

Comments on the Yang-Yendall Equation of State

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The recent article by Yang and Yendall (1) proposes an interesting modification of the Eyring-Hirschfelder-Flory equation of state for calculation of phase equilibria. The success claimed by the authors for their equation to predict vapor pressures, saturated liquid and gas densities, and latent heats of vaporization is impressive and such that it may lead some people to conclude that therein lies an answer to the long search for a simple equation of state which correctly represents the gas and liquid behavior of pure substances. In order to assist those who may not be familiar with the inherent characteristics of the proposed equation, it is well to point out some limitations gleaned from a study made many years ago.

One form in which the Yang-Yendall equation may be displayed is

$$P = \frac{(P^*V^*/T^*)T}{V - V^*(V/V^*)^m} - \frac{P^*}{(V/V^*)^n} \quad (1)$$

Here P^* , V^* , and T^* are characteristic constants determined by trial specifically for each substance. The exponents m and n are empirical decimal numbers for each substance with $1/3 < m \leq 2/3$ and $1 < n \leq 2$. Flory used $m = 2/3$ and $n = 2$, as originally developed by Eyring and Hirschfelder, in representing the liquid phase of chain molecules. Yang and Yendall not only generalized the allowable values of m and n , but they extended the application to the gas phase. In so doing they stipulated that the equation must reduce to the ideal-gas law at low pressure which requires that

$$P^*V^* = RT^* \quad (2)$$

Thus, Equation (1) may be written

$$P = \frac{RT}{V - V^*(V/V^*)^m} - \frac{P^*}{(V/V^*)^n} \quad (3)$$

With $m = 0$ and $n = 2$, this equation is that of Van der Waals, so it innocently appears to be quite acceptable. It is unfortunate, however, that although Yang and Yendall forced the equation to reduce to ideal-gas law, they failed to examine the *manner* or path along which it approaches the ideal-gas state.

As an example of an impending severe drawback for general use of the equation, let us calculate the compressibility $Z = PV/RT$ for several states of argon whose constants are given by Yang and Yendall as

$$\begin{aligned} P^* &= 65.91794(82.0567/1.98719) \text{ atm.} \\ V^* &= 22.59613 \text{ cc./(g.) (mol)} \\ T^* &= 749.5464^\circ\text{K.} \\ m &= 0.477594 \\ n &= 1.822936 \end{aligned}$$

With T and V as the independent variables, the results are as follows:

$T, ^\circ\text{K.}$	$V, \text{cc./g. mol}$	Z
150.86	2259.613	0.9868
150.86	11298.07	1.0106
150.86	16947.098	1.0111
150.86	22596.13	1.0110

150.86	45192.26	1.0097
150.86	225961.3	1.0057

Now 150.86°K. is the critical temperature of argon. Along the critical temperature line on a compressibility chart (Z versus P) there is no known substance—and in particular, argon—whose value of Z exceeds unity unless the volumes are much less than the critical volume. For argon the critical volume is 74.7 cc./g. mol. , a number vastly smaller than any of the values tested. It is readily noted that the calculated values of Z do not differ much from unity, but the differences are real since the calculations were carried out with eight significant figures. Similar calculations, not reported here, showed the same erroneous behavior at temperatures both above and below the critical temperature.

In order further to study the questionable behavior of the equation an average value of m was taken as 0.5 and n as 1.8, so that

$$P = \frac{RT}{V - V^{*0.5}V^{0.5}} - \frac{P^*V^{*1.8}}{V^{1.8}} \quad (4)$$

Multiplying by the inverse of the first term on the right-hand side and rearranging gives

$$Z = \frac{PV}{RT} = 1 + \frac{V^{*0.5}PV^{0.5}}{RT} - \frac{P^*V^{*1.8}}{RTV^{0.8}} + \frac{P^*V^{*2.3}}{RTV^{1.3}} \quad (5)$$

Letting $P \rightarrow 0$ and $V \rightarrow \infty$ reduces to $PV/RT = 1$, as it should from the requirement that the ideal-gas law is to be followed at infinite attenuation. Thus, V may be replaced with RT/P at low pressure so that

$$Z = 1 + \frac{V^{*0.5}P^{0.5}}{(RT)^{0.5}} - \frac{P^*V^{*1.8}P^{0.8}}{(RT)^{1.8}} + \frac{P^*V^{*2.3}P^{1.3}}{(RT)^{2.3}} \quad (6)$$

This may be differentiated with respect to P and rearranged slightly to

$$\frac{dZ}{dP} = \frac{\frac{0.5V^{*0.5}}{(RT)^{0.5}} - \frac{0.8P^*V^{*1.8}P^{0.3}}{(RT)^{1.8}}}{P^{0.5}} + \frac{1.3P^*V^{*2.3}P^{0.3}}{(RT)^{2.3}} \quad (7)$$

Letting $P \rightarrow 0$ for all real temperatures shows that $dZ/dP \rightarrow \infty$. But dZ/dP is related to the second virial coefficient as

$$B = RT \frac{dZ}{dP} \quad (8)$$

Thus, the proposed equation predicts that the second virial coefficient is infinity for all real temperatures, which of course is patently in contradiction with the experimental evidence. Additionally the equation gives linear isometrics which is not in accordance with the facts.

One must conclude from the above analysis that although the Yang and Yendall equation may serve some purpose for calculation of certain equilibria, it fails to behave properly in its approach to the ideal gas state. It is, therefore believed that any future users of the equation

may find it desirable to keep its spurious behavior well in mind particularly if potential applications are at low pressures.

LITERATURE CITED

1. Yang, Chang-Lee, and E. F. Yendall, *AIChE J.*, **17**, 596 (1971).

Wall-to-Bed Heat Transfer in Fluidized Beds

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A model has been proposed by Gabor (1) for relating the rate of wall-to-bed heat transfer in a fluidized bed to the particle residence time at the heat-transfer surface. In that model, a bed of spherical particles was approximated by a series of alternate slabs representing the solid and gas phases. The model was solved numerically by the method of Dusenberre (2).

The predictions of the alternate-slab model, using a gas slab thickness of $0.1d$ and a solid slab thickness of $2/3d$, were in good agreement with data by Botterill et al. (3), Harakas and Beatty (4), and Hampshire (5) on heat transfer from a wall to moving packed beds of glass and copper particles. However, existing data on heat transfer in fluidized beds are either incomplete or were not taken under applicable conditions for a satisfactory test of the model (1). Therefore, to test the applicability of the alternate-slab model to fluidized beds, measurements were made of heat-transfer coefficients as a function of particle residence time in fluidized beds.

EXPERIMENT

Heat transfer measurements made in two 18-in. high columns operated at the same conditions were compared. One column was semicylindrical, and the other was cylindrical. The semicylindrical column was constructed by cutting a 4-in. diam. brass tube in half lengthwise. A 1-in. thick glass plate coated with an electrically conducting mixture of antimony and tin oxides to reduce static charges in the fluidized bed was attached to form a flat face. A 1-in. by 1-in. heater surrounded by guard heaters was mounted in the back curved surface 6 in. above the sintered metal gas distributor plate at the bottom of the column. Air at the bed minimum fluidization velocity was introduced through the gas distributor. Bubbles were periodically injected from a tube mounted in the gas distributor plate adjacent to the midpoint of the base of the glass wall. A bubble that formed at the injection point was assumed to have a diameter equivalent to the dimension observed through the glass wall and was presumed to be a half-bubble whose radius dimension into the bed (perpendicular to the glass wall) was half that of the observed bubble diameter. The half bubble retained its identity as it rose along the axis of the column on the glass wall. Because of axial symmetry, the particle motion at the edges of the column (which was observed through the glass wall) was assumed to be identical to the particle motion within the bed at the heater surface. The effects of bubbling on both particle motion and heat transfer were studied simultaneously.

The cylindrical column was constructed from a 4-in. diameter stainless steel tube. This column had a 2-in. high by 1½-in. wide glass window that was interchangeable with a heater of

the same dimensions. From an injection tube installed in the center of the base of the column, individual axisymmetric bubbles were injected into the bed. The cylindrical column had to be operated twice under identical conditions, once for measurement of heat-transfer rates and once for observation of particle movement. Comparison of the results for the two columns was used to check the validity of the assumption that particle behavior is axisymmetric in the semicylindrical column.

The particle movement was photographed with a Milliken Model DBM-5 motion picture camera at 120 frames/sec. The particles fluidized were two sizes of glass beads, 1.51×10^{-3} ft. and 1.17×10^{-3} ft. in diam., with colored glass particles as visual tracers and 1.93×10^{-3} ft. copper shot with 1.0 weight percent nickel particles as visual tracers. The alternate-slab model predicts that the addition of 1.0 weight percent nickel particles, which have the same density as copper particles, to the bed would affect the data by only 0.1 percent.

Bubbles of 1- to 1½-in. diam. were injected into both columns with the beds at minimum fluidization at frequencies of 45 to 90 per min. by means of a solenoid valve and an electric timer. To obtain frequencies higher than 90 per min., the gas for bubble formation was introduced at a uniform flow rate through the injector tube to form bubbles freely. These bubbles were not uniform in size but were formed at a higher frequency ($\sim 120 \text{ min.}^{-1}$) than could be achieved with the timer.

DETERMINATION OF PARTICLE RESIDENCE TIME

The particles along the wall moved upward during bubble formation at the injector tube. The particles then moved downward as the bubble rose up the column; after the bubble passed, they remained stationary until the next bubble formed. The particle residence time was determined by the following equation:

$$t = \frac{L(t_u + t_d + t_r)}{V_{ut}u + V_{dt}d} \quad (1)$$

Equation (1), which is based on the assumption that all particles above or below the heater are at bed temperature, is derived by dividing the inventory of particles at the heater surface by the rate of particle flow past the heater.

The particle velocities and residence times during the different stages of bubble injection, formation, and rising were determined by a frame-by-frame analysis of the motion picture film for 15 bubbles. For the freely formed bubbles, there was essentially no upward particle movement. The downward movement of particles into the heat-transfer region was at a higher velocity than the downward movement at the bottom of the heat-transfer region. Some particles were observed to leave in the direction approximately perpendicular to the heater surface; this accounted for the difference in downward particle velocities at the top and bottom of the heat-transfer region. If