

CALCULATION OF ORTHOBARIC DENSITIES FROM EQUATIONS OF STATE

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A numerical method for calculation of densities of saturated vapour and liquid phases, and of saturated vapour pressure using an equation of state is proposed. The method proved to be both robust and efficient using the Redlich-Kwong equation of state for methane. The method can be straightforwardly extended for the case of multicomponent systems.

Key words: Equations of state; Saturated pressure; Saturated densities; Gas-liquid equilibrium; Thermodynamic functions.

Equations of state may be used not only for calculations of p - V - T properties of fluids but also for the determination of other thermodynamic functions. In particular, they may be used for the determination of properties of coexisting vapour and liquid phases. The first step is the calculation of saturated vapour pressure and densities of the coexisting phases.

For the sake of simplicity, we will concentrate here on one-component system. In equilibrium between vapour and liquid phases at given temperature T , the phases are under the same pressure p

$$p = p(T, \rho^{(g)}) = p(T, \rho^{(l)}), \quad (1)$$

and fugacities f of the phases must be equal

$$f(T, \rho^{(g)}) = f(T, \rho^{(l)}), \quad (2)$$

where ρ is molar density, and superscripts (l) and (g) denote the liquid and the vapour phase, respectively. Orthobaric molar densities $\rho^{(g)}$ and $\rho^{(l)}$ are obtained by solving this set of two non-linear equations (1) and (2). After obtaining the solution, saturated vapour pressure is directly calculated from a given equation of state using Eq. (1).

The Newton–Raphson Method

For simplicity we will use an abbreviated notation $p^{(g)} = p(T, \rho^{(g)})$, $p^{(l)} = p(T, \rho^{(l)})$, $f^{(g)} = p(T, \rho^{(g)})$, $f^{(l)} = p(T, \rho^{(l)})$. Typically, the set of equations (1) and (2) is solved using the Newton–Raphson method, *i.e.*, by iterative solving of

$$\begin{aligned} \left(\frac{\partial p}{\partial \rho}\right)^{(g)} \Delta \rho^{(g)} - \left(\frac{\partial p}{\partial \rho}\right)^{(l)} \Delta \rho^{(l)} &= p^{(l)} - p^{(g)} \\ \left(\frac{\partial f}{\partial \rho}\right)^{(g)} \Delta \rho^{(g)} - \left(\frac{\partial f}{\partial \rho}\right)^{(l)} \Delta \rho^{(l)} &= f^{(l)} - f^{(g)}, \end{aligned} \quad (3)$$

where $\Delta \rho = \rho_{i+1} - \rho_i$ and i is the iteration step number. Convergence of the iteration process depends on initial estimates $\rho_0^{(l)}$ and $\rho_0^{(g)}$. It can be easily shown (see, *e.g.*, ref.¹) that the necessary condition of convergence is the condition of mechanical stability

$$\left(\frac{\partial p}{\partial \rho}\right)_T > 0 \quad (4)$$

that must be met in both phases (see Fig. 1a).

However, the condition of stability must be obeyed not only for the initial estimates but also in each iteration step. If the increments $\Delta \rho^{(l)}$ and $\Delta \rho^{(g)}$ are large, the iterations may diverge. For this reason, it is useful to damp the increments

$$\Delta \rho_{\text{damp}}^{(l)} = k \Delta \rho^{(l)}, \quad \Delta \rho_{\text{damp}}^{(g)} = k \Delta \rho^{(g)}. \quad (5)$$

In this work, we have chosen the following damping constant k

$$k = 0.2 / \left[\left(\frac{\Delta \rho^{(l)}}{\rho^{(l)}} \right)^2 + \left(\frac{\Delta \rho^{(g)}}{\rho^{(g)}} \right)^2 \right].$$

In Fig. 1b the area of first estimates of $V_m^{(l)} = 1/\rho^{(l)}$ and $V_m^{(g)} = 1/\rho^{(g)}$ is schematically depicted. Line A corresponds to the condition $(\partial p / \partial \rho)_T = 0$ for the liquid side, *i.e.*, the set of Eqs (3) does not converge for initial estimates of liquid volumes greater than V_A . Similarly, line C restricts the range of initial

estimates of gas densities, *i.e.*, the equations do not converge for initial estimates $V^{(g)} < V_C$. Line B is not dictated by thermodynamics but by numerics. It corresponds to the highest initial estimates of liquid densities for which the set of damped equations converges within 50 iteration steps, when the damping constant k is employed, and the convergence is reached when $k \leq 10^{-8}$. The line was found by trials.

The Proposed Method

The main source of problems with the convergence of Eqs (1) and (2) is the existence of an infinite number of non-physical trivial solutions

$$\rho^{(l)} = \rho^{(g)} .$$

These undesirable solutions may be eliminated using a similar approach to that proposed in ref.² for calculation of compositions of two liquid phases in equilibrium. Equations (1) and (2) may be rewritten to

$$\frac{p^{(g)} - p^{(l)}}{(\rho^{(g)} - \rho^{(l)})^n} = 0 \quad (6)$$

$$\frac{f^{(g)} - f^{(l)}}{(\rho^{(g)} - \rho^{(l)})^n} = 0 , \quad (7)$$

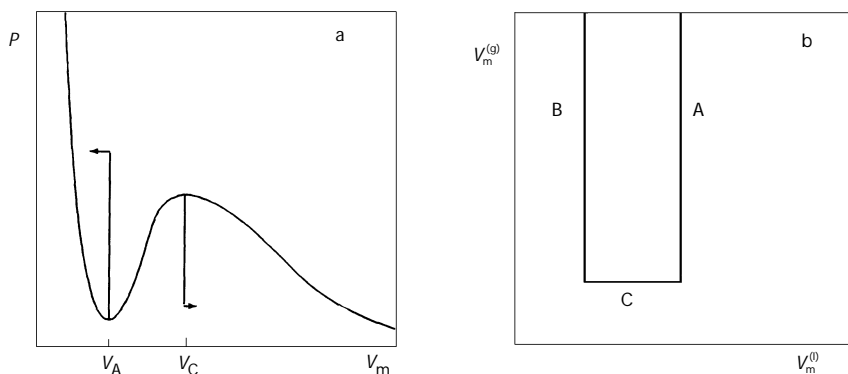


FIG. 1

a An isotherm at a subcritical temperature. V_A and V_C are volumes in the minimum and maximum, respectively. b Region of the first estimates of $V_m^{(l)} = 1/\rho^{(l)}$ and $V_m^{(g)} = 1/\rho^{(g)}$ for which the proposed equations either converge or diverge. Physical meaning of lines A, B and C is described in the text

where n is the multiplicity of the trivial solutions that is *a priori* unknown³. The equations may be solved using the Newton–Raphson method.

$$\begin{aligned} \left[\left(\frac{\partial p}{\partial \rho} \right)^{(g)} + n \frac{p^{(g)} - p^{(1)}}{[\rho^{(1)} - \rho^{(g)}]} \right] \Delta \rho^{(g)} - \left[\left(\frac{\partial p}{\partial \rho} \right)^{(1)} + n \frac{p^{(g)} - p^{(1)}}{[\rho^{(1)} - \rho^{(g)}]} \right] \Delta \rho^{(1)} &= \\ &= p^{(1)} - p^{(g)} \\ \left[\left(\frac{\partial f}{\partial \rho} \right)^{(g)} + n \frac{f^{(g)} - f^{(1)}}{[\rho^{(1)} - \rho^{(g)}]} \right] \Delta \rho^{(g)} - \left[\left(\frac{\partial f}{\partial \rho} \right)^{(1)} + n \frac{f^{(g)} - f^{(1)}}{[\rho^{(1)} - \rho^{(g)}]} \right] \Delta \rho^{(1)} &= \\ &= f^{(1)} - f^{(g)} \end{aligned} \quad (8)$$

These equations reduce to Eqs (3) for $n = 0$.

We performed a number of numerical tests of the efficiency and the robustness of the iterative solutions of Eqs (3) and (8) for methane using the Redlich–Kwong equation of state. The increments in densities were damped using Eqs (5). Table I shows numbers of iterations in dependence on the trivial solution multiplicity n .

It can be seen from Table I that the optimum value of n (*i.e.*, n corresponding to the minimum number of iteration steps n_{step}) is 20, suggesting that multiplicity of trivial solutions is surprisingly large. This is probably not true, and one should not call n the multiplicity but a free parameter. The change of Eqs (1) and (2) to equivalent equations (6) and (7) eliminates not only the trivial solutions but changes also their convergence properties. In other words the trivial solutions can be, for example, eliminated already for $n = 1$, but the use of larger n improves the convergence. We wish to note that the optimum value $n = 20$ (shown in Table I) is just a particular num-

TABLE I

Number of iteration steps as a function of the trivial solution multiplicity n (methane, $T = 150$ K, initial estimates $V_m^{(l)} = 55$ cm³/mol, $V_m^{(g)} = 10\,000$ cm³/mol), n_{step} is a number of iteration steps

n	0	1	2	3	4	5	10	20	50	100	200
n_{step}	29	25	22	19	18	17	13	10	11	18	31

ber depending on a state point, on a criterion on convergence, and on the equation of state used.

Robustness of the proposed method, *i.e.*, its relative insensitivity to initial estimates, has been tested for $n = 1, 2$ and 3 at $T = 130, 150$ and 170 K. The

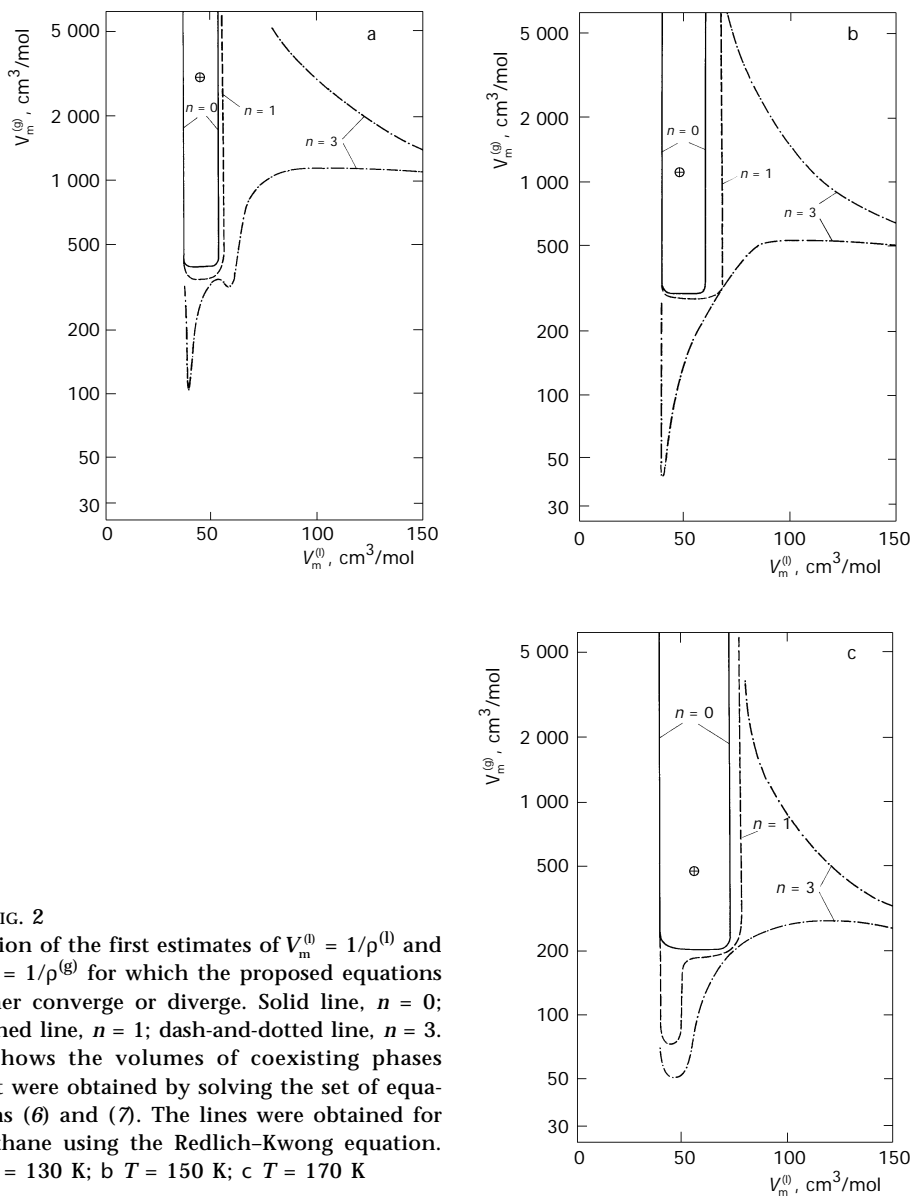


FIG. 2

Region of the first estimates of $V_m^{(l)} = 1/\rho^{(l)}$ and $V_m^{(g)} = 1/\rho^{(g)}$ for which the proposed equations either converge or diverge. Solid line, $n = 0$; dashed line, $n = 1$; dash-and-dotted line, $n = 3$. \oplus shows the volumes of coexisting phases that were obtained by solving the set of equations (6) and (7). The lines were obtained for methane using the Redlich-Kwong equation. a $T = 130$ K; b $T = 150$ K; c $T = 170$ K

results are shown in Fig. 2. The figure shows that the region of initial estimates, at which the set of equations (6) and (7) converges, increases with increasing n . We note that for $n > 0$, solutions can be obtained even if the inequality (4) is not obeyed. For example, a solution was found at $T = 150$ K starting from very bad estimates $V_m^{(l)} = 45$ cm³/mol and $V_m^{(g)} = 46$ cm³/mol if $n = 3$ was used.

Despite of the fact that the proposed method is less sensitive to initial estimates, it is reasonable to use the estimates as close to the solution as possible. Often a value of the saturated vapour pressure at a given temperature is known, for example from the Antoine equation. Values of the liquid and the gas densities calculated from an equation of state at this pressure are usually very good estimates. Also, if the orthobaric densities are calculated at several temperatures, the results for close temperature are excellent estimates (see ref.⁴).

CONCLUSIONS

A modification of Eqs (1) and (2) into (6) and (7) for calculation of gas-liquid equilibria which eliminates undesirable trivial solutions for liquid and gas orthobaric densities has been proposed. The modification is combined with the Newton-Raphson method to solve the set of non-linear equations. Using the Redlich-Kwong equation of state for methane as an example, it was shown that the proposed method is more efficient (requiring less iteration steps) and more robust (less sensitive to initial estimates) than the Newton-Raphson method applied to the original set of equations.

The method can be used for any equation of state and it can also be easily extended to mixtures.

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