Flash calculation is essential in solving nonlinear simultaneous algebraic equations. This problem has been solved by the Newton-Raphson method or by the successive substitution method, which is simple but time-consuming because of its iterative features. New algorithms of flash calculation using the Newton-Raphson method have been presented by Holland and Hirose. In this paper, the new algorithms are further improved. The non-idealities of both vapor and liquid phases are considered and the Newton-Raphson loop, which is necessary to obtain the compressibility factor by the equation of state, is combined with the principal flash calculation loop, which is related to other dependent variables. Consequently, the proposed method has only one Newton-Raphson loop. The usefulness of this new algorithm is illustrated by a simulation of a part of an air separation process.

1. Basic Equations

The residual functions required to describe an equilibrium stage are summarized in Table 1. The application of the Newton-Raphson method to these residual functions may be expressed in compact form as

\[
\frac{\partial F}{\partial X} \cdot \Delta X = -F
\]

where \( F \) is the vector of the residual functions, \( X \) is the vector of the dependent variables and \( \Delta X \) is the vector of the Newton-Raphson corrections. The Jacobian matrices \( \left[ \frac{\partial F}{\partial X} \right] \) are as follows for each case:

1) Isothermal flash (to calculate \( x_i, y_i, r, q, \) and \( z \) under given temperature \( T \) and \( P \))

\[
D = f(T, P, y_i, \text{physical properties}, z)
\]

For example,

\[
D = \frac{z}{z-B^s P - \frac{A^s P^2}{B^s z+B^s P - z}}
\]

2) Liquid cooling or heating (to calculate \( x_i, y_i, P, T, \) and \( z (q=1) \) under given enthalpy \( H_P \))

3) Bubble point calculation (to calculate \( x_i, y_i, T, \) and \( z (q=1) \) under given \( P \))

4) Flash at constant \( q \) (to calculate \( x_i, y_i, T, \) and \( z \) under given \( q \) and \( P, 0 \leq q < 1 \) (\( q=0; \) Dew point calculation))

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Table 2 Computational results

<table>
<thead>
<tr>
<th>Initial stream</th>
<th>Liquid cooling</th>
<th>Joule-Thomson expansion</th>
<th>Bubble point cal.</th>
<th>Dew point cal.</th>
<th>Flash at constant q</th>
<th>Isothermal flash</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P$ [atm]</td>
<td>6.00</td>
<td>4.18</td>
<td>1.3</td>
<td>1.3</td>
<td>1.3</td>
<td>1.3</td>
</tr>
<tr>
<td>$T$ [K]</td>
<td>100.4</td>
<td>96.27</td>
<td>83.26</td>
<td>82.94</td>
<td>86.83</td>
<td>83.79</td>
</tr>
<tr>
<td>$h_f$ [J/mol]</td>
<td>4869</td>
<td>4631</td>
<td>3919</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$s_f$ [J/mol]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$q$ [-]</td>
<td>1</td>
<td>0.8750</td>
<td>0</td>
<td>0.7</td>
<td>0.3647</td>
<td>0.3953</td>
</tr>
<tr>
<td>$z$ [-]</td>
<td>0.8975</td>
<td>0.9553</td>
<td>0.9550</td>
<td>0.9589</td>
<td>0.9559</td>
<td>0.9572</td>
</tr>
<tr>
<td>Composition [%]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$x_1$</td>
<td>0.5944</td>
<td>0.5944</td>
<td>0.5613</td>
<td>0.5944</td>
<td>(0.2733)</td>
<td>0.5085</td>
</tr>
<tr>
<td>$x_2$</td>
<td>0.0165</td>
<td>0.0165</td>
<td>0.0174</td>
<td>0.0165</td>
<td>(0.0191)</td>
<td>0.0186</td>
</tr>
<tr>
<td>$x_3$</td>
<td>0.3891</td>
<td>0.3891</td>
<td>0.4213</td>
<td>0.3891</td>
<td>(0.0706)</td>
<td>0.4729</td>
</tr>
<tr>
<td>$y_1$</td>
<td>(0.7981)</td>
<td>0.8258</td>
<td>(0.8435)</td>
<td>0.5944</td>
<td>0.7948</td>
<td>0.7174</td>
</tr>
<tr>
<td>$y_2$</td>
<td>(0.0112)</td>
<td>0.0104</td>
<td>(0.0096)</td>
<td>0.0165</td>
<td>0.0117</td>
<td>0.0143</td>
</tr>
<tr>
<td>$y_3$</td>
<td>(0.1907)</td>
<td>0.1638</td>
<td>(0.1469)</td>
<td>0.3891</td>
<td>0.1935</td>
<td>0.2683</td>
</tr>
<tr>
<td>$\phi_1$ [-]</td>
<td>0.9097</td>
<td>0.9583</td>
<td>0.9579</td>
<td>0.9627</td>
<td>0.9590</td>
<td>1</td>
</tr>
<tr>
<td>$\phi_2$ [-]</td>
<td>0.8976</td>
<td>0.9531</td>
<td>0.9527</td>
<td>0.9580</td>
<td>0.9539</td>
<td>1</td>
</tr>
<tr>
<td>$\phi_3$ [-]</td>
<td>0.8950</td>
<td>0.9520</td>
<td>0.9515</td>
<td>0.9570</td>
<td>0.9528</td>
<td>1</td>
</tr>
<tr>
<td>$f_i^2/p_i^2$ [-]</td>
<td>0.8437</td>
<td>0.9243</td>
<td>0.9257</td>
<td>0.9059</td>
<td>0.9216</td>
<td>1</td>
</tr>
<tr>
<td>$f_i^2/p_i^2$ [-]</td>
<td>0.9318</td>
<td>0.9746</td>
<td>0.9752</td>
<td>0.9594</td>
<td>0.9733</td>
<td>1</td>
</tr>
<tr>
<td>$f_i^2/p_i^2$ [-]</td>
<td>0.9422</td>
<td>0.9815</td>
<td>0.9820</td>
<td>0.9663</td>
<td>0.9805</td>
<td>1</td>
</tr>
<tr>
<td>Iteration No.</td>
<td>3</td>
<td>5</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
</tbody>
</table>

---

- given value; ( ) apparent value
* vapor phase non-ideality is considered by the Redlich-Kwong equation.
** vapor phase non-ideality is considered by the virial equation whose coefficients are obtained from the experimental data.6)

Fig. 1 Flow chart of calculation procedure

5) Isenthalpic expansion (Joule-Thomson expansion) [to calculate $x_i, y_i, r, q, T,$ and $z$ under given enthalpy $H_f$ and $P$]

\[
\frac{\partial(M_1, \ldots, M_m, N_1, \ldots, N_m, E, S_1, S^*), D)}{\partial(x_1, \ldots, x_m, y_1, \ldots, y_m, T, r, q, z)} \quad [2(m+4)\text{matrix}]\]

\[
\sum_{i=1}^{\infty} (M_i + N_i^2) + S_i^2 + S_i^* + D^2 + E^2 < \text{convergence tolerance}
\]

The calculation procedure of the proposed method is shown in Fig. 1. The proposed method has only one Newton-Raphson loop and no successive substitution procedures.

2. Numerical Examples

Every case listed above is illustrated in a simulation of a part of an air separation process. Figure 2, in which a schematic diagram of temperature-entropy is shown, may help one to visualize each state of the numerical examples. Physical properties and equations of vapor pressure, the activity coefficient, and the enthalpy for the ternary system N2-Ar-O2 are presented in Reference (2).

The computational results are shown in Table 2.
A liquid air stream from the bottom of the lower column of a dual distillation tower is cooled by a heat exchanger (Fig. 2) and then is flashed through an expansion valve, following the principle of the Joule-Thomson effect (Fig. 2), flash calculations at constant q, bubble point calculation, and an isothermal flash calculation, respectively. A comparison of the computational result with actual data (Kobe Steel, Ltd.) for the temperature change due to Joule-Thomson expansion shows good agreement.

In each case, convergence is achieved in fewer than six iterations. As shown in the computational results of the isothermal flash calculation, there are some differences between the values of the dependent variables obtained by assuming that both the vapor and liquid phases are ideal and those obtained by using the Redlich-Kwong equation or the virial equation whose coefficients were determined by experimental data to evaluate the fugacity coefficient of the vapor and by Prausnitz’s method to calculate the fugacity of liquid. If another equation of state is used to consider the nonideality of vapor phase, we need only one procedure, that is, we replace the residual function Eq. (6) or (7) with its residual function.

This result indicates that the effect of the nonidealities of both vapor and liquid phases cannot be ignored for rigorous flash calculations.

For comparison, the proposed method is applied to a problem (isothermal flash calculation; system [methanol-ethanol-water]) which required 23 iterations for a converged solution by the previously presented successive substitution method. Convergence of the same problem is achieved in 3 iterations by the proposed method.

A new algorithm of the general flash calculation by the Newton-Raphson method is presented. Numerical examples indicate that the proposed method is useful and is easily programmed.

**Nomenclature**

- $A^i, A^i_1$, $B^i, B^i_1$, $B_{12}$: constants in the Redlich-Kwong equation
- $D^i$: residual function related to equation of state
- $E^i$: residual function defined by Eq. (8)
- $F^i$: vector of residual functions
- $f^i_{p, v}$: fugacity of component i in the liquid phase
- $H_{p, v}$: enthalpy per mole of mixture in the vapor state
- $H_M$: enthalpy per mole of mixture in the liquid state
- $M_i$: residual function defined by Eq. (1)
- $m$: number of components
- $N_i$: residual function defined by Eq. (2)
- $P$: total pressure
- $p^i_{p, v}$: vapor pressure of component i
- $q$: fraction of liquid to feed
- $R$: gas constant
- $r$: $1 - q$
- $S_i$: residual function defined by Eq. (3)
- $S_i$: residual function defined by Eq. (4)
- $T$: absolute temperature
- $X$: vector of variables
- $x_i$: mole fraction of component i in the liquid phase
- $x_i$: mole fraction of component i in the feed
- $y_i$: mole fraction of component i in the vapor phase
- $z$: compressibility factor
- $\gamma_i$: activity coefficient of component i in the liquid phase
- $\phi_i$: fugacity coefficient of component i in the vapor phase

**Literature Cited**