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Dilute-Gas Mixture Properties from Pure-Component Data

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The second virial coefficient, dilute-gas viscosity, and binary diffusion coefficients of some binary-gas mixtures are predicted from potentials which have been fitted to the properties of the pure components. It has been noted that the SSR-MPA potential for polyatomic and the MSK potential for monatomic molecules together with a suitable set of universal combination rules are adequate to make predictions essentially within the inaccuracy of the data.

KEY WORDS: binary diffusion coefficient; dilute gas; mixtures; second virial coefficient; viscosity.

1. INTRODUCTION

In recent publications [1–3] it was shown that the gas-state properties of simple linear molecules can be accurately correlated by potential models containing no more than three adjustable parameters, when the long-range angle-dependent forces and the anisotropy of the molecular shape are properly taken into account. We refer to this type of potential model as SSR-MPA (site–site repulsion/multipole attraction). Together with our earlier results on monatomic gases with the MSK potential [4, 5], we thus dispose of a physically consistent representation of the pure-gas data of a fair number of simple molecules with only three empirically adjusted parameters, which can be used for interpolation and extrapolation purposes. In particular, such an approach can potentially predict the thermophysical properties of gaseous mixtures from properties of the pure component data. In this paper, we determine the level of accuracy with

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which this can actually be done for the simplest gaseous systems consisting of monatomic and simple linear polyatomic molecules such as Ne, Ar, Kr, Xe and N_2, O_2, and C_2H_6.

2. MODEL FOR THE BINARY INTERACTIONS

The SSR-MPA potential model, which we use in this work for the simple linear molecules, is based on the well-known long-range contributions to the intermolecular forces according to quantum mechanical perturbation theory and the multipole expansion [6]. Full account is taken of multipole, induction, and dispersion forces, the latter being restricted to the Lennard–Jones r^{-6}-term plus anisotropic contributions. The short-range repulsive forces are modeled by a site–site interaction model, using the Lennard–Jones repulsive term, i.e.,

$$\phi^{\mathrm{rep}}_{\alpha_i\beta_j}(r_{\alpha_i\beta_j}, \omega_{\alpha_i}, \omega_{\beta_j}) = \sum_{\mathrm{a,b}} 4\varepsilon_{\mathrm{a}_\alpha \mathrm{b}_\beta}\sigma^{12}_{\mathrm{a}_\alpha \mathrm{b}_\beta} r^{-12}_{\mathrm{a}_{\alpha_i} \mathrm{b}_{\beta_j}} \tag{1}$$

where $\varepsilon_{\mathrm{a}_\alpha \mathrm{b}_\beta}$ and $\sigma_{\mathrm{a}_\alpha \mathrm{b}_\beta}$ are the potential parameters of the site–site interaction and $r_{\mathrm{a}_{\alpha_i} \mathrm{b}_{\beta_j}}$ is the distance between site a in molecule α_i and site b in molecule β_j. While in the form of Eq. (1) the repulsive potential is not explicit in the desired coordinates $r_{\alpha_i\beta_j}$, ω_{α_i}, and ω_{β_j}, i.e., the center-to-center distance and the orientational angles of the molecules, it can be transformed into such a form including also the elongation of the molecule by standard mathematical methods [6]. The model contains three adjustable parameters, $\sigma_{\alpha\beta}$ and $\varepsilon_{\alpha\beta}$, i.e., the center-to-center distance and energy parameters, and the eccentricity r^*_{a} of the molecule, which arises when the site–site model is transformed into the $r_{\alpha_i\beta_j}$, ω_{α_i}, ω_{β_j} coordinate system. For the symmetric linear molecules considered here, all parameters for the site–site repulsive interactions are eliminated by the following rule:

$$\sum_{\mathrm{a,b}} \varepsilon_{\mathrm{a}_\alpha \mathrm{b}_\beta}\sigma^{12}_{\mathrm{a}_\alpha \mathrm{b}_\beta} = \varepsilon_{\alpha\beta}\sigma^{12}_{\alpha\beta} \tag{2}$$

The monatomic gases are described with sufficient accuracy by the MSK potential, which is fully defined in Refs. 4 and 5 but not by the Lennard–Jones (12 – 6) potential. Clearly the SSR-MPA does not reduce to the MSK for vanishing elongation but, instead, to the Lennard–Jones (12 – 6) potential. This introduces an element of inconsistency in those calculations, where one pure component is a monatomic and the other a polyatomic molecule. Since we insist on describing the pure component adequately, this inconsistency is unavoidable. It turns out to be practically unimportant, however, when we evaluate all binary interactions between a monatomic and a polyatomic molecule by using effective Lennard–Jones

Table I. The Energy Parameter for Effective Viscosity and Second Virial Coefficient Lennard–Jones Interaction

Gas	ε/k (K)	
	For viscosity	For second virial coefficient
Ne	56.850	35.519
Ar	140.671	119.105
Kr	199.843	173.242

parameters for the monatomic molecule and SSR-MPA parameters for the polyatomic molecule. The effective Lennard–Jones parameters are found by fitting this potential to the MSK values for a given physical property. They are thus different for virial coefficients and viscosities. This does not disturb us here, since they all arise from the common satisfactory MSK representation. The appropriate combination rules for the center-to-center parameters are

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

and

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

as discussed in Ref. 5. With these prescriptions, all binary interactions are fully defined. Tables I and II summarize the potential parameters as obtained from the above procedure for the noble gases using the MSK parameters of Ref. 1. For the linear molecules and like interactions the potential parameters are those of Ref. 5. Unlike interaction parameters

Table II. The Distance Parameter for Effective Viscosity and Second Virial Coefficient Lennard–Jones Interaction

Gas	σ (Å)	
	For viscosity	For second virial coefficient
Ne	2.6740	2.8016
Ar	3.3217	3.4292
Kr	3.5545	3.6115

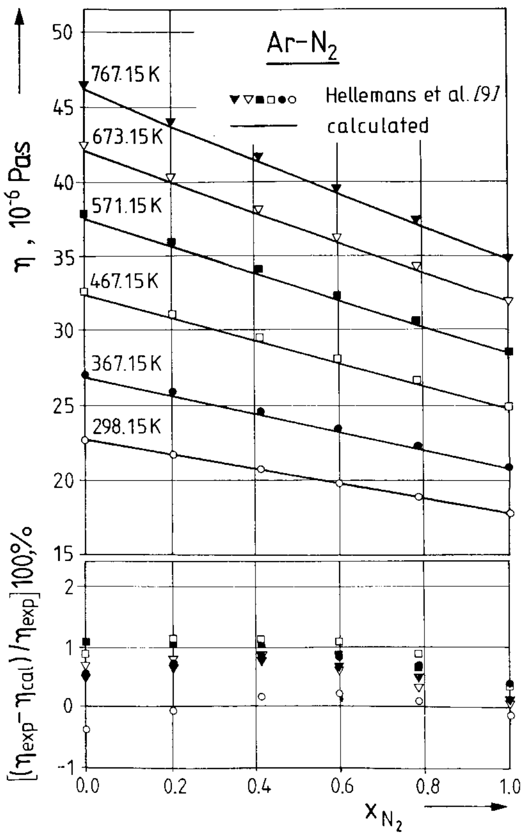

Fig. 1. Predicted viscosities of the Ar–N$_2$ system.

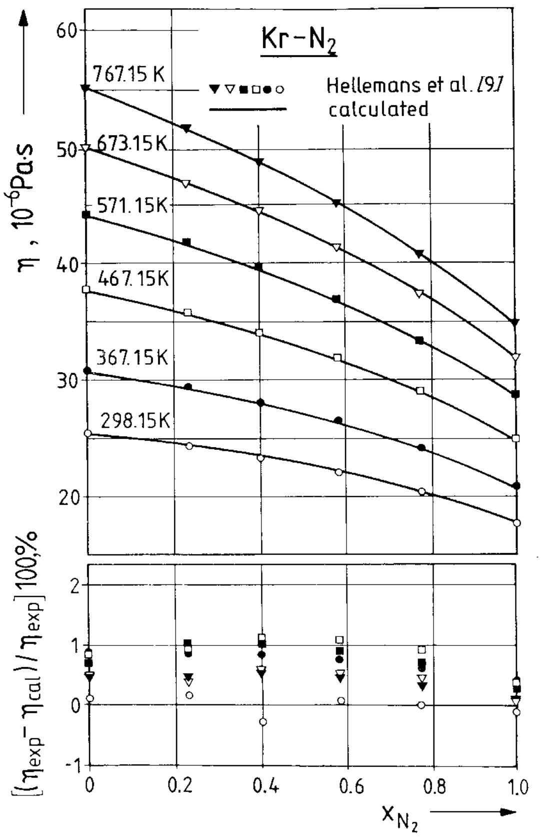

Fig. 2. Predicted viscosities of the Kr–N$_2$ system.

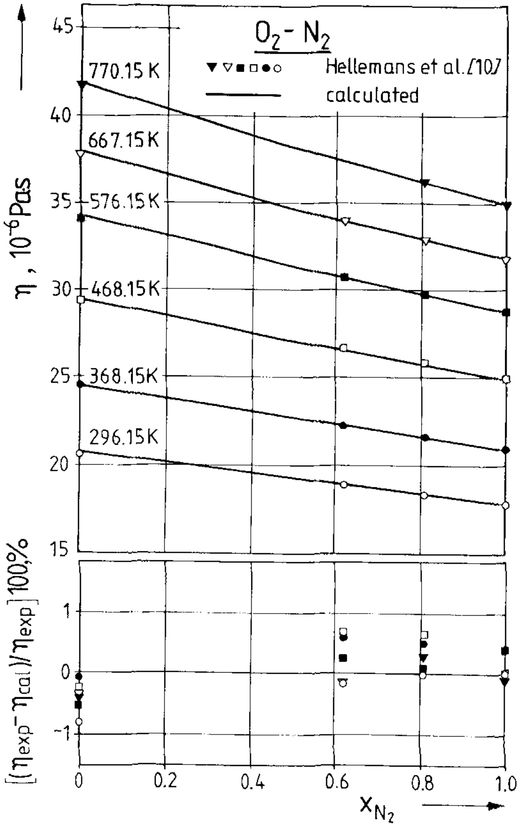

Fig. 3. Predicted viscosities of the O_2–N_2 system.

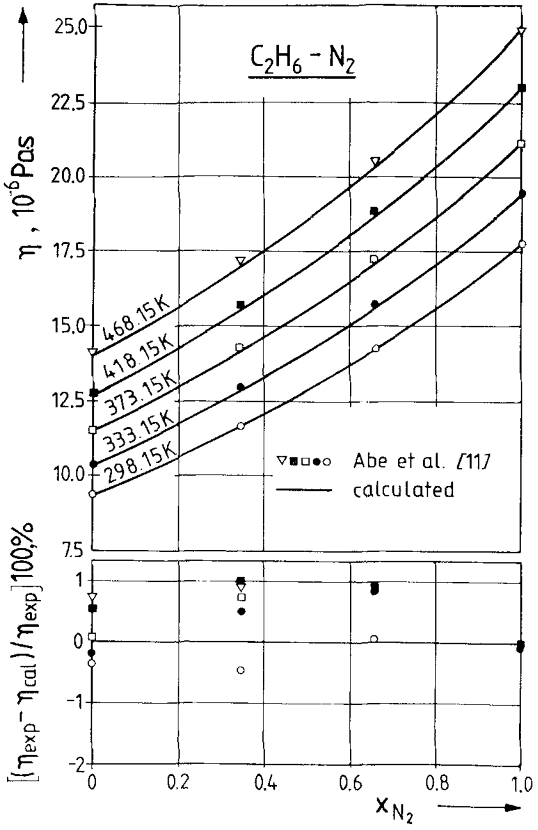

Fig. 4. Predicted viscosities of the C_2H_6–N_2 system.

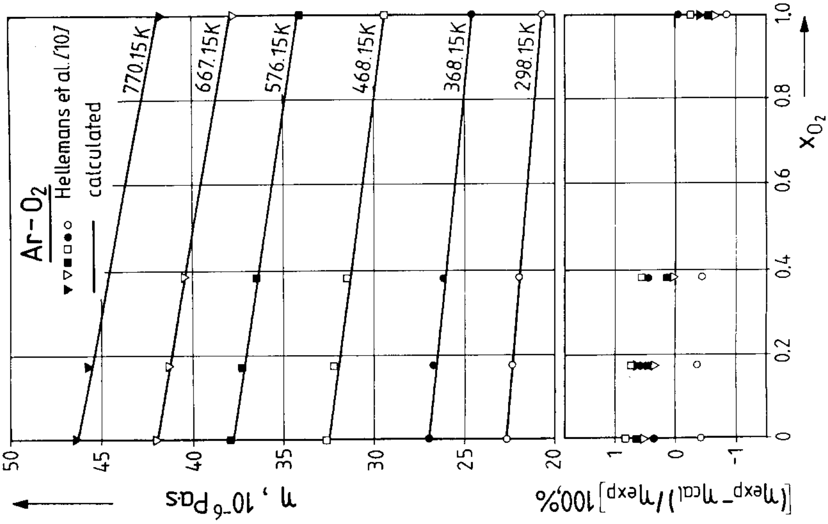

Fig. 5. Predicted viscosities of the Ar–O_2 system.

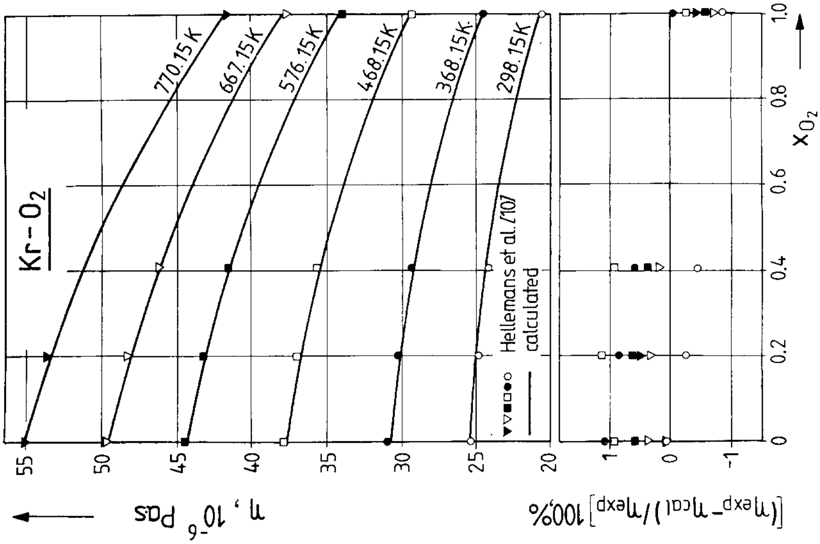

Fig. 6. Predicted viscosities of the Kr–O_2 system.

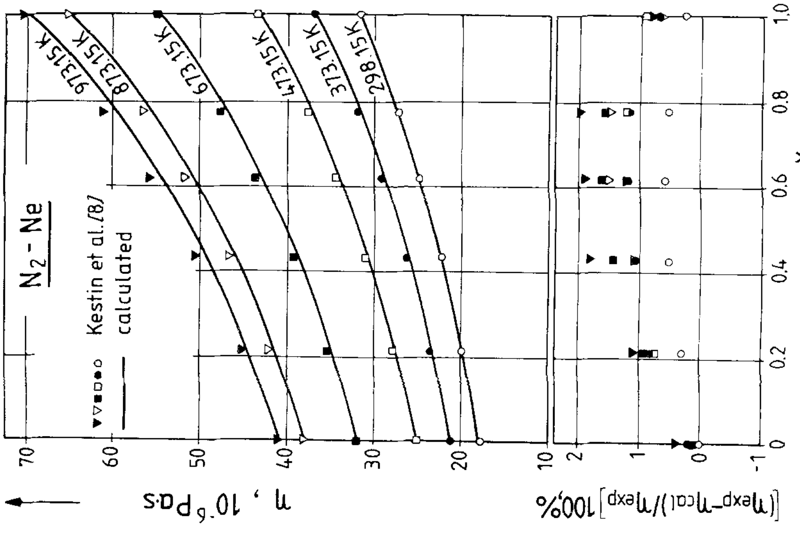

Fig. 7. Predicted viscosities of the N_2–Ne system.

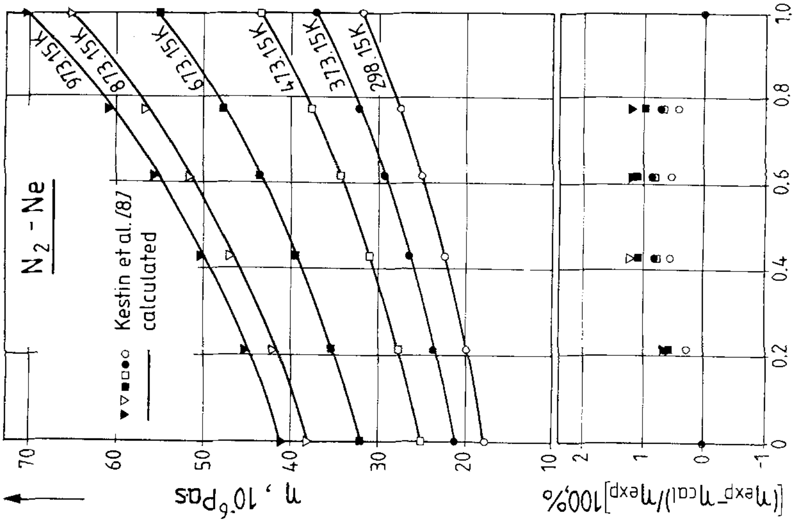

Fig. 8. Predicted mixture viscosities of the N_2–Ne system with pure-component data used to fit potential parameters.

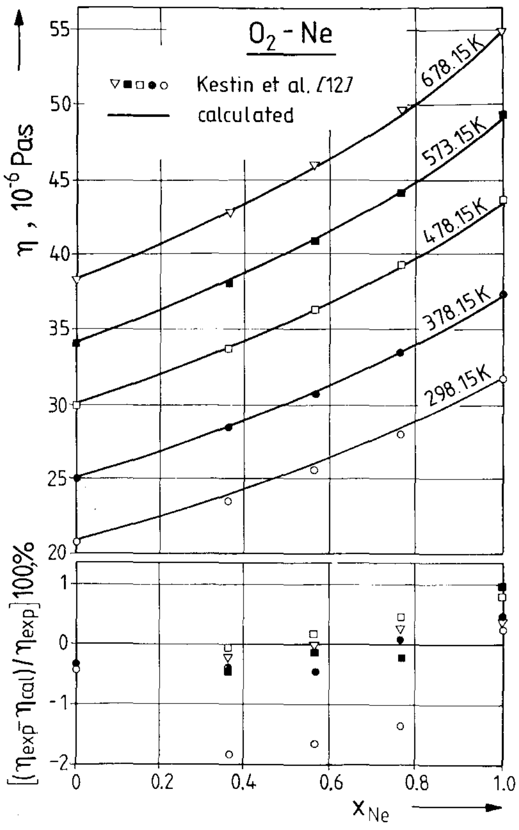

Fig. 9. Predicted viscosities of the O_2–Ne system.

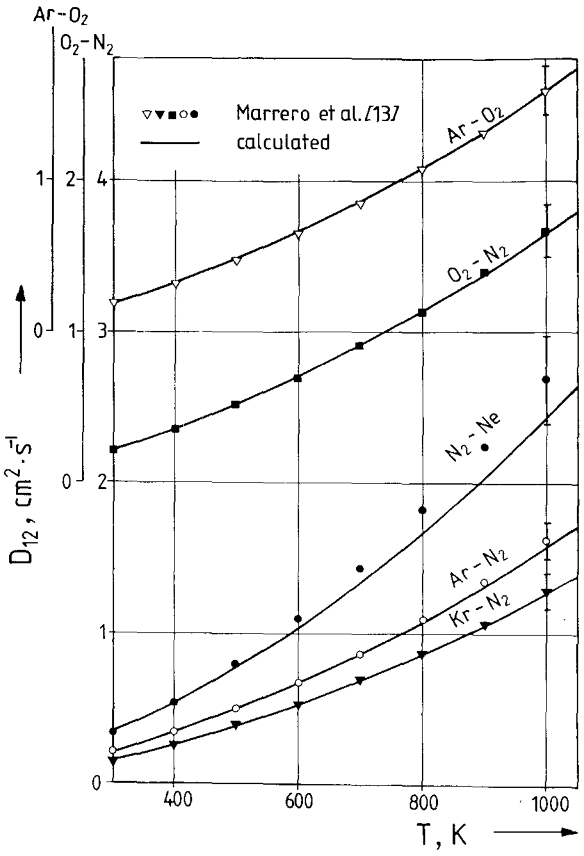

Fig. 10. Predicted binary diffusion coefficients of various systems.

were calculated from the equations of this paper. All further molecular parameters are taken from independent sources and are summarized in Refs. 1 and 5.

3. RESULTS AND CONCLUSIONS

We consider the dilute-gas viscosity, diffusion coefficient, and second virial coefficient of some binary mixtures, for which accurate data are available. Figures 1 to 12 show the predicted thermophysical properties for the systems.

It can be seen that generally errors in the predicted mixture viscosity do not rise above 1 %, which is essentially within experimental error. Here, it must be remembered that all potential parameters used in these calculations were fitted exclusively to pure-component second virial coefficients and Joule–Thomson coefficients [1, 5]. Thus, pure-gas viscosities already represent an extrapolation, and mixture-gas viscosities even more so. Clearly, the introduction of experimental pure-gas viscosities will give

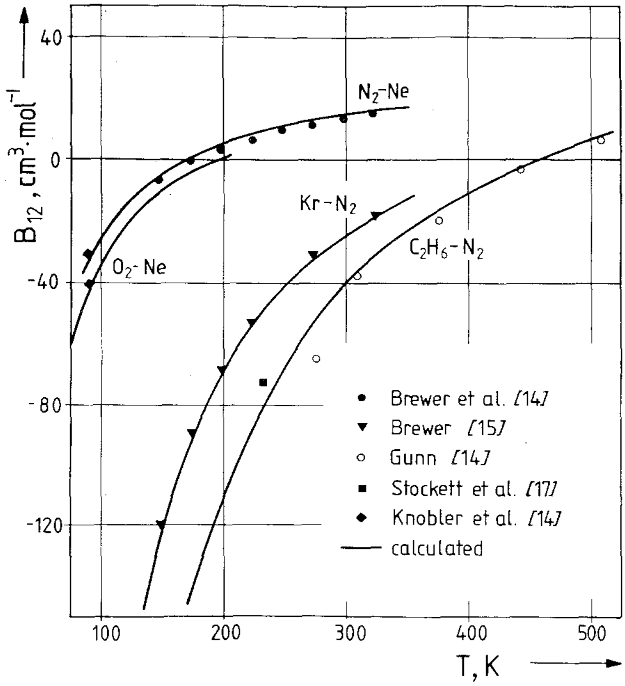

Fig. 11. Predicted second interaction virial coefficients for N_2–Ne, O_2–Ne, Kr–N_2, and C_2H_6–N_2.

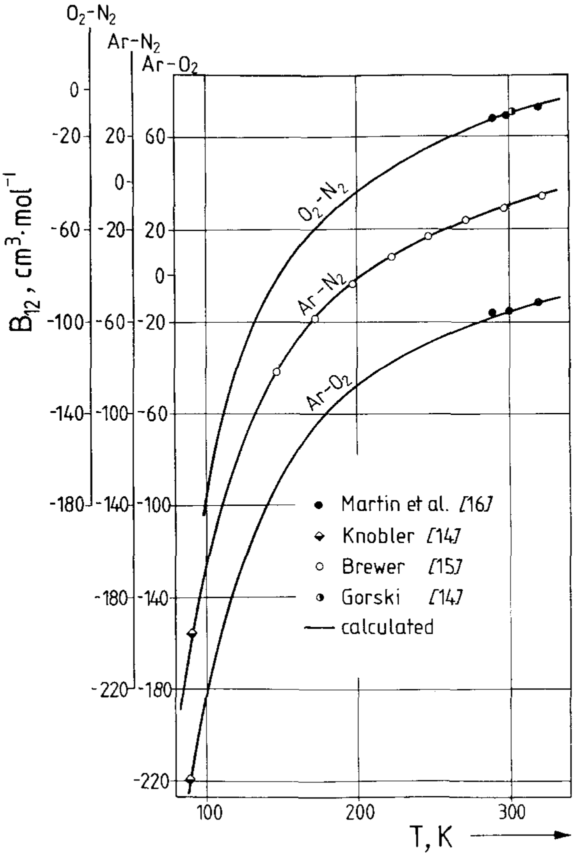

Fig. 12. Predicted second interaction virial coefficients for O_2–N_2, Ar–N_2, and Ar–O_2.

an even better extrapolation to mixtures. We demonstrate this in Figs. 7 and 8 for the example of N_2–Ne, where extrapolation errors for pure neon of about 1 % and a particular strong request for the combination rules add up to a maximum error of 2 %, which is considered to be too high. Introducing the experimental pure-gas viscosities, as shown in Fig. 8, leads to errors in the predicted mixture viscosity of about 1 %, which is again tolerable. Similar conclusions also apply to O_2–Ne, which, too, is not satisfactory. Predicted binary diffusion coefficients agree with the data very well. The same may be said of the interaction second virial coefficients that are shown in Figs. 11 and 12.

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