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Dilute-Gas Properties of the Monatomic Gases and Their Mixtures from the MSK Potential

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The three-parameter MSK potential is used to calculate the dilute-gas properties of the monatomic gases and their mixtures. The parameters are fitted to data of the second virial coefficient and the Joule–Thomson coefficient; the calculations of all other thermophysical properties are predictions. For mixtures, universal combination rules for the potential parameters are used. It is shown that a consistent representation of the gas data of the monatomic systems is possible.

KEY WORDS: dilute gas; mixtures; pair potentials; statistical mechanics.

1. INTRODUCTION

In a recent publication [1], we proposed a new pair potential for gaseous and liquid argon. It is based on the Maitland–Smith form [2], extended by a spherical hard core in the spirit of Kihara [3] and, therefore, referred to as the MSK potential. When determining the three adjustable parameters of this potential from a consistent set of data for the second virial coefficient and the Joule–Thomson coefficient, it was possible to predict the dilute-gas viscosity and, after adding three-body dispersion forces, the third virial coefficient of argon essentially within their experimental inaccuracy [1]. In view of this remarkable success for argon, it was decided to apply the new MSK potential to other monatomic gases as well. In this paper, we report the results for the dilute-gas properties of the monatomic gases and their mixtures. The purpose is to show that using an adequate potential model with only three parameters permits the prediction of some ther-

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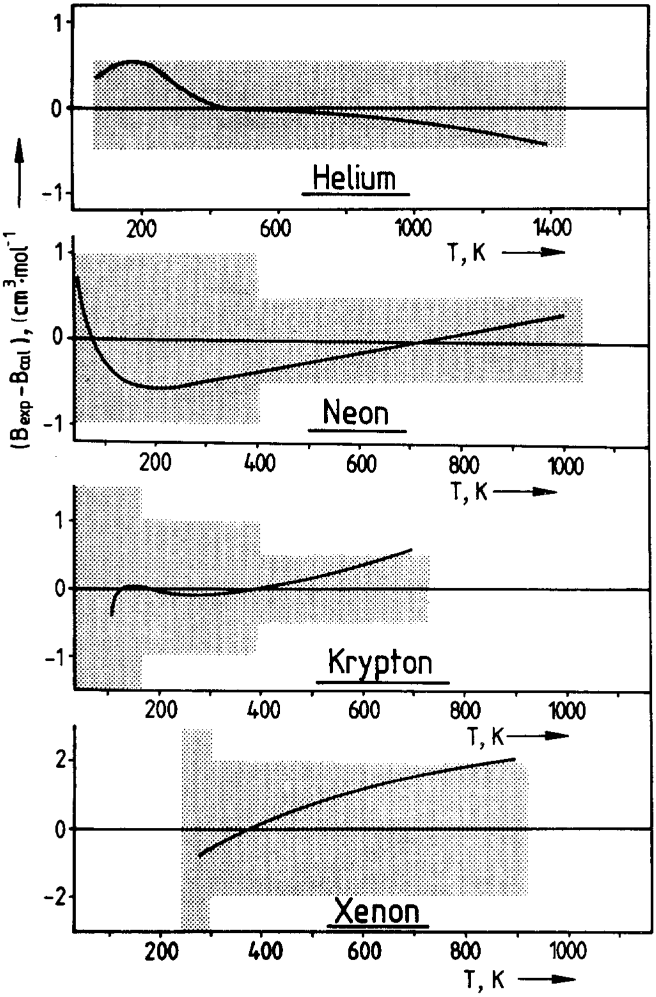

Fig. 1. Deviation plot of experimental second virial coefficients for helium, neon, krypton, and xenon. Data: Ne recommended values of Dymond and Smith [8]; He, Kr, and Xe [9].

mophysical properties from others, while the addition of some simple and universal mixing rules yields acceptable predictions of mixture properties from those of pure components.

2. POTENTIAL MODEL FOR LIKE AND UNLIKE INTERACTIONS

The MSK potential has the following form:

$$\phi(r) = \frac{6}{n-6}\,\varepsilon\left[\left(\frac{r_m - d}{r-d}\right)^n - \frac{n}{n-6}\left(\frac{r_m - d}{r-d}\right)^6\right] \tag{1}$$

with

$$n = 12 + 5\left(\frac{r}{r_m} - \frac{d}{r_m} - 1\right) \tag{2}$$

It contains three adjustable parameters, i.e., the depth of the potential ε, the associated distance between the atoms r_m, and the hard spherical core

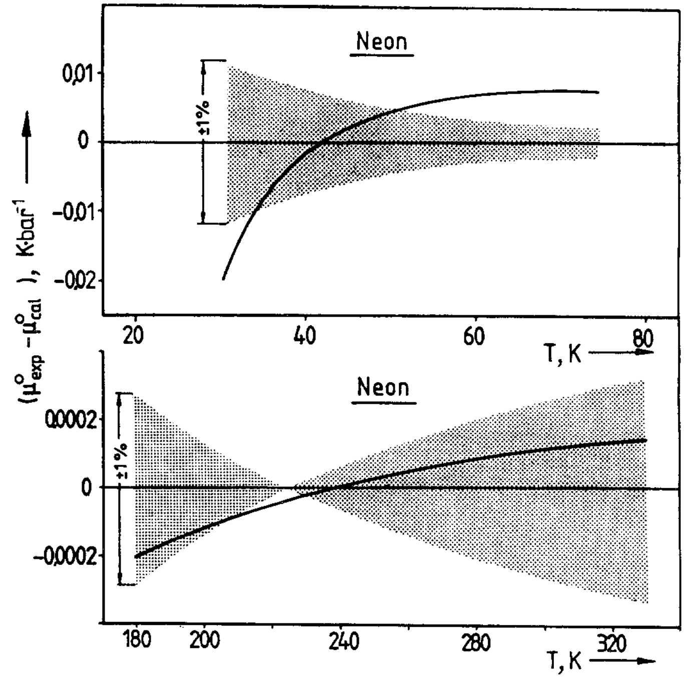

Fig. 2. Deviation plot of experimental Joule–Thomson coefficients for neon. Data: Ne [10, 11].

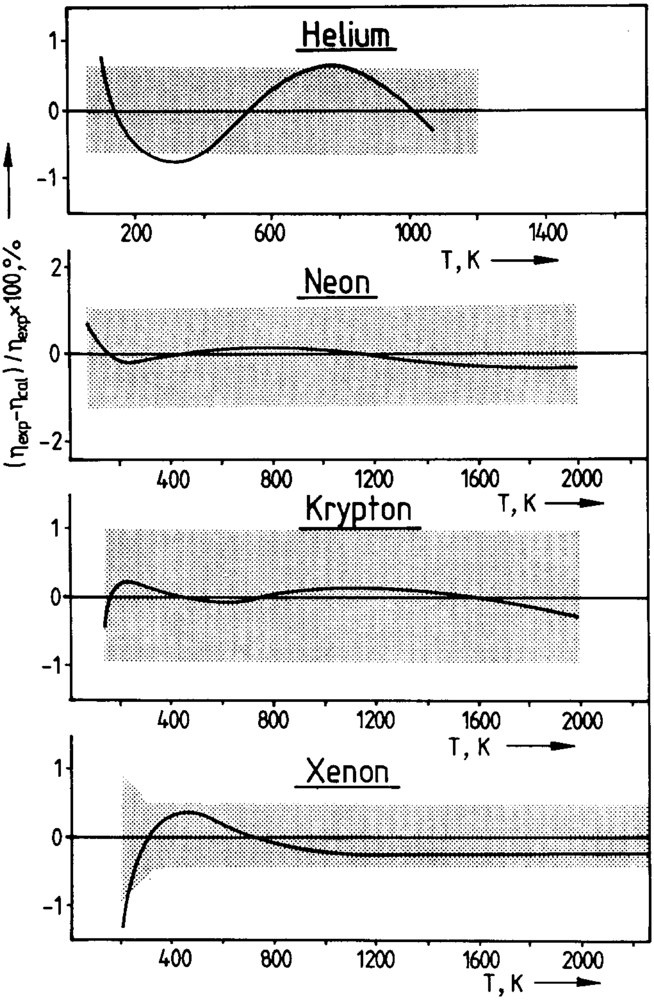

Fig. 3. Percentage deviation plot of experimental dilute gas viscosity coefficients of helium, neon, krypton, and xenon compared to theoretical values. Data: Ne and Kr [12]; He and XE [13].

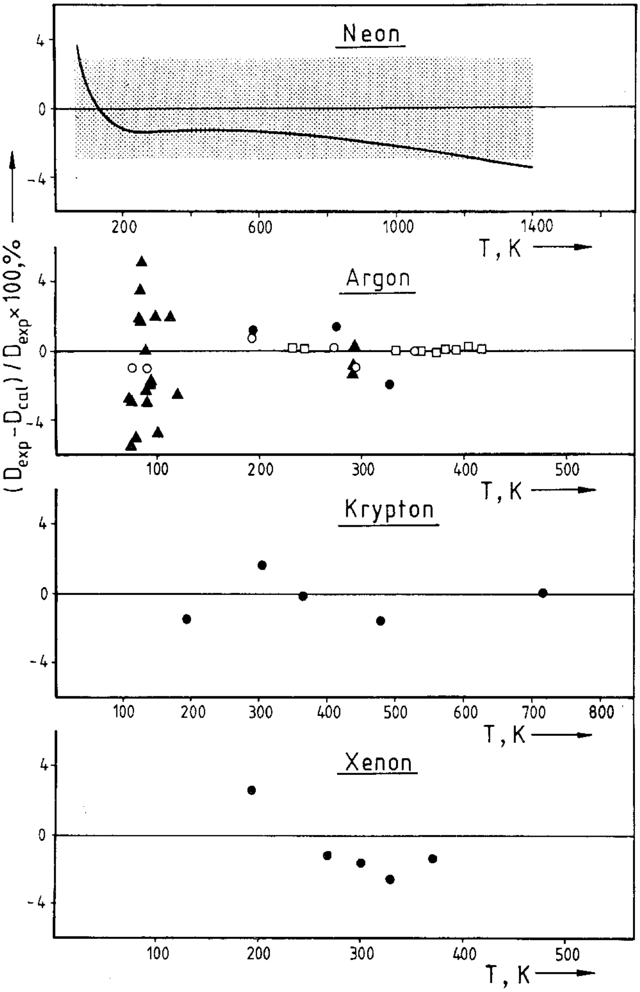

Fig. 4. Percentage deviation plot of experimental self-diffusion coefficients of neon, argon, krypton, and xenon. Data: Ne [14]; Ar (▲) [15], (●) [16], (○) [17], (□) [18] [Note: The data from Ref. 18 are relative to D at 298.15 K. We correlated the other experimental self-diffusion coefficients and used the value $D_{11}(T=298.15\text{ K})=0.183\text{ cm}^2\cdot\text{s}^{-1}$ for this reference point]; Kr [19]; Xe [20].

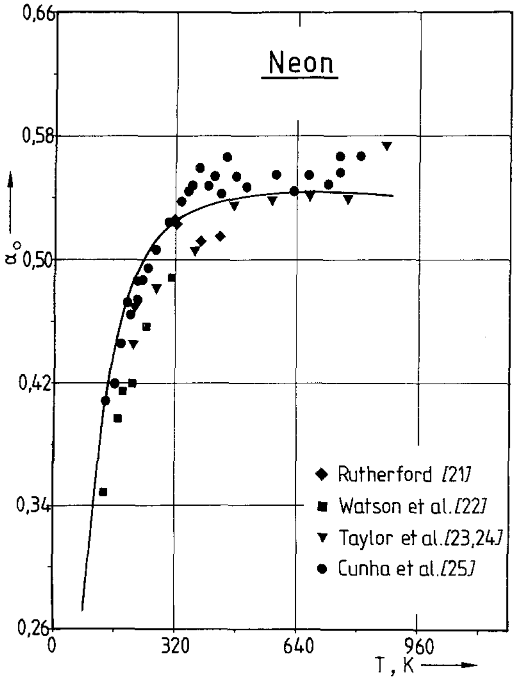

Fig. 5. Experimental and theoretical thermal diffusion factors for neon.

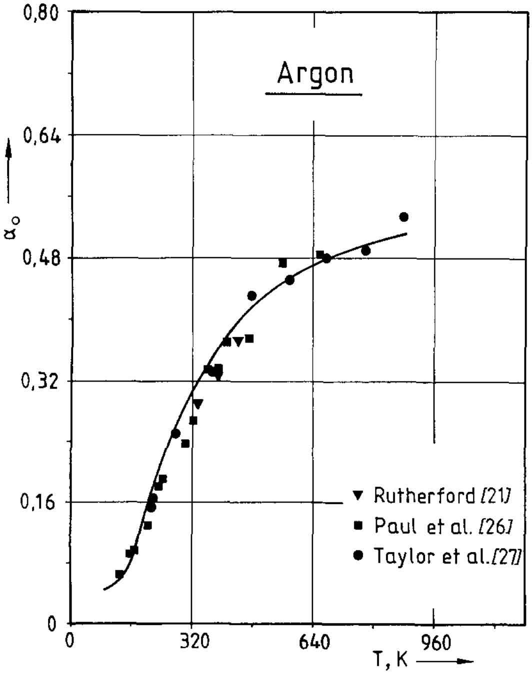

Fig. 6. Experimental and theoretical thermal diffusion factors for argon.

diameter *d*. It has been suggested [4] to use a consistent set of data for the second virial coefficient and the Joule–Thomson coefficient to determine the parameters of a pair potential. We have followed this suggestion in Ref. 1 for argon with very good results. In this paper, we determined the parameters for neon by the same manner. For krypton, xenon, and helium no Joule–Thomson coefficients were available, so we used the dilute-gas viscosity instead.

Since we wish to predict the properties of the gas mixtures, we need combination rules for the potential parameters. For $\varepsilon_{\alpha\beta}\sigma_{\alpha\beta}^6$ we use a combination rule emerging from the London theory of dispersion interactions when applied to a Lennard–Jones potential:

$$\varepsilon_{\alpha\beta}\sigma_{\alpha\beta}^6 = \frac{2(\varepsilon_{\alpha\alpha}\sigma_{\alpha\alpha}^6)(\varepsilon_{\beta\beta}\sigma_{\beta\beta}^6)}{\varepsilon_{\alpha\alpha}\sigma_{\alpha\alpha}^6\alpha_\beta^2 + \varepsilon_{\beta\beta}\sigma_{\beta\beta}^6\alpha_\alpha^2}\,\alpha_\alpha\alpha_\beta \qquad (3)$$

We refer to this rule as Kohler's rule, since an equivalent form was suggested by Kohler [5]. Representing the repulsive forces between two

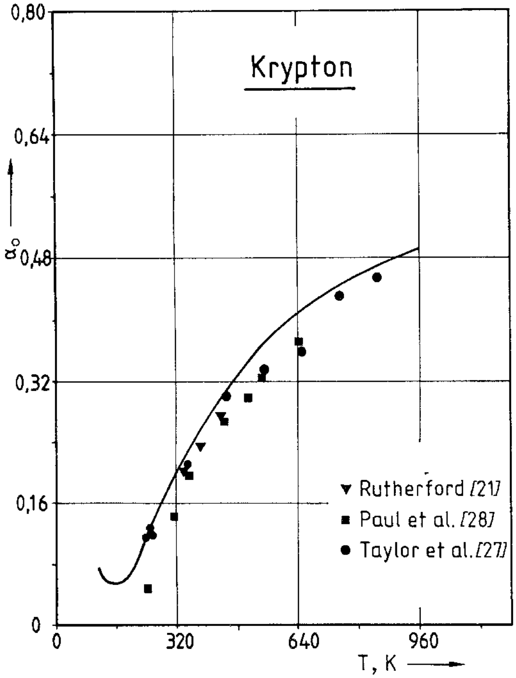

Fig. 7. Experimental and theoretical thermal diffusion factors for krypton.

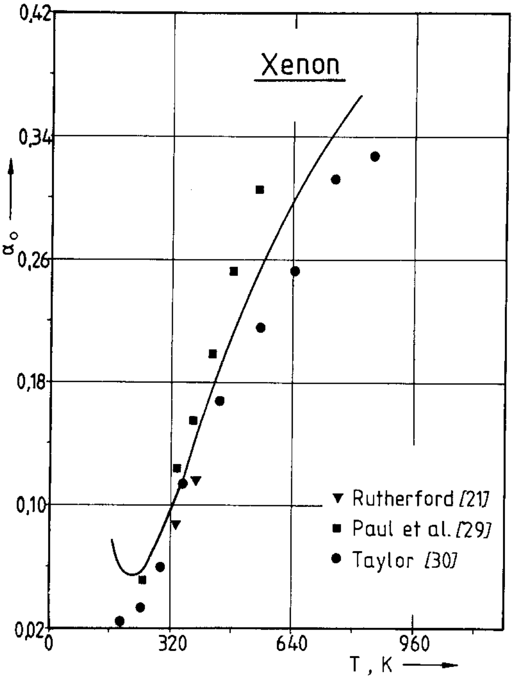

Fig. 8. Experimental and theoretical thermal diffusion factors for xenon.

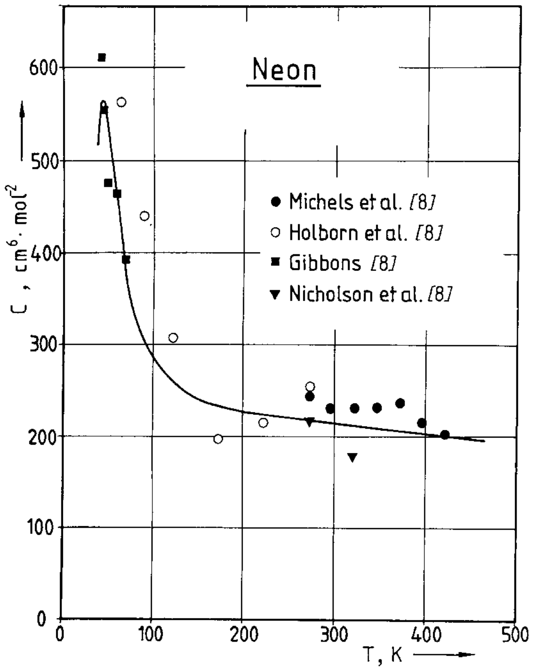

Fig. 9. Experimental and theoretical third virial coefficient for neon.

atoms by a spring model [3], we can derive a second combination rule for the parameters of a Lennard–Jones potential according to

$$\varepsilon_{\alpha\beta}\sigma_{\alpha\beta}^{12}=\left[\frac{(\varepsilon_{\alpha\alpha}\sigma_{\alpha\alpha}^{12})^{1/13}+(\varepsilon_{\beta\beta}\sigma_{\beta\beta}^{12})^{1/13}}{2}\right]^{13} \tag{4}$$

The hard spherical core diameter of the unlike pair interaction is obviously calculated from

$$d_{\alpha\beta}=\frac{1}{2}\,(d_{\alpha\alpha}+d_{\beta\beta}) \tag{5}$$

Equations (1) to (5) fully define all pair interactions in the systems considered here. Calculations of the third virial coefficient require nonadditive dispersion forces to be taken into account. We have convinced ourselves that it is sufficient to use the Axilrod–Teller term [6], because all higher terms tend to cancel each other [7]. The three-body dispersion coefficient is calculated in the usual way from the pair interaction parameters and the polarizabilities [34].

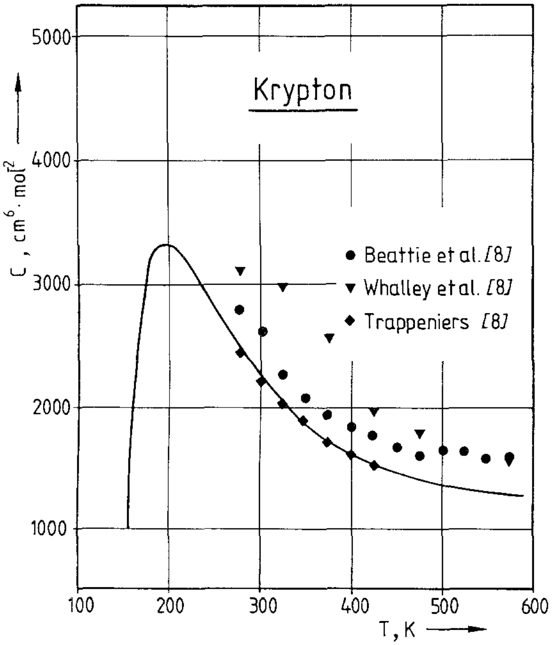

Fig. 10. Experimental and theoretical third virial coefficient for krypton.

3. RESULTS FOR THE PURE GASES

We look at the following thermophysical properties: second virial coefficient B, Joule–Thomson coefficient μ^0, viscosity η, diffusion coefficient D, thermal diffusion factor α_0, and third virial coefficient C. The properties B, μ^0, η, and C for argon have already been discussed in Ref. 1. Thus only D and α_0 are included for argon in this work. Also, for reasons of space, only a selection of results is shown for helium. This gas exhibits quantum effects at low temperatures and was included mainly to demonstrate the power of combination rules (3), (4), and (5) under extreme conditions. Figure 1 shows deviation plots for the second virial coefficients of helium, neon, krypton, and xenon; Fig. 2, the deviation plots for the Joule–Thomson coefficients of neon at low and normal temperatures. Figure 3 shows the predictions of the viscosities for neon and the correlation for the other three gases; Fig. 4, the predictions of the diffusion coefficient. Shaded areas in the figures represent the extimated accuracy of the data. Figures 5 to 8 show the predictions of the thermal diffusion factor. A particularly difficult property to predict is the third virial coefficient. There is a considerable amount of scatter in the data, but it may be concluded from Figs. 9 to 11

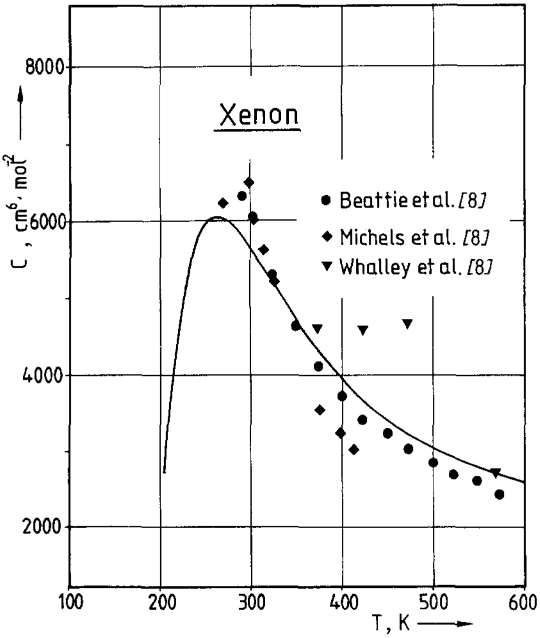

Fig. 11. Experimental and theoretical third virial coefficient for xenon.

that the MSK potential is able to predict these coefficients also quite reliably. We can conclude that, essentially although not quite, all dilute-gas properties of the monatomic gases are described within their estimated experimental uncertainties by the MSK potential, with parameters either from $B+\mu^0$ data or from $B+\eta$ data.

4. RESULTS FOR THE MIXTURES

Using the combination rules, Eqs. (3) to (5), we are now in the position to predict the dilute-gas properties of the mixtures of monatomic gases. We concentrate on the second virial coefficient and the viscosity, for

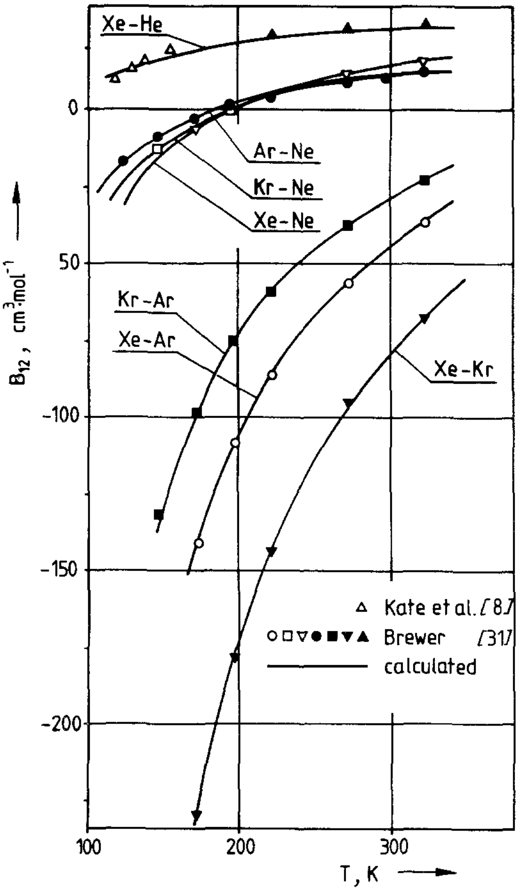

Fig. 12. Experimental and theoretical second virial interaction coefficient.

which reliable data are available. Figure 12 shows typical results for the second virial interaction coefficient for all investigated binary interactions; Fig. 13, the analogous results for the viscosity interaction coefficient. These results tend to establish a high degree of reliability for the combination rules used in this work. It should be noted that the prediction capacity does not deteriorate at large differences of the potential parameters, e.g., for Xe–He. Clearly, since the mixing rules are exactly known for dilute-gas mixtures, the total properties are also in satisfactory agreement with the data. Figure 14 shows as an example the predicted viscosity of the ternary mixture krypton–argon–neon.

5. CONCLUSIONS

We conclude that the MSK potential in connection with the universal combination rules, Eqs. (3) to (5), is a powerful tool to correlate and extrapolate the dilute-gas properties of the monatomic gases and their

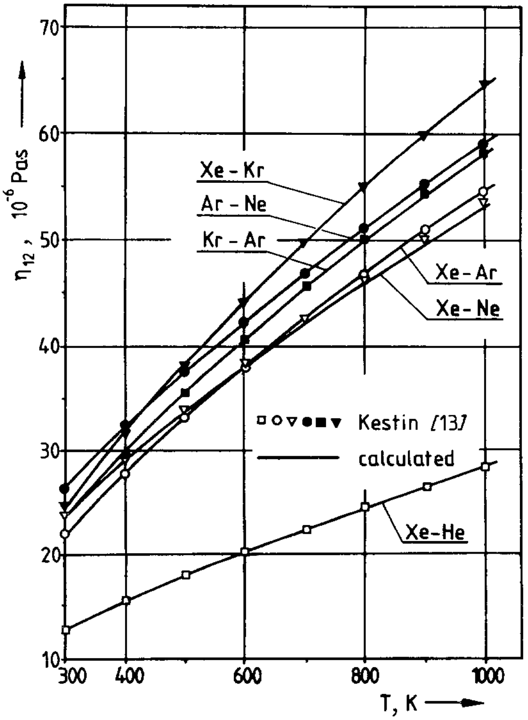

Fig. 13. Experimental and theoretical viscosity interaction coefficient.

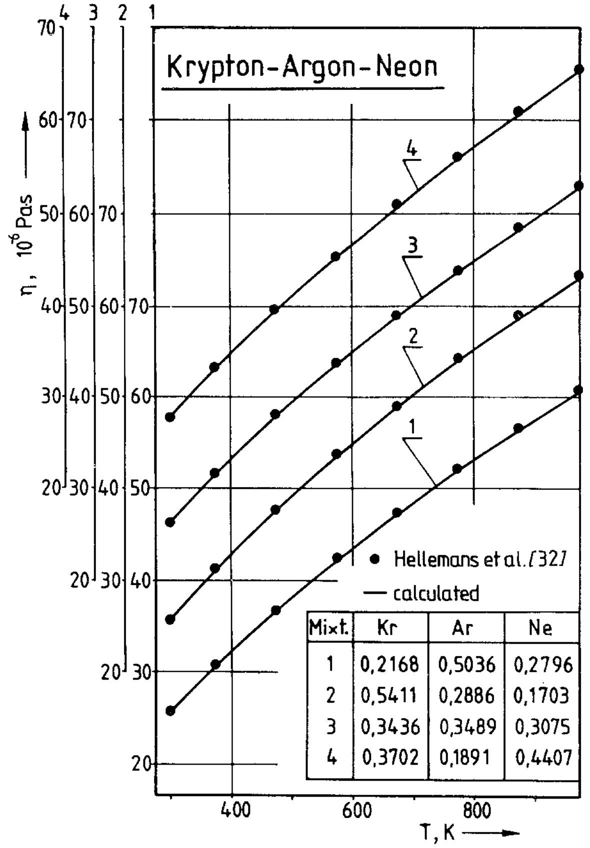

Fig. 14. Comparison between calculated and measured values of the viscosity for the system krypton–argon–neon.

Table I. Values of the Parameters of the MSK-Potential Function (Polarizabilities Are Taken from Ref. 35)

Interaction		ε/k (K) This work	ε/k (K) Aziz [33]	r_m (Å) This work	r_m (Å) Aziz [33]	d/r_m
He	He	10.6600	10.8	2.97624	2.9673	−0.043645
Ne	Ne	40.8546	42.25	3.10020	3.087	0.040348
Ar	Ar	141.6116	143.224	3.74563	3.759	0.058644
Kr	Kr	212.9198	199.9	3.93798	4.012	0.092412
Xe	Xe	296.0421	282.35	4.27841	4.3634	0.103115
He	Xe	30.6212	30.0	3.93247	3.947	0.039577
Ne	Ar	64.0275	69.181	3.49118	3.417	0.049374
Ne	Kr	70.4675	70.7	3.63543	3.63	0.067256
Ne	Xe	69.9164	72.2	3.88618	3.87	0.072855
Ar	Kr	171.3391	167.3	3.84802	3.881	0.075828
Ar	Xe	191.2239	188.63	4.04362	4.0668	0.081713
Kr	Xe	245.7570	233.48	4.11777	4.174	0.097758

mixtures. In Table I we finally summarize the binary interaction parameters obtained in this work. It can be seen that they are reasonably close to those values that have been established by much more involved theoretical and experimental efforts. Clearly, fitting parameters of a simple potential to gas data alone will not normally yield a potential that can also be used for the liquid state. In Ref. 1 we have shown that the MSK is useful for the whole thermodynamic surface for argon. In fact the potential parameters for argon are particularly close to the correct ones. For the other fluids fine-tuning by the use of liquid-state data will be required to obtain parameters which are valid in the whole-state surface.

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