partial difference equation such as Equation (15), (22), or (42), the memory requirement of the present approach should be about the same order of magnitude as the traditional methods. It should be noted that we encounter the dimensionality difficulty only when we solve Equation (11) directly on the computer.

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NOTATION

b = given initial condition
c = given final condition
D = distillate rate
J = Jacobian matrix
K = equilibrium ratio
L = flow rate of L phase
$l_i(k)$ = moles per hour of component i in the L phase from stage k
m = number of components or total number of state variables
N = total number of stages
n = stage number, a parameter
r = missing final or missing initial condition
V = flow rate of V phase
$v_i(k)$ = moles per hour of component i in the V phase entering stage k
$x_i(k)$ = concentration of i^{th} component leaving the k^{th} stage in the L phase
$y_i(k)$ = concentration of i^{th} component entering the k^{th} stage in the V phase
η, ζ, ν = functions defined by Equation (24) or (46)

Subscripts

D = distillate
f = feed
H = heavy key
i = i^{th} component
k = k^{th} iteration, assumed known
$k + 1$ = $(k + 1)$ iteration, assumed unknown
L = light key

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COMMUNICATIONS TO THE EDITOR

Vapor-Liquid Equilibria of the Hydrochloric Acid-Water System

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According to the criterion that the chemical potential of a component is the same in all phases at equilibrium, one writes

$$\mu_v = \mu_L \tag{1}$$

From the definition of activity and fugacity, these are given by

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$$\mu_v = \mu_v^0 + RT \ln f \qquad (2)$$

$$\mu_L = \mu_L^0 + RT \ln a \qquad (3)$$

Since hydrochloric acid is a 1-1 electrolyte, its activity is

$$a = (a_+)(a_-) = a_\pm^2 = X_\pm^2 \ \gamma_\pm^2 \qquad (4)$$

where $a_\pm$ is the mean ionic activity, $X_\pm$ denotes the mean mole fraction of the ions, and $\gamma_\pm$ is the mean ionic activity coefficient. Combining Equations (2), (3), and (4), we get

$$\mu_v^0 + RT \ln f = \mu_L^0 + 2RT \ln X_\pm + 2RT \ln \gamma_\pm \qquad (5)$$

If we let

$$\mu_L^0 - \mu_v^0 = RT \ln K$$

then

$$f = K \, X_\pm^2 \ \gamma_\pm^2 \qquad (6)$$

If the pressure in the system is so low that the vapors are nearly ideal gases, the fugacity may be replaced by the partial vapor pressure of hydrochloric acid; thus

$$p_{\mathrm{HCl}} = y_{\mathrm{HCl}} \ P_t = K \ X_\pm^2 \ \gamma_\pm^2 \qquad (7)$$

The partial vapor pressure of water is given by

$$p_{\mathrm{H_2O}} = y_{\mathrm{H_2O}} \ P_t = P^0_{\mathrm{H_2O}} \ X_{\mathrm{H_2O}} \ \gamma_{\mathrm{H_2O}} \qquad (8)$$

where $P^0_{\mathrm{H_2O}}$ is the vapor pressure of pure water, $X_{\mathrm{H_2O}}$ is the mole fraction of water in the liquid phase based on all the species present in the solution, and $\gamma_{\mathrm{H_2O}}$ is the activity coefficient of water. From Equations (7) and (8), one obtains

$$y_{\mathrm{HCl}}/[1 - y_{\mathrm{HCl}}] = K \ X_\pm^2 \ \gamma_\pm^2 / P^0_{\mathrm{H_2O}} \ X_{\mathrm{H_2O}} \ \gamma_{\mathrm{H_2O}} \qquad (9)$$

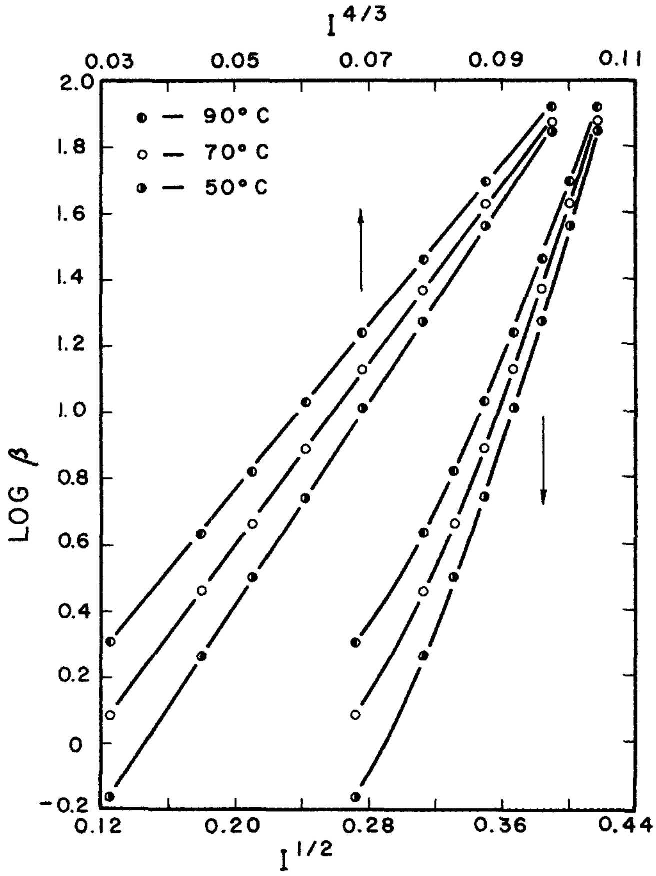

Fig. 1. Log β vs. $I^{1/2}$ and $I^{4/3}$ for the hydrochloric acid-water system:

$\log \beta = 24.50 \, I^{4/3} - 0.46$ (90°C.)
$\log \beta = 27.17 \, I^{4/3} - 0.76$ (70°C.)
$\log \beta = 30.39 \, I^{4/3} - 1.10$ (50°C.)

If we let

$$\beta = y_{\mathrm{HCl}} \ X_{\mathrm{H_2O}} / [1 - y_{\mathrm{HCl}}] \ X_\pm^2 \qquad (10)$$

Equation (9) becomes

$$\beta = [K/P^0_{\mathrm{H_2O}}] \ [\gamma_\pm^2/\gamma_{\mathrm{H_2O}}] \qquad (11)$$

that is

$$\log \beta = \log[K/P^0_{\mathrm{H_2O}}] + \log [\gamma_\pm^2/\gamma_{\mathrm{H_2O}}] \qquad (12)$$

Hala et al. (*1*) suggested that

$$\log [\gamma_\pm^2/\gamma_{\mathrm{H_2O}}] = b_0 \ I^{1/2} + b_1 \qquad (13)$$

and thus

$$\log \beta = \log [K/P^0_{\mathrm{H_2O}}] + b_0 \ I^{1/2} + b_1 = b_0 \ I^{1/2} + b_2 \qquad (14)$$

If the variation of the total vapor pressure is small, as is the case for the present system, the effect of pressure on the mean activity coefficient is negligible, and b_0, b_1, and b_2 can thus be considered as constant for a given temperature. It has been found that the vapor-liquid equilibria of the hydrochloric acid-water system do not obey Hala's equation. As is seen from Figure 1, for data taken from Perry's Handbook (*2*), the relationship between log β and $I^{1/2}$ for the hydrochloric acid-water system is not linear. Instead, log β varies with $I^{4/3}$ linearly. $X_{\mathrm{H_2O}}/X_\pm^2$ and I were calculated according to the following equations, respectively:

$$X_{\mathrm{H_2O}}/X_\pm^2 = [1 - x_{\mathrm{HCl}}^2]/x_{\mathrm{HCl}}^2 \qquad (15)$$

$$I = \frac{1}{2} \cdot [1 + 1] \ x_{\mathrm{HCl}} = x_{\mathrm{HCl}} \qquad (16)$$

The vapors of the present system have a negative deviation from Raoult's law; that is, the vapor pressure of each constituent is less than that required by the Raoult equation.

NOTATION

a = activity
b_0, b_1, b_2 = constants
f = fugacity
I = ionic strength
K = constant
P = vapor pressure
P_t = total vapor pressure
R = gas constant
T = absolute temperature
x = mole fraction in the liquid phase
X = mole fraction in the liquid phase based on all the species present
y = mole fraction in the vapor phase
β = dimensionless group
γ = activity coefficient
μ = chemical potential

Subscripts

L = liquid phase
v = vapor phase
$\pm$ = mean value

Superscripts

0 = standard state

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