D_{MD} are the dimer self-diffusion coefficient and the binary diffusion coefficient of the gaseous mixture, respectively, given by

$$[D_{\text{D}}]_1 = \frac{3}{8P} \left(\frac{\pi k_{\text{B}}^3 T^3}{m_{\text{D}}} \right)^{1/2} \frac{1}{\left\langle \Omega_{\text{D}}^{(1,1)}(T) \right\rangle} \tag{16.29}$$

$$[D_{\text{MD}}]_1 = \frac{3}{16P} \left(\frac{\pi k_{\text{B}}^3 T^3 \, (m_{\text{M}} + m_{\text{D}})}{2 m_{\text{M}} m_{\text{D}}} \right)^{1/2} \frac{1}{\left\langle \Omega_{\text{MD}}^{(1,1)}(T) \right\rangle} \tag{16.30}$$

Here, ρ is the molar density of the mixture, $C^{\text{id}}_{V\text{D,int}}$ is the internal heat capacity at constant volume of the dimer, which for dilute gases is given by

$$C^{\text{id}}_{V,\text{D,int}} = C^{\text{id}}_{V,\text{D,rot}} + C^{\text{id}}_{V,\text{D,vib}} \tag{16.31}$$

$C^{\text{id}}_{V,\text{D,rot}}$ and $C^{\text{id}}_{V,\text{D,vib}}$ are the contributions of rotational and vibrational degrees of freedom, respectively, to the molar heat capacity at constant volume. The rotational contribution to the heat capacity can be considered classical, because $T \gg \theta_{\text{rot}}$, where θ_{rot} is the characteristic rotational temperature, and the dimer is assumed to be a rigid rotor – a hypothesis commensurate with the use of the Eucken approximation. Hence,

$$C^{\text{id}}_{V,\text{D,rot}} = R \tag{16.32}$$

The vibrational contribution can be calculated assuming that the vibration is that of a linear harmonic oscillator

$$C^{\text{id}}_{V,\text{D,vib}} = R \left(\frac{\theta_{\text{vib}}}{T} \right)^2 \frac{\exp\left(\theta_{\text{vib}}/T\right)}{\left[\exp\left(\theta_{\text{vib}}/T\right) - 1\right]^2} \tag{16.33}$$

where θ_{vib} is a characteristic vibrational temperature, given in Table 16.3 for each of the alkali metal dimers.

The vapor of the alkali metal is considered to be a chemical reacting mixture of monomers and dimers, in equilibrium

$$\text{M} \; + \; \text{M} \quad \rightleftharpoons \quad \text{D}$$

Table 16.3. *Spectroscopic values for the wavenumber and the characteristic vibrational temperature for the dimers of the alkali metals.*

Metal	$\frac{\tilde{\nu}_e}{\mathrm{cm}^{-1}}$	$\frac{\theta_{\mathrm{vib}}}{\mathrm{K}}$
Lithium	351.39	505.58
Sodium	159.11	228.93
Potassium	92.021	132.40
Rubidium	57.747	83.086
Cesium	42.0194	60.4571

It is well known that these vapors cannot be considered as ideal gases, as the second virial coefficients are different from zero, except in the case of cesium at high temperatures (Nieto de Castro *et al.* 1990). However, the quasi-chemical equilibrium hypothesis can be used that states that the imperfection has its origin in the atom association, and therefore the mixture of monomers and dimers can be considered a perfect gas mixture (Ewing *et al.* 1967). Assuming also local chemical equilibrium, Stogryn & Hirschfelder (1959) considered that the heat of reaction could affect the 'reactive' contribution and found that the chemical reaction component is given by

$$\lambda_{\mathrm{r}} = \rho\,[D_{\mathrm{MD}}]_1 \frac{\left(\Delta H^0(T)\right)^2 y_{\mathrm{M}} y_{\mathrm{D}}}{RT^2\,(1+y_{\mathrm{D}})^2} \tag{16.34}$$

where R is the universal gas constant and $\Delta H^0(T)$ is the standard enthalpy of reaction at temperature T. The viscosity coefficient can be calculated from equations (16.6)–(16.10). It is convenient to write it in a dimensionless form by dividing by $[\eta_{\mathrm{M}}]_1$, in which case equations (16.7)–(16.9) are rewritten in terms of the ratios

$$\beta_1^2 = \frac{\left\langle\Omega_{\mathrm{MD}}^{(2,2)}(T)\right\rangle}{\left\langle\Omega_{\mathrm{D}}^{(2,2)}(T)\right\rangle}, \quad \beta_{12}^2 = \frac{\left\langle\Omega_{\mathrm{MD}}^{(2,2)}(T)\right\rangle}{\bar{\Omega}_{\mathrm{M}}^{(2,2)}(T)}, \quad \beta_2^2 = \frac{\beta_{12}^2}{\beta_1^2} \tag{16.35}$$

Correspondingly, the thermal conductivity of the mixture can be rewritten in the dimensionless form

$$\lambda^*(y_{\mathrm{D}}, T) = \frac{[\lambda_{\mathrm{mix}}]_1}{[\lambda_{\mathrm{M}}]_1} = \lambda^*_{\mathrm{tr}}(y_{\mathrm{D}}) + \lambda^*_{\mathrm{int}}(y_{\mathrm{D}}, T) + \lambda^*_{\mathrm{r}}(y_{\mathrm{D}}, T) \tag{16.36}$$

The various contributions can be rearranged into the forms:

a) Translational:

The translational contribution is given by equation (16.15), reduced by $[\lambda_{\mathrm{M}}]_1$. Expressions (16.16)–(16.22) apply, and where ratios of thermal conductivities for different species occur, these are rewritten in terms of the ratios given by equation (16.35).

b) Internal:

$$\lambda_{\mathrm{int}}^{*} = \frac{2\sqrt{2}A_{\mathrm{D}}^{*}\left(C_{V,\mathrm{D,rot}}^{\mathrm{id}} + C_{V,\mathrm{D,vib}}^{\mathrm{id}}\right)}{25R\left(\beta_2^2 + \frac{\sqrt{2}A_{\mathrm{D}}^{*}y_{\mathrm{M}}}{\sqrt{3}A_{\mathrm{MD}}^{*}y_{\mathrm{D}}}\beta_{12}^2\right)} \tag{16.37}$$

c) Chemical Reaction:

$$\lambda_{\mathrm{r}}^{*} = \frac{2\sqrt{3}}{25}A_{\mathrm{MD}}^{*}\left(\frac{\Delta H^0(T)}{RT}\right)^2 \frac{y_{\mathrm{M}}y_{\mathrm{D}}}{(1+y_{\mathrm{D}})^2}\beta_{12}^{-2} \tag{16.38}$$

The prediction of the viscosity and thermal conductivity coefficients of the mixtures on purely theoretical grounds is not possible at present, as the interaction viscosity, η_{MD}, thermal conductivity, λ_{MD}, and the ratios of collision integrals, A_{MD}^{*} and B_{MD}^{*}, cannot be theoretically evaluated in the absence of reliable pair potentials for the monomer-dimer interactions. Similarly, the 'pure' dimer viscosity, η_{D}, and thermal conductivity, λ_{D}, cannot be determined either experimentally or theoretically, without resort to an accurate pair potential for the dimer-dimer interaction.

However, a data assessment procedure based on the above model is devisable, which is endowed with a fairly sound theoretical basis. Testing the compliance of the data and the mutual consistency of viscosity and thermal conductivity to the outlined model needs the establishment of a practical procedure. Namely, the collision integrals, or rather their ratios, involving the dimer species will have to be calculated by fitting the model expressions to the experimental data. For this purpose, some further simplifications of the model were necessary:

(i) the ratios A_{MD}^{*}, B_{MD}^{*} are taken as independent of the type of interaction, and calculated by replacing the ratio of collision integrals in (16.10) and (16.23) by the corresponding monomer-monomer collision integrals, such that $A_{\mathrm{MD}}^{*} = A_{\mathrm{M}}^{*} = A_{\mathrm{D}}^{*}$ and $B_{\mathrm{MD}}^{*} = B_{\mathrm{M}}^{*} = B_{\mathrm{D}}^{*}$. This approximation is supported by the well-known result that these ratios are weakly dependent on the intermolecular pair potential for spherical models.

(ii) the parameters β_i^2 (where $i = 1,\ 2,\ 12$) were assumed to be temperature-independent, as proposed by Vargaftik & Yargin (1985). This is probably the most questionable approximation at the moment, but the unavailability of information about the interaction M-D makes it necessary.

In spite of these assumptions, one cannot proceed without the use of some experimental information. Most of the published data on the viscosity and thermal conductivity of the alkali metal vapors are collected in the works of Vargaftik & Yargin (1985) and Fialho *et al.* (1993). It has been shown that the viscosity and the thermal conductivity data must be treated on different grounds, because of the much higher theoretical complexity and measurement difficulty of the latter. In particular, a poorer precision and, especially, a much higher level of corrections to the raw data, affecting the accuracy of the results, are found for the thermal conductivity, when compared to the viscosity measurements. In order to make the best use of the minimum necessary experimental information on the collision integral ratios, Fialho *et al.* (1993) applied the following procedure to each viscosity data set:

(i) for each datum at a certain temperature and pressure, the monatomic viscosity, $[\eta_M]_1$, has been calculated, using the equations described in Section 16.2,

(ii) the respective dimer mole fractions have been calculated using the values published by Vargaftik & Yargin (1985). Interpolation between those values was performed using the fitting equation

$$\ln\left(K_d'\right) = \ln\left(\frac{y_M^2 P}{y_D P^0}\right) = E - \frac{\Delta H_0^0}{RT} + \frac{A}{R}\ln(T) + \frac{B}{R}T + \frac{C}{2R}T^2 + \cdots \tag{16.39}$$

where P is the pressure, P^0 is the standard state reference pressure ($P^0 = 0.1$ MPa), $y_M \approx 1 - y_D$ is the monomer mole fraction, and the coefficients A, B, C and E are fitting coefficients (Table 16.4); ΔH_0^0 is the standard enthalpy of formation of the dimer at 0 K (Vargaftik & Voljak 1985), whose values are tabulated in Table 16.5. The calculated values for y_D and y_M are dependent on

Table 16.4. *Parameters necessary for the use of equation (16.39). Limits of validity of the parameters in the temperature range. Pressures should be less than 1.0* MPa.

Metal	$\frac{T}{\text{K}}$	$\frac{A}{\text{J mol}^{-1}\text{K}^{-1}}$	$\frac{B}{\text{J mol}^{-1}\text{K}^{-2}}$	$\frac{10^6 \cdot C}{\text{J mol}^{-1}\text{K}^{-3}}$	$10^{-1} \cdot E$
Lithium	1200 – 2000	9.945835	-6.634476	1.864750	1.355096
Sodium	800 – 1300	7.711819	-5.631470	1.652149	1.492893
Potassium	800 – 1900	3.939518	-1.732501	1.804059	1.686225
Rubidium	700 – 1200	6.502770	-6.845959	4.091932	1.504084
Cesium	800 – 1200	5.557522	-5.990512	4.135396	1.545305

Table 16.5. *Ionization energy and dissociation enthalpy for the alkali metals (Vargaftik & Voljak 1985).*

Metal	$\frac{10^{-4} \cdot I/k_B}{\text{K}}$	$\frac{\Delta H_0^0}{\text{kJ mol}^{-1}}$
Lithium	6.256	107.8
Sodium	5.964	71.38
Potassium	5.036	53.8
Rubidium	4.847	48.57
Cesium	4.514	44.38

the validity of the assumptions made by Vargaftik & Voljak (1985), namely, that the systems behave as a perfect gas mixture, and that the ionization of the atomic species is comparatively of no practical consequence in the temperature ranges covered by the data. This can be shown by using the result of Vargaftik & Voljak (1985) for the equilibrium constant K_e for the ionization process

$$K_e = 3.33 \cdot 10^{-7} T^{5/2} \exp(-I/k_{\mathrm{B}}T) \tag{16.40}$$

where I is the ionization energy (see Table 16.5). For the present calculations, the maximum error due to ionization is of the order of 0.15% of y_{D}.

(iii) The 'best values' of β_1^2 and β_{12}^2 were calculated by a nonlinear multiparametric fitting procedure to the whole set of data, using the Marquard method (Press *et al.* 1986). For the purpose of calculating β_1^2 and β_{12}^2, the experimental data are expressed as the relative deviation from the corresponding monomer property

$$\frac{\Delta\eta}{[\eta_{\mathrm{M}}]_1} = \frac{\eta_{\mathrm{exp}}(y_{\mathrm{D}}, T) - [\eta_{\mathrm{M}}]_1}{[\eta_{\mathrm{M}}]_1} \tag{16.41}$$

which is a function of β_1^2 and β_{12}^2. These parameters have been determined for each data set.

This model, which is a modification of the procedure adopted by Vargaftik & Yargin (1985), in order to apply the kinetic theory for binary reacting mixtures of gases to the study of alkali metal vapors, will herewith be referred to as Modified Vargaftik and Yargin Approximation (MVYA). The viscosity data were analyzed and used to calculate those parameters, which were impossible to evaluate theoretically. The procedure is illustrated here with sodium vapor.

The available data for the viscosity coefficients of sodium vapor are plotted in the form of deviations from the monomer viscosities versus the corresponding dimer mole fractions in Figure 16.2. Data giving rise to positive deviations greater than the nominal precision of the experimental method have been discarded from the analysis, as the presence of dimers decreases the viscosity of the mixture in comparison with the monomer. The quality of the data was primarily assessed by testing their compliance to the model. Subsequently the highest–quality data sets for each were selected according to that criterion. The best parameters selected are shown in Table 16.6. In case of doubt, the data obtained with the more precise experimental method have been selected. Details of the discussion can be found in the work of Fialho *et al.* (1994a,b). It was not possible to optimize the fits for cesium, because both sets of data available are in mutual disagreement, deviating from the MVYA approximation; therefore this metal is excluded from the present analysis.

The deviations between the experimental data for the viscosity of sodium vapor and values calculated using the MVYA model as a function of the dimer mole fraction are presented in Figure 16.3. In this figure, Stefanov *et al.* (1966) data are in good agreement at low dimer fractions and deviate by almost −15% at a dimer mole fraction of 0.1.

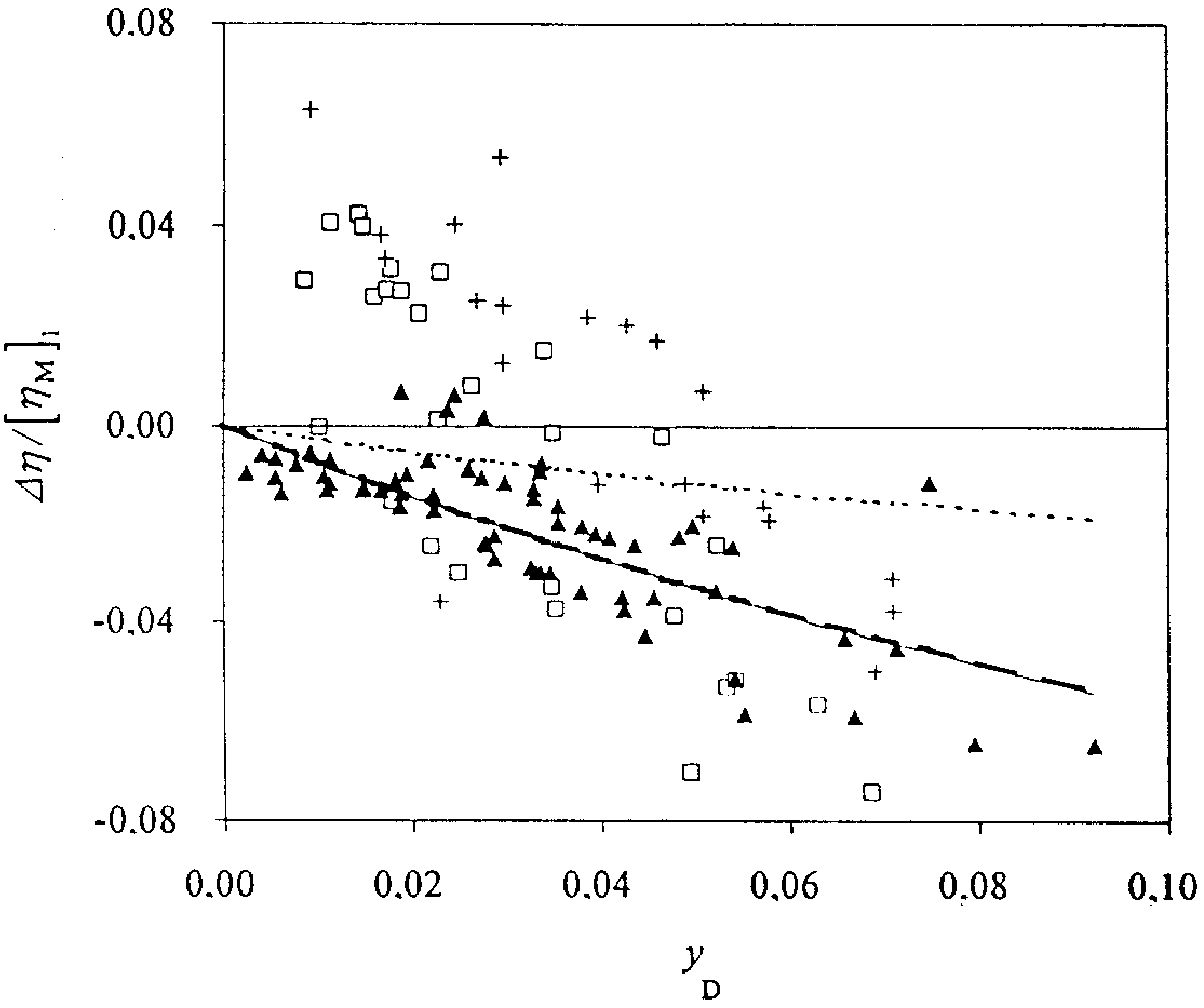

Fig. 16.2. Deviations from the monomeric behavior for the viscosity of the vapor of sodium. The symbols represent the experimental data and the lines correspond to the fitting of the MVYA model. □, - - - annular gap, Vargaftik *et al.* (1992). +, · · · falling body, Vargaftik & Yargin (1985). ▲, —— oscillating disc, Timrot & Varava (1977).

Table 16.6. *Parameters obtained by the best fit to the viscosity data, of the alkali metal vapors available in the literature, to the model MVYA (Fialho et al. 1994a).*

Metal	Ref.	β_1^2	β_{12}^2
Lithium	Stepanenko *et al.* (1986)	1.19±0.04	1.42±0.02
Sodium	Timrot & Varava (1977)	0.87±0.02	1.092±0.008
Potassium	Stefanov *et al.* (1966), Vargaftik *et al.* (1975)	1.18±0.05	1.64±0.02
Rubidium	Sidorov *et al.* (1975)	1.3±0.2	1.48±0.06

The data obtained with higher–precision techniques, namely, oscillating disc (Timrot & Varava 1977) and concentric cylinders (Vargaftik *et al.* 1992) used to determine β_1^2 and β_{12}^2, agree well with the prediction, within the claimed uncertainties.

The assessment of the thermal conductivity data was performed, comparing the experimental values with the results calculated through the model equations using the values of β_1^2 and β_{12}^2, obtained from the selected viscosity data, and the spectroscopic

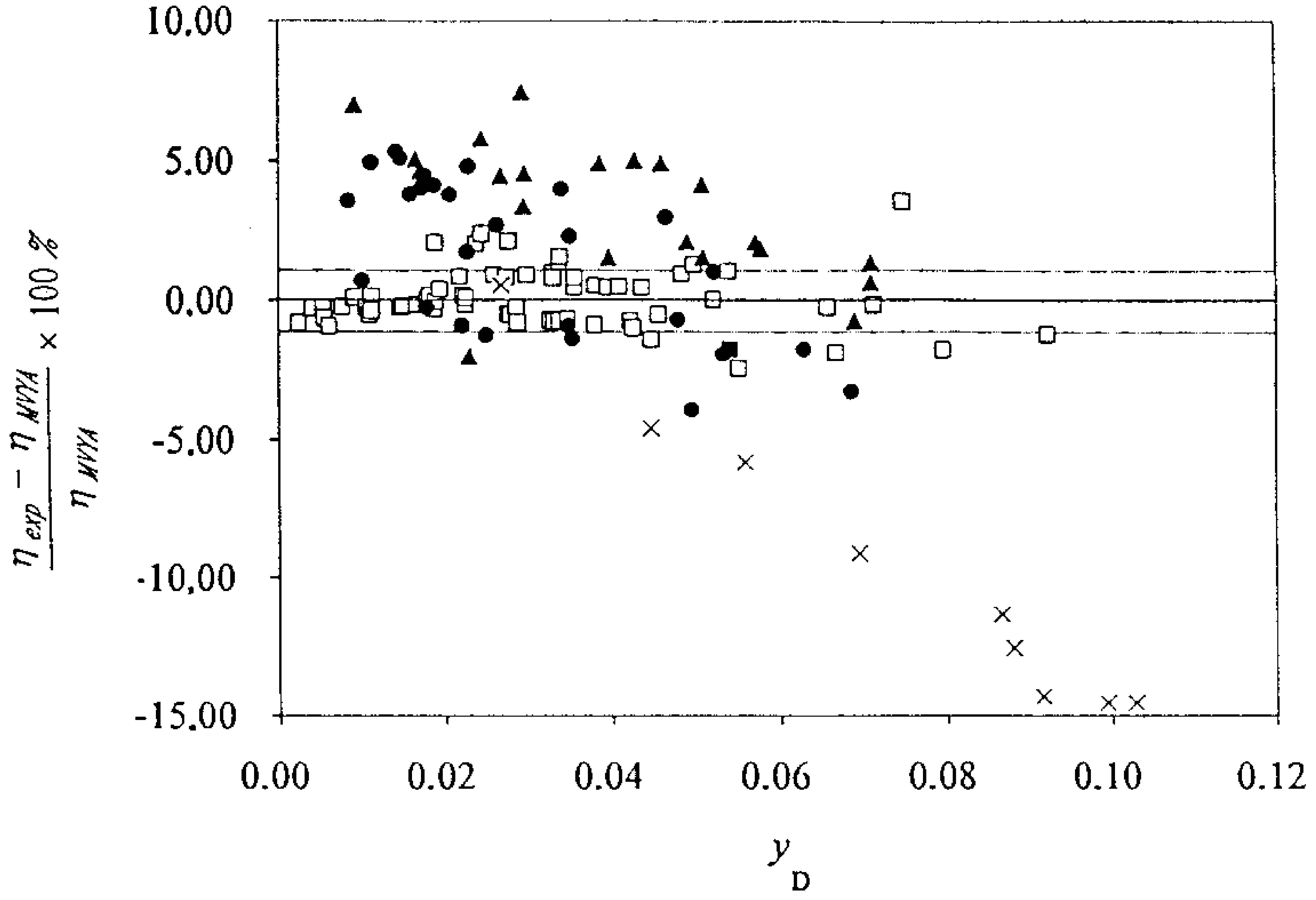

Fig. 16.3. Deviations between the experimental data and the model for the viscosity of sodium. The parameters used in the model were taken from the viscosity data of Timrot & Varava (1977). The dotted lines (+1.1 and -1.1 %) represent the claimed experimental accuracy. □ - oscillating disc, Timrot & Varava (1977). ▲ - falling body, Vargaftik & Yargin (1985). x - capillary tube, Stefanov *et al.* (1966). ● - annular gap, Vargaftik *et al.* (1992).

information collected in Tables 16.3 and 16.5. As for viscosity the thermal conductivity results are expressed as deviations from the monomer properties, in the form

$$\frac{\Delta\lambda}{[\lambda_M]_1} = \frac{\lambda_{exp}(y_D, T) - [\lambda_M]_1}{[\lambda_M]_1} \qquad (16.42)$$

A comparison of the thermal conductivity data with the model predictions, using the selected β_{12}^2 and β_1^2 parameters for sodium, is presented in Figure 16.4.

This figure shows that the deviations from the data obtained by Vargaftik & Voshchinin (1967) agree well with the predictions within the mutual uncertainties involved in the comparison. Higher positive deviations are found for the data published with the steady-state hot-wire technique by Timrot *et al.* (1976), especially for low y_D. The results obtained by Timrot & Totskii (1967) show large systematic discrepancies with the present model. However, it should be noted that, despite the systematic deviations found for the latter data, and its large scatter (±10%), the variation with the dimer concentration does not differ substantially from the one predicted by this model. Applying the model previously described (MVYA) with the parameters defined in Tables 16.3 to 16.6, the transport property surfaces for lithium, sodium and potassium can be generated (Fialho *et al.* 1994a,b).

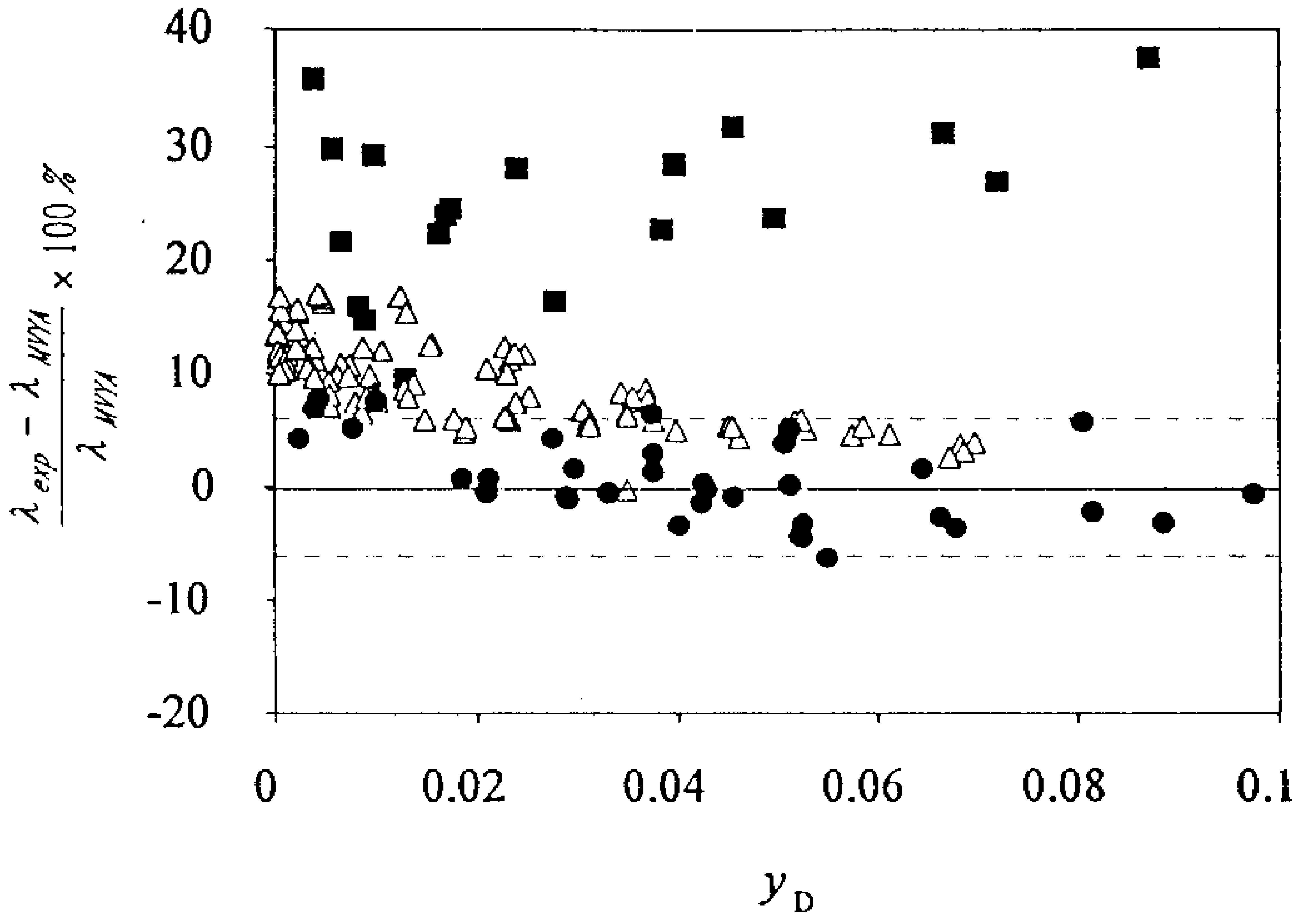

Fig. 16.4. Deviations between the experimental data and the model for the thermal conductivity of sodium. The parameters used in the model were taken from the viscosity data of Timrot & Varava (1977). The dotted lines (+6% and −6%) represent the claimed experimental accuracy. ■ - steady–state concentric cylinders, Timrot & Totskii (1967). △ - steady–state hot wire, Timrot *et al.* (1976). ● - steady–state concentric cylinders, Vargaftik & Voshchinin (1967).

16.4 Conclusions

The preceding sections have shown how it is possible to use the available kinetic theory of low–density reacting binary mixtures to calculate the viscosity and thermal conductivity of the alkali metal vapors. The model can also be applied to the binary diffusion coefficient in the mixture. It can be easily shown that, for this model, the ratio $[\mathcal{D}_{\mathrm{MD}}]_1 / [\mathcal{D}_{\mathrm{M}}]_1 = \sqrt{3}\beta_{12}^{-2}/2$. This result says that the density and temperature dependence of both diffusion coefficients is the same. From the results of the self–diffusion coefficient of the monomer reported by Fialho *et al.* (1993) and the value of β_{12}^{-2} from Table 16.6, the binary diffusion coefficient can be obtained. It is also possible on the basis of this model to verify the internal consistency of all the experimental information available on the transport properties of these vapors and to select precise data and propose accuracy classes (Fialho *et al.* 1994). The results obtained suggest that there is still a lot to be done on the experimental measurement of thermal conductivity of these vapors, where radiation effects at high temperatures play a significant role, most of the time difficult to estimate (Wakeham *et al.* 1991). The data selected can be used to produce a consistent set of transport property tables for the alkali metal vapors, lithium, sodium and potassium, with a confidence level commensurate with the uncertainty of the selected data. This work was performed by the authors and will be the subject of a future publication. For the case of rubidium it is still possible to produce such tables, but with a decrease in the confidence level. For cesium it was not possible to construct such tables (Fialho *et al.* 1994a,b). In order to illustrate the applications presented in this chapter, a small sample of the tables is shown in the Appendix below (Table 16.7).

Appendix

Table 16.7. *Calculated values for the viscosity and thermal conductivity for sodium vapor using the MVYA model (Fialho 1993).*

$\frac{T}{\mathrm{K}}$	$\frac{\eta_M}{\mu\mathrm{Pa\,s}}$	$P = 1$ kPa	$P = 10$ kPa	$P = 100$ kPa	$P = 1000$ kPa
900	18.18	18.00			
1000	19.80	19.72	19.18		
1200	22.91	22.89	22.73	21.64	
1500	27.39	27.38	27.34	26.91	25.07
$\frac{T}{\mathrm{K}}$	$\frac{\lambda_M}{\mathrm{mW\,m^{-1}K^{-1}}}$	$P = 1$ kPa	$P = 10$ kPa	$P = 100$ kPa	$P = 1000$ kPa
900	24.66	28.93			
1000	26.86	28.31	38.57		
1200	31.08	31.35	33.60	47.50	
1500	37.15	37.20	37.60	41.19	55.35

References

Davies, R. H., Mason, E. A. & Munn, R. J. (1965). High temperature transport properties of alkali metal vapours. *Phys. Fluids*, **8**, 444–452.

Ewing, C. T., Stone, J. P., Spann, J. R. & Miller, R. R. (1967). Molecular association in sodium, potassium and cesium vapors at high temperature. *J. Phys. Chem.*, **71**, 473–477.

Fialho, P. S. (1993). *Propriedades Termofísicas de Fluidos. Sua Previsão, Estimativa e Correlação.* Ph.D. thesis, Faculty of Sciences, University of Lisbon, Portugal.

Fialho, P. S., Fareleira, J. M. N. A., Ramires, M. L. V. & Nieto de Castro, C. A. (1993). The thermophysical properties of alkali metal vapours. Part IA - Prediction and correlation of transport properties for monatomic systems. *Ber. Bunsenges. Phys. Chem.*, **97**, 1487–1492.

Fialho, P. S., Ramires, M. L. V., Fareleira, J. M. N. A. & Nieto de Castro, C. A. (1994b). Viscosity, thermal conductivity and thermal diffusion ratio of the alkali metal vapours, in *Thermal Conductivity 22*, ed. T. W. Tong, Lancaster, USA: Technomic Pubs. Co., 126–135.

Fialho, P. S., Ramires, M. L. V., Nieto de Castro, C. A., Fareleira, J. M. N. A. & Mardolcar, U. V. (1994a). The thermophysical properties of alkali metal vapours. Part II - Assessment of experimental data on thermal conductivity and viscosity. *Ber. Bunsenges. Phys. Chem.*, **98**, 92–102.

Hirschfelder, J.O., Curtiss, C. F. & Bird, R.B. (1954). *Molecular Theory of Gases and Liquids.* New York: John Wiley & Sons.

Holland, P. N. & Biosi, L. (1987). Calculation of the transport properties of ground state sodium atoms. *J. Chem. Phys.*, **87**, 1261–1266.

Holland, P. N., Biosi, L. & Rainwater, J. C. (1986). Theoretical calculations of the transport properties of monatomic lithium vapor. *J. Chem. Phys.*, **85**, 4011–4018.

Maitland, G.C., Rigby, M., Smith E.B. & Wakeham, W.A. (1987). *Intermolecular Forces: Their Origin and Determination*. Oxford: Clarendon Press.

Mies, F. H. & Julienne, P. S. (1982). The thermodynamic properties of diatomic molecules at elevated temperatures: Role of continuum and metastable states. *J. Chem. Phys.*, **77**, 6162–6176.

Nieto de Castro, C.A., Fareleira, J.M.N.A., Ramires, M.L.V., Canelas Pais, A.A.C. & Varandas, A.J.C. (1990). The thermophysical properties of alkali metal vapours. Part I - Theoretical calculation of the properties of monatomic systems. *Ber. Bunsenges. Phys. Chem.*, **94**, 53–59.

Ohse, R. W. (Ed.). (1985). *IUPAC Handbook of Thermodynamic and Transport Properties of Alkali Metals*. Oxford: Blackwell Scientific Publications.

Polishchuk, A. J., Sphilrain, E. E. & Yacubov, I. T. (1980). Thermal conductivity and viscosity of lithium vapours. *J. Eng. Phys.*, **38**, 247–250.

Press, W. H., Flannery, S. A., Teukolvsky, S. A. & Vetterling, W. T. (1986). *Numerical Recipes. The Art of Scientific Computing*. Cambridge: University Press.

Sannigrahi, A. B., Mohammed, S. N. & Mookhejee, D. C. (1976). Second virial coefficients of alkali vapours. *Mol. Phys.*, **31**, 963–970.

Sidorov, N. I., Tarkalov, Y. V. & Yargin, Y. S. (1975). *Izv. VUZOV. Energetica*, **4**, 96–101, quoted in Vargaftik, V. B. & Yargin, V. S. (1985).

Sinanoglu, O. & Pitzer, K. S. (1959). Equation of state and thermodynamic properties of gases at high temperatures I. Diatomic molecules. *J. Chem. Phys.*, **31**, 960–967.

Stefanov, B. (1980). Generalisation of thermal conductivity and viscosity data for monatomic alkali metal vapours. *High Temp.-High Press.*, **12**, 189–194.

Stefanov, B. I., Timrot, D. L., Totskii, E. E. & When-Hao, C. (1966). Viscosity and thermal conductivity of the vapours of sodium and potassium. *Teplofiz. Vys. Temp.*, **4**, 141–142.

Stepanenko, I. F., Sidorov, N. I., Tarkalov, Y. V. & Yargin, V. S. (1986). Experimental study of the viscosity of lithium vapour at high temperatures. *Int. J. Thermophys.*, **7**, 829–835.

Stogryn, D. E. & Hirschfelder, J. O. (1959). Initial pressure dependence of thermal conductivity and viscosity. *J. Chem. Phys.*, **31**, 1545–1554.

Timrot, D. L., Makhrov, V. V. & Sviridenko, V. I. (1976). Method of the heated filament (incorporating a new section) for use in corrosive media, and determination of the thermal conductivity of sodium vapour. *Teplofiz. Vys. Temp.*, **14**, 67–94.

Timrot, D. L. & Totskii, E. E. (1967). Measurements of the thermal conductivity of sodium and potassium vapours as a function of temperature and pressure. *Teplofiz. Vys. Temp.*, **5**, 793–801.

Timrot, D. L. & Varava, A. N. (1977). Experimental investigation of the viscosity of sodium vapors. *Teplofiz. Vys. Temp.*, **15**, 750–757.

Varandas, A. J. C. (1980). Hybrid potential function for bound diatomic molecules. *J. Chem. Soc. Faraday Trans. II*, **76**, 129–135.

Varandas, A. J. C. & Brandaõ, J. (1982). A simple semiempirical approach to the intermolecular potential of van der Waals systems I. Isotropic interactions: Application to the lowest triplet state of the alkali dimers. *Mol. Phys.*, **45**, 857–875.

Varandas, A. J. C. & Dias da Silva, J. (1986). Hartree-Fock approximate correlation energy (HFACE) potential for diatomic interactions. Molecules and van der Waals molecules. *J.Chem. Soc. Faraday Trans. II*, **82**, 593–608.

Varandas, A. J. C. & Dias da Silva, J. (1992). Potential model for diatomic molecules including the United-Atom Limit, and its use in a multiproperty fit for argon. *J. Chem. Soc. Faraday Trans.*, **88**, 941–954.

Vargaftik, V. B., Vinogradov, Y. K., Dolgov, V. I., Dzis, V. G., Stepanenko, I. F., Yakimovitch, Y. K. & Yargin, V. S. (1992). Viscosity and thermal conductivity of alkali metal vapours at temperatures up to 2000 K. *Int. J. Thermophys.*, **12**, 85–103.

Vargaftik, V. B. & Voljak, L. D. (1985). Thermodynamic properties of alkali metal vapours at low pressures. Chapter 7.6.6.1 of *IUPAC Handbook of Thermodynamic and Transport Properties of Alkali Metals*, ed. R. W. Ohse. Oxford: Blackwell Scientific Pubblications.

Vargaftik, V. B. & Voshchinin, A. A. (1967). Experimental study of the thermal conductivity of sodium and potassium as vapours. *Teplofiz. Vys. Temp.*, **5**, 802–811.

Vargaftik, N. B., Sidorov, N. I., Tarkalov, Y. V. & Yargin, V. S. (1975). Viscosity of potassium vapour. (Russ.). *Teplofiz. Vys. Temp.*, **13**, 974–978.

Vargaftik, V. B. & Yargin, V. S. (1985). Thermal conductivity and viscosity of the gaseous phase. Chapter 7.4 of *IUPAC Handbook of Thermodynamic and Transport Properties of Alkali Metals*, ed. R. W. Ohse. Oxford: Blackwell Scientific Publications.

Wakeham, W. A., Nagashima, A. & Sengers, J. V. (Eds.). (1991). *Measurement of the Transport Properties of Fluids*. Oxford: Blackwell Scientific Publications.