REMARKS ON SOLUTION METHODS OF VIRIAL-TYPE EQUATIONS OF STATE

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Received December 10, 1984

Summary

The paper gives an unconditionally successful and rapidly converging procedure to solve virial-type EOS for the unknown vapor and liquid densities, and presents methods to improve the convergence of the vapor-liquid equilibrium ratios and of the vapor-liquid rate.

Knowing the $F(P, T, z_1, z_2, \ldots, z_i, \ldots) = 0$ equation of state and the ideal gas heat capacities $(C^*_{p,i} = C_{p,i}(p=0, T))$ all important thermodynamic data may be calculated. The general spread of the electronic computers enabled the establishment and usage of virial equations—being fit both for the vapor and liquid phase—instead of the previous, more simple equations of state. We give some remarks about the usage of the virial equation in this paper.

Let us consider the following task! Given are the pressure (P), temperature (T) and the over-all mole fractions (Z_i); we look for the vapor rate (V), for the mole fractions in vapor and liquid phase $(Y_i$ and $X_i)$, for the vapor and liquid densities (ϱ_v, ϱ_l), enthalpies (h_v, h_l) and entropies (s_v, s_l). The well-known block-scheme of the solution is shown in Fig. 1.

Our remarks concern about steps ③, ④ and ⑤ in Fig. 1. Step ⑤, the most decisive part of the calculation gives rapid convergence, according to the literature. But our experience is that convergence often oscillates

$$(K_i^{(m-2)} > K_i^{(m-1)} < K_i^{(m)} \quad \text{or} \quad K_i^{(m-2)} < K_i^{(m-1)} > K_i^{(m)}).$$

We assume in this cases that the absolute value of the deviation from the proper $K_i = K_i^{(\infty)}$ value—as a function of iteration-step-number—diminishes exponentially; then we don't continue the calculation with $K_i^{(m)}$ in the m-th step, but with

$$K_i^{(m*)} = \frac{K_i^{(m-2)} K_i^{(m)} - K_i^{(m-1)} K_i^{(m-1)}}{K_i^{(m)} - 2K_i^{(m-1)} + K_i^{(m-2)}} \tag{1}$$

① INPUT: P, T, Z_i

② Estimation of $K_i^{(0)} = Y_i/X_i$ equilibrium ratios. (e.g. $K_i^{(0)} = P_{si}/P$, P_{si} is the vapor pressure of i-th component at temperature T)

③ Flash calculation using the following equations:

$$\sum \frac{Z_i(K_i-1)}{V(K_i-1)+1} = f(V) = 0$$

$$X_i = \frac{Z_i}{V(K_i-1)+1}$$

$$Y_i = K_i X_i$$

④ Making use of P, T, Y_i and X_i, construction of $\sum_j V_j(T)\varrho^j - P = 0$ and seeking for its largest/least positiv root (ϱ_l, ϱ_v, respectively), and calculation of the vapor/liquid fugacities ($F_{i,v}, f_{i,l}$).

⑤ Correction of the equilibrium ratios:

$$K_i^{(m+1)} = K_i^{(m)} \cdot f_{i,l}/f_{i,v}$$

⑥ IF $K_i^{(m+1)} \neq K_i^{(m)}$ THEN GO TO ③

⑦ Entalpy and entropy calculation

⑧ END

Fig. 1

The details are shown in Fig. 2. Using correction (1) in the m-th step only if it was not used in steps $(m-1)$ and $(m-2)$, the speed of convergence increases considerably in case of oscillation. However, it would lead to convergence in most cases of oscillating divergence too.

The $F(V)=0$ equation in step ③ is often solved by Newton's tangent method to get the $0 \leq V \leq 1$ root, if it exists. Since $f(V)$ decreases monotonously in the interval (0, 1) the existence of the root may be determined using the signs of $f(0)$ and $f(1)$. In all steps of reiteration, the fastest way to approach the root
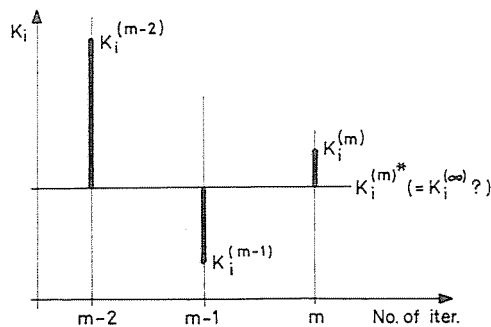

Fig. 2

is to seek for the root of the wire (V_1 in Fig. 3.), for the roots of the tangents of $f(V)$ on the borders of the narrowest known interval containing the root (V_2 and V_3 in Fig. 3). If V_2 and/or V_3 is not in this interval we assume them/it being on the nearer border.

We combine the central root (V_2 in Fig. 3.) with the center of the interval (V_0) so, that the weight of V_0 decreases rapidly during the successive
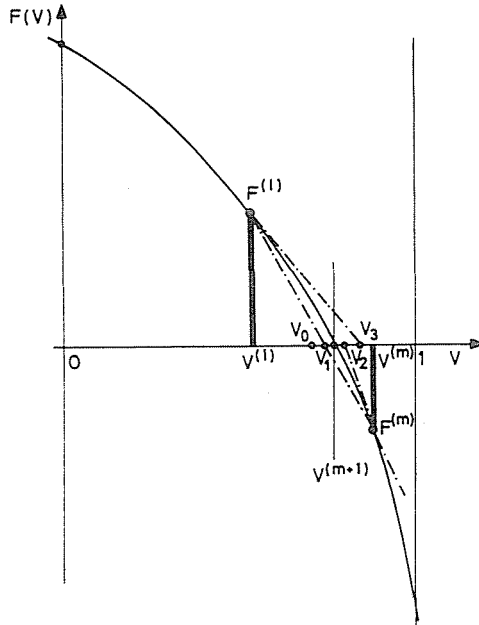

Fig. 3

approximation. We regard the value V got in this way ($V^{(m+1)}$) as the new approximation of the root and this V is one of the borders of the interval containing the root in the next step of the approximation.

In step ④, the task is to find the least/largest positive root of equation:

$$\overline{f(\varrho)} = \sum_{j} V_j(T)\varrho^j = P \tag{2}$$

to get the density of the vapor/liquid phase. Since the well known methods are either slow (e.g. Johnson, Colver, Hydrocarbon Processing, 1968/12. p. 79—83) or do not lead to the solution in all cases (e.g. Starling, Fluid Thermodynamic Properties..., Gulf, 1973), we give a relatively fast and unconditionally stable procedure (see Fig. 4).

An $f_n(\rho) = P$ and an $f_k(\rho) = P$ ($f_n(\rho) \geq f(\rho) \geq f_k(\rho), 0 \leq \rho$) is to solve first for getting a (ρ_k, ρ_n) interval that contains all positive roots of eq. (2). Then we use
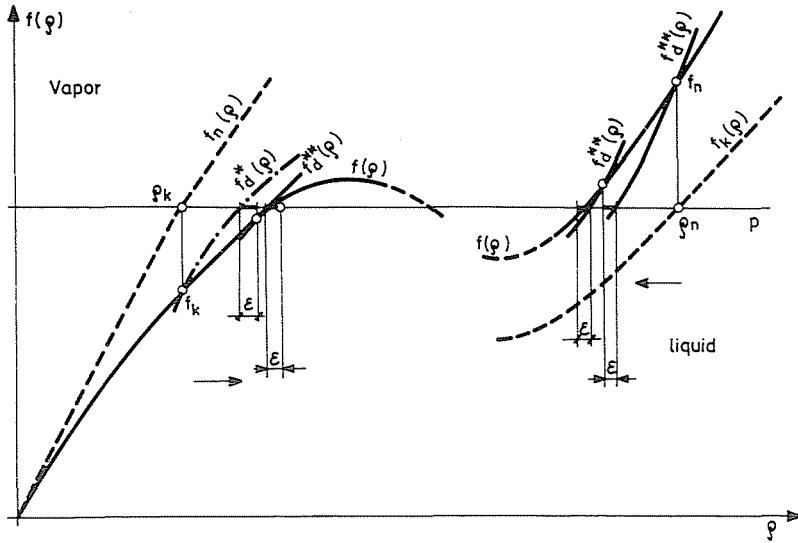
Fig. 4

Newton's tangent method—based on ρ_k (in case of vapor) or ρ_n (in case of liquid)—with two modifications. These are as follows:

a) The corrections are greater than the calculated ones by ε ($\varepsilon \approx 0$).

b) The first derivatives of the $f_d^*, f_d^{**}, \ldots$ functions are not equal to the derivative of $f(\rho)$ in the base point, but $\dfrac{\mathrm{d} f_d^*}{\mathrm{d}\rho} \geqq \dfrac{\mathrm{d} f}{\mathrm{d}\varrho}, \dfrac{\mathrm{d} f_d^{**}}{\mathrm{d}\rho} \geqq \dfrac{\mathrm{d} f}{\mathrm{d}\varrho}, \ldots$ in the whole interval. We used as the f_d^*, f_d^{**} functions polynominals of third degree.

Repeating this procedure, we get in some steps an interval with a width of ε, that contains only the wished root. Then we can find the root with any suitable method.

In step ④, it is necessary to calculate the coefficients of the mixture's equation of state. That is very time-consuming for multicomponent mixtures, so it is suitable to make use of symmetries. E.g. the second virial-coefficient is

$$B = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j B_{i,j} \quad \text{where} \quad B_{i,j} = B_{j,i}$$

So it is better to use the following form:

$$B = \sum_{i=1}^{n} x_i x_i B_{i,i} + 2 \sum_{i=1}^{n-1} x_i \sum_{j=i+1}^{n} x_j B_{i,j}.$$

Organizing suitably the calculation described above, it is easy to write simple subroutines to calculate different equipments (e.g. heat exchangers, separators, compressors, ets.); their results are the data of the exhaust streems

while input data are the data of the inlet streems and some characteristics of the equipments (e.g. thermal efficiency, effectiveness of separation, internal efficiency and back-pressure). Having a main program that directs the callings of the subroutines calculating the equipments and coordinates the inlet and exhaust streems, it is possible to calculate whatever cycles or processes (e.g. natural gas processing, sorption cooling machine, etc.).
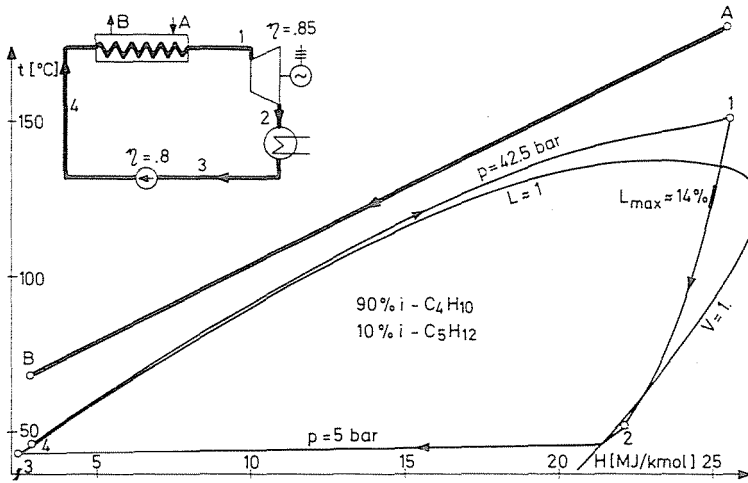

Fig. 5

Table 1

Point		1	2	3	4
Z1	—	.9	.9	.9	.9
Z2	—	.1	.1	.1	.1
V	—	1	1	0	0
P	bar	42.5	5	5	42.5
T	C°	152	51.9	42.4	45.1
ρ	kg/m^3	208.7	12.51	530.4	535.0
H	MJ/kmole	25.57	22.11	2.42	2.94
S	kJ/kmole, K	633.754	635.879	573.830	574.160
M	kg/kmole	59.52	59.52	59.52	59.52

$\eta_{eff} = 13\%$ $P_{eff} = 45$ MW
Heat consumption $= 27.72$ MJ/kWh
Water consumption $= 57.9$ kg/kWh
Process fluid $= 72.9$ kg/kWh   (3.28×10^6 kg/h)

We examined a simple Rankine-cycle with a process fluid containing 90% i-C_4H_{10} and 10% i-C_5H_{12} for utilization of geothermal energy using such a program—based on the equation of state of Starling. The cycle is taken from EPRI Journal, 1983/12, p. 34.

Our results are shown in Table 1., the cycle is shown in Fig. 5. The agreement to the published data is satisfactory. It may be seen that the method above enables thermodynamic calculation with reasonable speed and accuracy.

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