

Inapplicability of the keesom potential to define second virial coefficient of polar molecules

© **Ikhtier H. Umirzakov**

The Laboratory of Modeling. Kutateladze Institute of Thermophysics of Siberian Branch of Russian Academy of Sciences. Prospect Lavrenteva, 1. Novosibirsk, 630090. Russia.

Phone: +7 (383) 354-20-17. E-mail: tepliza@academ.org

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Abstract

Temperature-dependent potentials for practical applications were obtained by Keesom by averaging over all orientations of the molecules of electrostatic interaction potentials of the constant electric multipoles of molecules. It is shown that averaged over all the mutual orientations of the constant dipole moments of the interacting polar molecules and the temperature-dependent potential of the Keesom can not be used to describe the second virial coefficient of the polar molecules instead of the interaction potential of the electric dipoles, which depends on their mutual orientation; the use of the Keesom potential gives an overestimation of the absolute value of the second virial coefficient and an overestimated value of the Boyle temperature, an incorrect value of the Boyle volume, in describing the experimental data on the second virial coefficient of polar substances it can lead to an erroneous conclusion about the dependence of the dipole moment on temperature and to the underestimated value of dipole moment; The Keesom potential cannot also be used to calculate other virial coefficients; Electrostatic potentials averaged over mutual orientations of molecules cannot be used to calculate virial coefficients. It is also shown that to describe the interaction of polar molecules it is necessary to take into account not only the anisotropic electrostatic interaction of the electric dipole moments of molecules but also the Debye-Falkenhagen induction energy describing the interaction of the constant electric dipole moment of one molecule and the moments induced by this dipole in another molecule, because at high temperatures the induction energy can become comparable with the energy of the electrostatic interaction of the electric dipole moments of the molecules. The obtained results are correct when the interaction potential between molecules is equal to the sum of the centrally symmetric potential and the interaction potential of the constant multipole moments with each other, as well as their interactions with the multipole moments induced by them.

References

- [1] J. Hirschfelder, Ch. Curtiss, R. Byrd. Molecular theory of gases and liquids. *Moscow: Foreign Literature Edition. 1961.* 930p. (russian)
- [2] E. Mason, T. Sperling. The Virial Equation of State. *Moscow: Mir. 1972.* 280p. (russian)