An Approach to Organizing the EOS Model in Process Simulators

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When using an equation-of-state (EOS) technique, it becomes a serious problem to handle specifications, which are infeasible depending on the equation being used and occurs as a result of the iterative nature of higher-level algorithms in a process simulator. Such situations can be dealt with either by higher-level algorithms or by the EOS model. The former approach tends to result in unnecessary complexity and could well interrupt orderly progress toward the solution, while the latter is more appropriate for a general-purpose simulator (Mathias et al., 1984). The EOS model has to be organized to allow for a specified phase: to recognize infeasible specifications (usually that of the pressure) and to supply values for the volume and derived properties at all conditions.

One approach to solving the above-stated problems on the basis of a new representation of the P-v behavior of the liquid and vapor phase at infeasible conditions is presented in the paper. The workability of the method is demonstrated on the example of Redlich-Kwong-Soave EOS.

Approach to the Problem

The EOS model interacts with the higher-level algorithms through changing values of composition (and temperature) with each call and through a specified value of the pressure and phase type. Solving an EOS for the volume of a liquid or a vapor phase leads to two problems: the "liquid-phase" and the "vapor-phase" problem.

Liquid-phase problem

An infeasible pressure specification is recognized for the liquid phase, if it satisfies the inequality $P_{spec} < P_{lim}$. For temperatures below the pseudocritical P_{lim} is a coordinate of the stationary point of the isotherm, satisfying

$$\left(\frac{\partial P}{\partial v}\right)_{T,x} = 0 \text{ and } \left(\frac{\partial^2 P}{\partial v^2}\right)_{T,x} > 0 \qquad (1)$$

Its value is obtained directly from the (second-order) Newton-Raphson volume-finding procedure. For temperatures above the pseudocritical, P_{lim} is determined from:

$$P_{lim} = \frac{RT}{v_{TC} - b_m} - \frac{a(T)}{v_{TC}\,(v_{TC} + b_m)} \qquad (2)$$

The true critical volume, v_{TC}, can be estimated, for instance, with the correlation of Elliot and Daubert (1987).

Solutions of the EOS corresponding to the volume of a liquid phase lie in the interval $b_m < v < v_{lim}$. For temperatures below pseudocritical, v_{lim} satisfies Eq. 1, while for temperatures above pseudocritical, $v_{lim} = v_{TC}$.

Once an infeasible pressure specification is recognized, the original EOS is replaced by a combination of P-v relationships, represented by:

- The equation of state itself: in the interval $(b_m - v_o)$
- A quadratic spline of the form $a_o + a_1 v + a_2 v^2$: in the interval $(v_o - v^*)$
- A cubic spline of the form $A_o + A_1 v + A_2 v^2 + A_3 v^3$: in the interval $(v^* - v'')$
- The equation of state itself: in the interval $(v'' - \infty)$

The arbitrary value v_o is chosen in the interval that is feasible for EOS solutions, where v^* is the volume of the liquid phase at $P = P_{spec}$ and v'' is the pseudocritical volume at $T < T_{pc}$ or the true critical volume of the liquid phase at $T > T_{pc}$ (Figures 1 and 2).

The new model is completely within the terms of the original EOS. It retains all its characteristic values (b_m, v_{lim}, v_{PC}/v_{TC}) and satisfies conditions of mechanical and thermal stability. The specified pressure then lies in its allowed region. Hence, the usual pattern of the EOS model can be followed:

1. Find a solution of the EOS for the molar volume of the specified phase.
2. Estimate the desired derived properties at the obtained volume and at the specified pressure.

A value v^* for the volume of the liquid phase at $P = P_{spec}$,

satisfying $b_m < v^* < v_{\text{lim}}$, is obtained solving the equation

$$P_{\text{spec}} = a_o + a_1 v + a_2 v^2. \tag{3}$$

The coefficients, a_o, a_1, and a_2, are determined by matching P and $(\partial P/\partial v)$ at point (v_o, P_{calc}) and postulating that $P = 0$ at $v = v_{\text{lim}}$.

The fugacity coefficients are calculated using the standard thermodynamic relationship (Michelsen, 1981), Appendix I:

$$\ln \phi_{li}^* = \frac{\partial}{\partial x_i} \int_{v^*}^{\infty} \left(\frac{P}{RT} - \frac{1}{v} \right) \cdot dv$$

$$- \ln z^* = \frac{\partial}{\partial x_i} \left\{ \int_{v^*}^{v''} \left[\frac{A_o + A_1 v + A_2 v^2 + A_3 v^3}{RT} - \frac{1}{v} \right] \cdot dv \right.$$

$$\left. + \int_{v''}^{\infty} \left(\frac{P}{RT} - \frac{1}{v} \right) dv \right\} - \ln z^* \tag{4}$$

The algorithm is straightforward:

1. The first term in the righthand side of Eq. 4 is a polynomial, and its integration is carried out analytically beforehand:

$$\int_{v^*}^{v''} \left[\frac{A_o + A_1 v + A_2 v^2 + A_3 v^3}{RT} - \frac{1}{v} \right] dv$$

$$= \frac{1}{RT} \left[A_o (v'' - v^*) + 0.5\, A_1 (v''^2 - v^{*2}) + \frac{1}{3} A_2 (v''^3 - v^{*3}) \right.$$

$$\left. + 0.25\, A_3 (v''^4 - v^{*4}) \right] - \ln (v''/v^*) \tag{4a}$$

The obtained result is substituted in Eq. 4.

2. The coefficients A_o, A_1, A_2, and A_3 are determined by matching P and $(\partial P/\partial v)$ at points (v^*, P_{spec}), (v_{pc}, P_{pc}) at $T < T_{pc}$ or at points (v^*, P_{spec}), $(v_{\text{lim}}, P_{\text{lim}})$ at $T > T_{pc}$.

3. A numerical differentiation is used to obtain the composition derivatives of the first term in the righthand side of Eq. 4, because of the complicated dependence of the A_i coefficients on composition. (An analytical differentiation is possible, but not efficient at this point.) The differentiation requires calculating

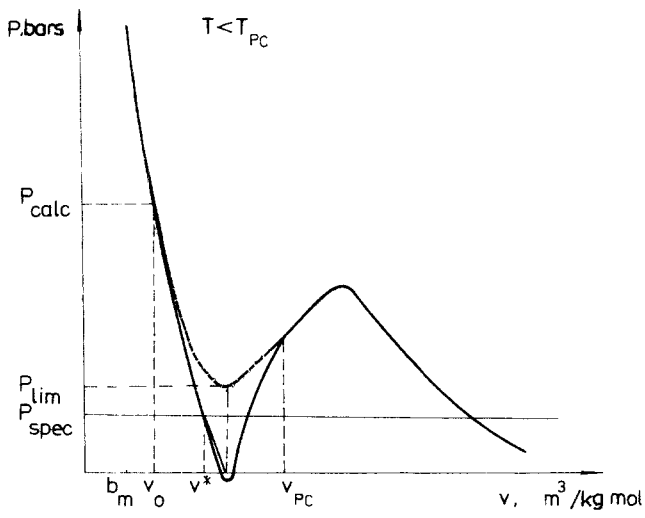

Figure 1. $P - v$ isotherm (- - - -), simulated by the liquid-phase model at $T < T_{pc}$ (—).

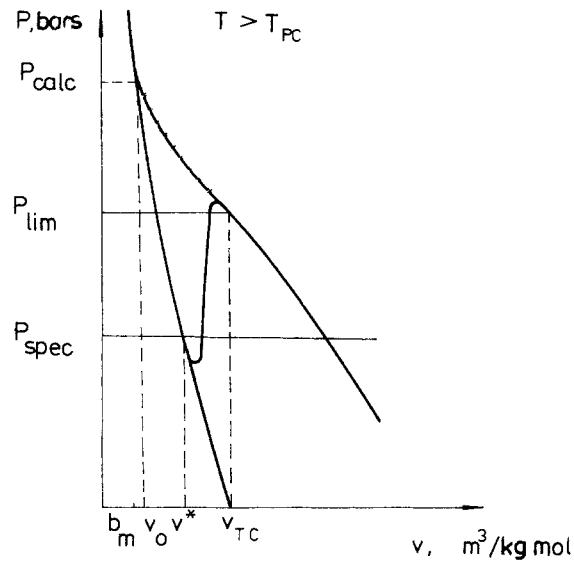

Figure 2. $P - v$ isotherm (- - - -), simulated by the liquid phase model at $T > T_{pc}$ (—).

twice the above analytical relations and is straightforward and not time-consuming.

4. The second term in Eq. 4 is:

$$\frac{\partial}{\partial x_i} \left[\int_{v''}^{\infty} \left(\frac{P}{RT} - \frac{1}{v} \right) dv \right] = \ln \phi_i(v'') + \ln z\,(v'') \tag{4b}$$

and is calculated directly with the original EOS.

Thus, the EOS model itself can be depicted as a simple two block structure.

In the first "standard" block, the volume-finding procedure converges in two, maximum of five iterations, either to the root of interest or to P_{lim}, v_{lim}. Thus, it includes diagnosis of pressure specification as well. If the latter is feasible, the desired derivative properties are calculated and returned to the higher-level simulation algorithms.

When infeasible pressure specifications are recognized, the second "extrapolating" block is triggered. The molar pseudovolume (Eq. 3) and the pseudofugacity coefficients (Eq. 4) are estimated at the specified pressure, using the proposed extrapolated $P - v$ relationships. The analytical formula for calculating $\ln \phi_i(v'')$ (Eq. 4b) is called from the first block. The pseudoproperties are then returned back to the higher-level simulation algorithm.

Thus, the structure of the EOS model is flexible and easily interwoven in the macrostructure of a general-purpose process simulator.

Vapor-phase problem

An infeasible pressure specification for the vapor phase is recognized, if $P_{\text{spec}} > P_{\text{lim}}$. P_{lim} satisfies either $(\partial P/\partial v)_{T,y} = 0$ $(\partial^2 P/\partial v^2)_{T,y} < 0$ for temperatures below the pseudocritical or Eq. 2 for temperatures above the pseudocritical. Then, a decision for triggering the extrapolating block is taken on the EOS level. The idea outlined above may be applied again (Figure 3). The model, however, can be simplified taking into consideration that a solution of the EOS, corresponding to a volume of a vapor phase satisfies the inequality $v_{\text{lim}} < v^* < \infty$.

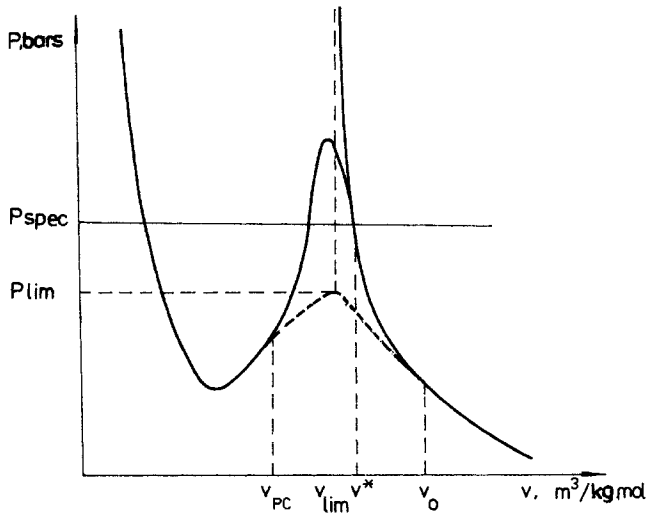

Figure 3. A representation of the vapor-phase behavior at infeasible pressure specifications.

The original EOS is replaced:

- In the interval $(v_{lim} - v_o)$, by an extrapolated $P - v$ relationship:

$$P = F/(v - v_{lim}) + c_o + c_1 v \tag{5}$$

- In the interval $(v_o - \infty)$, by the EOS itself (Figure 4).

The coefficients, c_o, c_1, are determined by matching P and $(\partial P/\partial v)$ at point (v_o, P_{calc}), where v_o is an arbitrary chosen value among the feasible solutions of the EOS. The coefficient F, empirically is assumed to be 1,000. A vapor molar volume at $P = P_{spec}$, satisfying $v_{lim} < v^* < \infty$, is found from Eq. 5. The desired derived properties, as in the liquid-phase case, are calculated at v^*, P_{spec}. For example:

$$\ln \phi_{i_v}^* = \frac{\partial}{\partial y_i}\int_{v^*}^{\infty}\left(\frac{P}{RT} - \frac{1}{v}\right)dv - \ln z^*$$

$$= \frac{\partial}{\partial y_i}\left\{\int_{v^*}^{v_o}\left[\frac{F/(v - v_{lim}) + c_o + c_1 v}{RT} - \frac{1}{v}\right]dv + \int_{v_o}^{\infty}\left(\frac{P}{RT} - \frac{1}{v}\right)dv\right\} - \ln z^* \tag{6}$$

for the vapor-phase pseudofugacity coefficients.

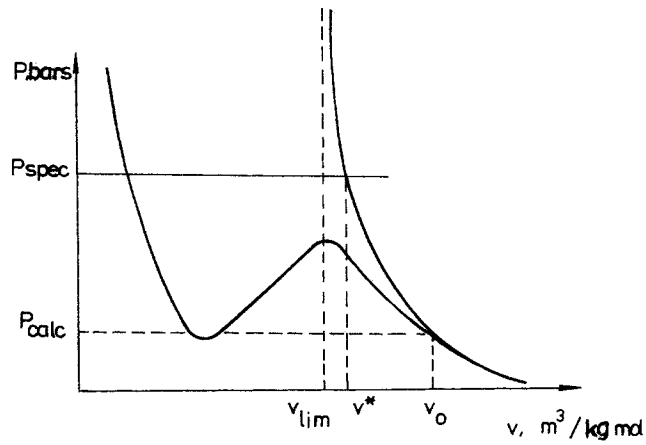

Figure 4. $P - v$ isotherm simulated by the vapor-phase model.

The result from the analytical integration of the first term in the righthand side of Eq. 6 is:

$$\int_{v^*}^{v_o}\left[\frac{F/(v - v_{lim}) + c_o + c_1 v}{RT} - \frac{1}{v}\right]dv = \frac{1}{RT}\left[F \cdot \ln\frac{(v_o - v_{lim})}{(v^* - v_{lim})} + c_o(v_o - v^*) + 0.5c_1(v_0^2 - v^{*2})\right] - \ln(v_o/v^*) \tag{6a}$$

The composition derivatives of Eq. 6a are found numerically, because of the complicated dependence of the c_i coefficients on composition.

The second term in the righthand side of Eq. 6 is:

$$\frac{\partial}{\partial y_i}\left[\int_{v_o}^{\infty}\left(\frac{P}{RT} - \frac{1}{v}\right)dv\right] = \ln\phi_i(v_o) + \ln z\,(v_o) \tag{6b}$$

and can be calculated directly with the original EOS.

The functional relations for $\ln \phi_{i_v}^*$ and $\ln \phi_{i_l}^*$ can be further differentiated numerically with respect to temperature, pressure, and composition at a very low computational cost.

Results and Discussion

The strategy discussed concerns only organizing the EOS model in a process simulator, but not the higher-level algorithms. While it will be useful to compare its efficiency with the efficiency of existing analogues, there are certain difficulties in estimating the CPU time required. Such data, as computer storage requirements and computational time needed, are either not published nor the data reported concern a higher-level algorithm. It, however, can illustrate the robustness and the ability of the method to provide trustworthy fugacity coefficients at infeasible pressure specifications. As an example, the equimolar ethane–*n*–heptane mixture, discussed by Mathias et al. (1984), may be used.

Fugacity coefficients, calculated by the proposed method, in the liquid and the vapor phase are shown on Figure 5 (temperature, below the pseudocritical) and Figure 6 (temperature above the true critical). The pseudofugacity coefficients calculated at infeasible pressure specifications are continuous with the true values and improve the convergence characteristics of the higher-level algorithms. For both components in the liquid and for *n*-heptane in the vapor phase, they completely follow the trend of the true values, as the pressure changes. The pseudofugacity coefficient of ethane in the vapor phase at $T = 420$ K does not quite maintain the expected trend with pressure; however this does not influence the orderly progress toward solution of a higher-level algorithm.

A second example, demonstrating the workability of the method in phase equilibrium calculations, is shown on Figure 7. The $P - T$ diagram of a nitrogen-propane binary (17.1 mol % nitrogen) is predicted with the Soave-Redlich-Kwong EOS (the binary coefficient $k_{ij} = 0.0763$). The phase behavior generated—a minimum in the bubble point curve and multiple bubble points at pressures higher than the true critical—fits fairly well with the experimental data of Schindler et al. (1966) and Grouslo et al. (1977).

The strategy described in this paper is applicable to all EOS models. The method has been extensively tested and proved to

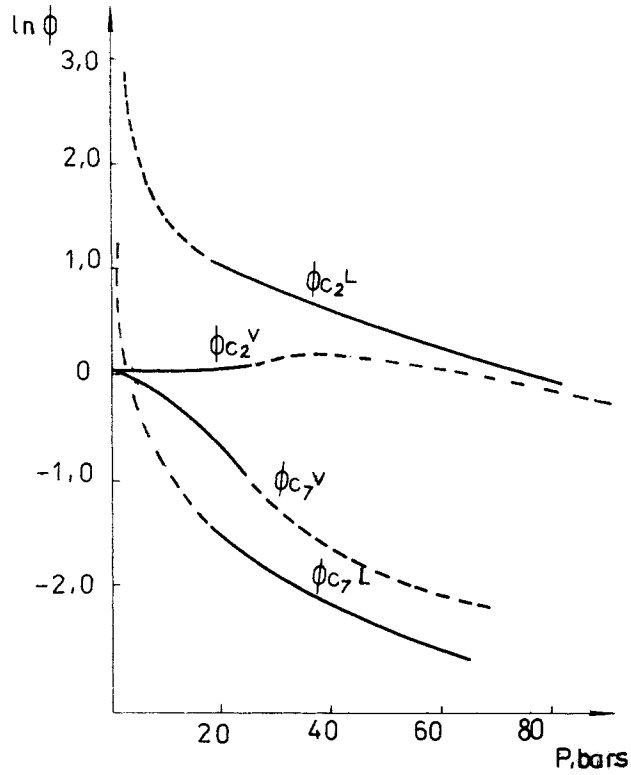

Figure 5. Fugacity coefficients of an equimolar ethane-*n*-heptane mixture at 420 K.

—, true values

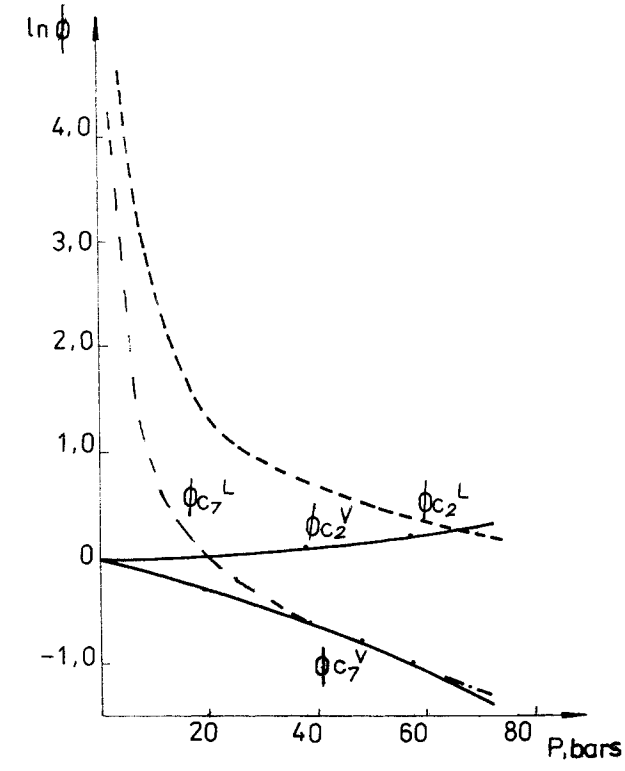

Figure 6. Fugacity coefficients of an equimolar ethane-*n*-heptane mixture at 500 K.

- - - -, pseudofugacity coefficients in the liquid phase

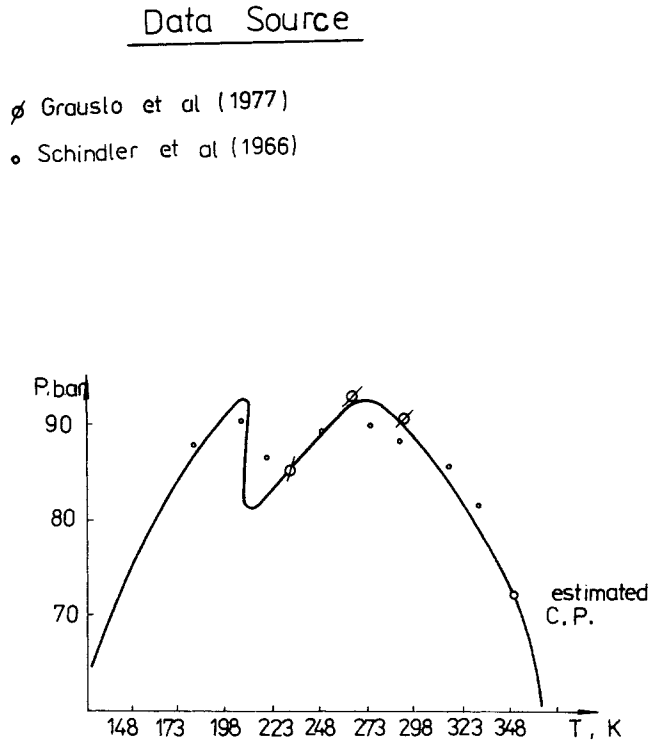

Figure 7. *P* – *T* diagram of a nitrogen-propane mixture (17.1 mol % nitrogen).

Predicted by the Redlich-Kwong-Soave EOS.

be reliable, robust, and efficient. It is embodied in the process simulator EQUILIBRIA (Bancheva and Stateva, 1987).

The method for estimation of the volume and derived properties at infeasible pressure specifications is unified for both phases. It does not need any additional corrections for the pseudofugacity coefficients to keep up with the tendency of the true values in the liquid phase. The method does not require expensive calculations, because the functional relations employed are of the lowest possible order and their integration and numerical differentiation are quite simple.

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Notation

b_m = van der Waals volume
k_{ij} = binary interaction parameter
P = pressure
R = universal gas constant
T = temperature
v = molar volume
x,y = component mole fractions in the liquid and vapor phase
z = compressibility factor

Greek letter

ϕ_i = fugacity coefficient, component i

Subscripts

calc = calculated from the EOS
eq = equilibrium
l = liquid

lim = limiting value
pc = pseudocritical
spec = specified value
TC = true critical
v = vapor

Superscript

$*$ = parameter value at the solution point

Literature Cited

Bancheva, Iv., and R. P. Stateva, "Organizing Thermophysical Properties Calculations in a Process Simulator," *Proc. Mediterranean Cong. on Chem. Eng.*, **II,** 540 (1987).

Elliot, J. R., and Th. E. Daubert, "Evaluation of an Equation of State Method for Calculating the Critical Properties of Mixtures," *Ind. Eng. Chem. Res.*, **26,** 1686 (1987).

Grauslo, L., A. Fredenslund, and J. Mollerup, "Vapor-Liquid Equilibria for Mixtures of Low Boiling Substances," H. Knapp, R. Doring, L. Oellrich, U. Plocker, and J. M. Prausnitz, eds., *DECHEMA Chemistry Data,* **VI,** Frankfurt, West Germany, 324.

Mathias, P. M., J. F. Boston, and S. Watanasiri, "Effective Utilization of Equations of State for Thermodynamic Properties in Process Simulation," *AIChE J.*, **30**(2), 182 (1984).

Michelsen, M. L., "Partial Derivatives of Thermodynamic Properties from Equations of State," *SEP 8109,* Instituttet for Kemiteknik (1981).

Schindler, D. L., G. W. Swift, and F. Kurata, "Vapor-Liquid Equilibria for Mixtures of Low Boiling Substances," H. Knapp, R. Doring, L. Oellrich, U. Plocker, and J. M. Prausnitz, eds., *DECHEMA Chemistry Data,* **VI,** Frankfurt, West Germany, 322.

Appendix I

Partial derivatives of component mole numbers (usually used in calculating fugacity coefficients) converted to those of mole fractions are derived from:

$$P = P(T, v, x)$$

$$P = \frac{RT}{v - b} - \frac{a(T)}{v(v + b)}$$

$$a = \Sigma\Sigma\, x_i x_j a_{ij}$$

$$b = \Sigma\, x_i b_i$$

$$F^* = \int_v^\infty \left(\frac{P}{RT} - \frac{1}{v}\right) dv$$

$$F_i^* = \frac{\partial}{\partial x_i}\left[\int_v^\infty \left(\frac{P}{RT} - \frac{1}{v}\right) dv\right]$$

$$\ln \phi_i^* = F_i^* - \ln z$$

$$P = P(T, V, N)$$

$$P = \frac{NRT}{V - B} - \frac{A(T)}{V(V + B)}$$

$$V = Nv \qquad N = \Sigma\, n_i$$

$$A = \Sigma\Sigma\, n_i n_j a_{ij}$$

$$B = \Sigma\, n_i b_i$$

$$F = \int_V^\infty \left(\frac{P}{RT} - \frac{N}{V}\right) dV$$

$$F_i = \frac{\partial}{\partial n_i}\left[\int_V^\infty \left(\frac{P}{RT} - \frac{N}{V}\right) dV\right]$$

$$\ln \phi_i = F_i - \ln Z$$

$$F_i = \frac{\partial}{\partial n_i}\left[\int_V^\infty \left(\frac{P(V)}{RT} - \frac{N}{V}\right) dV\right]$$

$$= \frac{1}{N}\frac{\partial}{\partial x_i}\left\{N \int_{V/N}^\infty \left[\frac{P(V/N)}{RT} - \frac{1}{V/N}\right] d\frac{V}{N}\right\}$$

$$= \frac{\partial}{\partial x_i}\left[\int_V^\infty \left(\frac{P(v)}{RT} - \frac{1}{v}\right) dv\right]$$

$$= F_i^*$$

after a change in the integration variable $v = V/N$ and taking into consideration that

$$\frac{\partial}{\partial n_i} = \frac{1}{N}\frac{\partial}{\partial x_i}.$$

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