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This Week's Citation Classic

O'Connell J P & Prausnitz J M. Empirical correlation of second virial coefficients for vapor-liquid equilibrium calculations.
Ind. Eng. Chem. Proc. Design Dev. **6**:245-50. 1967.
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A relatively simple, generalized correlation was developed for predicting the second virial coefficients of all types of substances to account for vapor-phase nonideality in vapor-liquid equilibrium calculations. Its principal advantage was reasonable reliability while requiring readily available parameters such as critical properties, dipole moment, etc. [The *SCI*® indicates that this paper has been cited over 105 times since 1967.]

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"With the widespread use of large storage, high-speed computers, there was a great increase in the capability of process chemical engineers to more carefully and completely design chemical process units and manufacturing plants. It has been estimated that for those processes requiring separation units for purification, over 70% of the capital investment and much of the energy requirements are involved with distillation, and to a lesser extent, extraction and other units The genera! design method involves calculating the number of ideal (equilibrium) stages which in turn requires means for adequately estimating pure-component properties and mixture nonidealities.

"Professor J. M. Prausnitz early recognized the need for better correlations, particularly for petrochemicals and organics, and the desirability to develop a complete scheme for predicting vapor-liquid equilibria which would be universally available (most previous methods were proprietary to single companies). C.A. Eckert, R.V Orye. and I were graduate students at the

University ot California. Berkeley, whom Prausnitz involved in various aspects of the general procedure which led to the book *Computer Calculations for Multi-component Vapor-Liquid Equilibria*.[1] My particular portions were for systems containing super-critical components and a predictive correlation for vapor nonidealitv using the second virial equation of state (the present article) Basically, I used appropriate molecular concepts to extend the previous correlation of Pitzer to polar and associating species

"Since the correlation was to be in the book and there were reservations about its generality, my own feeling was not to write a separate article. However. Prausnitz felt that it had enough 'stand-alone' value and the review process would help validate its worth, so it was submitted We did include here a few more examples and gave more thorough evidence for testing than in the book

"The passing years have shown that there has been value in the method because many more expressions for activity coefficients have been developed and their evaluation often required accurate description of vapor nonidealities Even more, correlation of experimental vapor-liquid equilibrium (VLE) data and parameter determination has the same need and apparently the method has often been used Finally, many competing virial coefficient correlations have been established, and the present method has been a standard of comparison (which, fortunately, has often been bettered, particularly by a later correlation of my own).[2]

"My own view of why **it** may have been cited so much is that it is the kind of work which gave a relatively simple general correlation (and the required parameters) for reliable prediction of a less important, but non-negligible, effect in systems where only one of several aspects was of principal concern As a result, the focus of the research, be it theory or correlation of experiment, could then be examined with little concern for errors introduced by such an ancillary quantity."

1. **Prausnjtz J M, Eckert C A, Orye R V & 0'Connell J.** *Computer calculations for multi-component vapor-liquid equilibria.* Englewood Cliffs. NJ: Prentice-Hall. 1967. 238 p.
2. **Hayden J** G & 0'Connell **J.** A generalized method for producing second virial coefficients. *Ind. Eng. Chem. Proc. Design Devel.* **14:**209-16. 1975.