The Virial Coefficients of Pure Gases and Mixtures. a Simply Additivity Scheme of Group Interactions

L. Lepori[C,S], E. Matteoli, A. Spanedda and G. C. Bussolino
Istituto Processi Chimico-Fisici, Pisa, Italy
lepori@ipcf.cnr.it

Many predicting methods have been proposed to evaluate virial coefficients B. Most of them are limited because they depend on the knowledge of molecular properties or on fitted parameters, which are often not available [1]. A few group parameterisation methods have been developed. The best known one [2] requires the critical temperature and is restricted to pure components. In the present work, a simple scheme based on additivity of group interactions is proposed with the aim of i) estimating second virial coefficients of both pure gases (B_{11}) and mixtures (B_{12}); ii) obtaining information on the interactions between molecules responsible of the deviations of gases from ideal behaviour.

It has been observed that the magnitude of B_{11} for both alkanes and perfluoroalkanes increases almost linearly with increasing cubic molecular surface area (as well as with volume and number of carbon atoms). On the basis of this finding, the following equation has been suggested to reproduce B_{12} values at a given temperature T for the general case of molecules 1 and 2. Calculations for pure gases are made by setting molecule 1 identical to molecule 2.

$$B_{12}(T) = \sum n_{ij} a_{ij}(T) s_i s_j \sqrt{S_1 S_2}$$

S_1 and S_2 are total surface areas of molecules, s_i and s_j are the surface areas of i and j groups (in units of CH_2 surface), respectively, n_{ij} is the number of i-j interactions, and a_{ij} is an adjustable parameter, that is, a measure of the interaction strength between i and j per unit interaction surface. B data were taken from Dymond and Smith [3], the surface areas S and s were computed from Bondi increments [4]. From preliminary calculations the following a_{ij} values ($cm^3\ mol^{-1}\ n_{CH2}^{-3}$) at 298.15 K have been obtained for the pair interactions: CH_2-CH_2 (-5.2), CF_2-CF_2 (-1.4), CH_2-CF_2 (-2.2), CH_2-OH (-12), OH-OH (-433), CH_2-O (+4), O-O (-297), CH_2-CO (-8.5), CO-CO (-214), CH_{ar}-CH_{ar} (-17). As function describing the temperature dependence of a_{ij} (and B) either an empirical equation or a semiempirical one based on the chemical theory has been employed. This latter was found more appropriate, requiring in most cases a lesser number of coefficients. A set of 350 selected B values for alkanes C_1 to C_8 and their mixtures in the temperature range 180-700 K were reproduced with a standard deviation of 30 cm^3/mole using three adjustable coefficients for the temperature dependence of only one interaction parameter $a_{ij}(T)$. The second virial coefficients B_M of multicomponents mixtures can be easily calculated from B_{ij} estimated with the above equation. The virial equation for such mixtures even when terminated at the second coefficient B_M, can furnish accurate PVT predictions up to a density of about one half of the critical.

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