Partial Derivatives of Thermodynamic Properties

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Introduction

It is generally recognized that the cost of single- or multistage, multicomponent equilibrium calculations is dominated by the requirement for evaluation of thermodynamic properties from rigorous and fairly complex models. This is particularly severe for nonideal mixtures, where conventional simulation methods based on the assumption of ideal behavior require a substantial number of iterations to converge.

Various alternatives have been proposed in order to reduce the cost of simulation and the number of iterations required, the most important being:

1. The use of Newton's method with either analytical or numerical derivatives (Naphtali and Sandholm, 1971; Fredenslund et al., 1977; Christiansen et al., 1979; Michelsen, 1982).
2. Quasi-Newton methods, where information from past iterations is used to build approximations to the Jacobian (Boston and Britt, 1978; Gallun and Holland, 1980; Lucia and Machietto, 1983; Westman et al., 1984).
3. Approximation with "local" simple models, in which the parameters are adapted to the rigorous model during the course of calculation (Chimowitch et al., 1983).

In the majority of cases Newton's method is superior with regard to robustness and the number of iterations required, but the alternative methods will often be less time-consuming than Newton's method if numerical differentiation is used to obtain the required derivatives. Analytical derivatives are generally not considered a possibility as they are claimed to be unavailable in physical properties subroutines or difficult and expensive to evaluate.

Superficially, these arguments are convincing, and also in earlier work from this department numerical differentiation (Fredenslund et al., 1977) or fairly complex expressions for analytical derivatives (Christiansen et al., 1979) have been proposed. Yet, the underlying thermodynamic structure in all cases we have encountered permits fairly simple and inexpensive evaluation of the needed derivatives. The aim of this note is to provide methods of evaluation and expressions for the required derivatives, and to demonstrate that their cost for a wide range of currently used models is far smaller than is commonly assumed.

Thermodynamic Properties for Process Simulation

The thermodynamic property routines required depend on whether, as in most low-pressure applications, an activity coefficient model is used for the liquid phase, or whether an equation of state is used for both fluid phases.

When activity coefficient models are used, nonideality in the vapor phase is usually of minor importance, and vapor phase thermodynamics is usually described using the ideal gas law or the virial equation (Prausnitz et al., 1980). The dominant source of nonideality is the liquid phase, and current activity coefficient models of widespread use comprise the Wilson equation (Wilson, 1964), the NRTL equation (Renon and Prausnitz, 1968), the UNIQUAC equation (Abrams and Prausnitz, 1975), and the UNIFAC group contribution method (Fredenslund et al., 1975, 1977). The partial derivatives of interest are the composition and temperature derivatives of the activity coefficients. Molar excess enthalpies are in turn obtained from the temperature derivatives of the activity coefficients.

For high-pressure calculations, nonideality in both phases is of importance, and most often thermodynamic properties for both fluid phases are obtained from the same equation of state. Cubic equations of state like the RKS equation (Soave, 1972) and the Peng-Robinson equation (Peng and Robinson, 1976) are widely used, but newer and much more complex equations like the GC-EOS (Skjold-Jørgensen, 1984) and the random/nonrandom equation of state (Mollerup, 1985) have recently been proposed. For equations of state, Newtonlike methods require partial composition derivatives of component fugacity coefficients with respect to composition and temperature. Again, the molar residual enthalpies are obtained from the temperature derivatives of the fugacity coefficients.

Activity Coefficient Derivatives

To develop expressions for activity coefficients and their composition derivatives, we write the model expression for the total excess Gibbs energy, $n_t g^E$, replacing mole fractions x_i by mole numbers n_i. The total excess Gibbs energy must of course be a homogeneous function of degree one in mole numbers. Activity coefficients are then found from

$$\ln \gamma_i = \frac{\partial}{\partial n_i}\left(\frac{n_t g^E}{RT}\right)_{T,P} \tag{1}$$

and their partial composition derivatives are found by repeating the differentiation.

As a simple, illustrative example, take the Wilson (1964) equation, for which

$$\frac{g^E}{RT} = -\sum_k x_k \ln\left(\sum_j x_j \Lambda_{kj}\right) \tag{2}$$

with

$$\Lambda_{kj} = \frac{v_j}{v_k}\exp\left(\frac{-\Delta\lambda_{kj}}{RT}\right) \tag{3}$$

where v_k and $\Delta\lambda_{jk}$ are the parameters of the equation.

We define

$$E_k = \sum_j n_j \Lambda_{kj} \tag{4}$$

and obtain

$$G^* \equiv \frac{n_t g^E}{RT} = -\sum_k n_k \ln\left(E_k/n_t\right) \tag{5}$$

Differentiation with respect to n_i yields

$$\ln \gamma_i = \left(\frac{\partial G^*}{\partial n_i}\right)_{T,P} = 1 - \ln\left(E_i/n_t\right) - \sum_k n_k \Lambda_{ki}/E_k \tag{6}$$

and, repeating the differentiation,

$$\left(\frac{\partial \ln \gamma_i}{\partial n_j}\right)_{T,P} = \frac{1}{n_t} - \frac{\Lambda_{ij}}{E_i} - \frac{\Lambda_{ji}}{E_j} + \sum_k n_k \Lambda_{ki}\Lambda_{kj}/E_k^2 \tag{7}$$

Reintroducing mole fractions and defining

$$\eta_i = \sum_k x_k \Lambda_{ik}, \quad \epsilon_{ik} = \Lambda_{ik}/\eta_i \tag{8}$$

yields the following simple expressions

$$\ln \gamma_i = 1 - \ln \eta_i - \sum_k x_k \epsilon_{ki} \tag{9}$$

and

$$n_t\left(\frac{\partial \ln \gamma_i}{\partial n_j}\right)_{T,P} = 1 - \epsilon_{ij} - \epsilon_{ji} + \sum_k x_k \epsilon_{ki}\epsilon_{kj} \tag{10}$$

As far as the effort is concerned, each element requires N multiplications for an N-component mixture (the product $x_k\epsilon_{ki}$ is already available from the calculation of $\ln \gamma_i$). The complete matrix thus requires about 0.5 N^3 multiplications, since we can take advantage of symmetry ($\partial \ln \gamma_i/\partial n_j = \partial \ln \gamma_j/\partial n_i$).

Temperature derivatives can be obtained by straightforward differentiation of the activity coefficient expressions, i.e.,

$$\frac{\partial \ln \gamma_i}{\partial T} = -\frac{1}{\eta_i}\frac{\partial \eta_i}{\partial T} - \sum_k x_k \epsilon_{ki}\frac{\partial \ln \epsilon_{ki}}{\partial T} \tag{11}$$

with

$$\frac{\partial \eta_i}{\partial T} = \sum_k x_k \Lambda_{ik}\frac{\partial \ln \Lambda_{ik}}{\partial T} = \frac{1}{RT^2}\sum_k x_k \Lambda_{ik}\Delta\lambda_{ik} \tag{12}$$

and

$$\frac{\partial \ln \epsilon_{ki}}{\partial T} = \frac{1}{RT^2}\Delta\lambda_{ki} - \frac{1}{\eta_k}\frac{\partial \eta_k}{\partial T} \tag{13}$$

Equation of State Models

Relations for the fugacity coefficients are derived from the total residual reduced Helmholz energy,

$$A^* = \frac{A^r(\underline{n}, T, V)}{RT} = \int_V^\infty \left(\frac{P}{RT} - \frac{N}{V}\right) dV \tag{14}$$

where V is the total volume.

The expressions are:

$$\ln \phi_i = \frac{\partial}{\partial n_i}(A^*)_{T,V} - \ln\left(\frac{PV}{n_t RT}\right) \tag{15}$$

$$\left(\frac{\partial \ln \phi_i}{\partial n_j}\right)_{T,P} = \left(\frac{\partial^2 A^*}{\partial n_i \partial n_j}\right)_{T,V} + \frac{1}{RT}\frac{\left(\frac{\partial P}{\partial n_i}\right)_{T,V}\left(\frac{\partial P}{\partial n_j}\right)_{T,V}}{\left(\frac{\partial P}{\partial V}\right)_{\underline{n},T}} + \frac{1}{n_t} \tag{16}$$

and

$$\left(\frac{\partial \ln \phi_i}{\partial T}\right)_{\underline{n},P} = \left(\frac{\partial^2 A^*}{\partial n_i \partial T}\right)_{V} + \frac{1}{RT}\frac{\left(\frac{\partial P}{\partial n_i}\right)_{T,V}\left(\frac{\partial P}{\partial T}\right)_{\underline{n},V}}{\left(\frac{\partial P}{\partial V}\right)_{\underline{n},T}} + \frac{1}{T} \tag{17}$$

The differentiation of A^* at constant total volume is unproblematic, and although compact expressions for the fugacity coefficient derivatives cannot conveniently be formulated, very rapid evaluation is normally possible. Examples and further details are given by Michelsen (1981).

We can finally mention that the fugacity coefficient expression for the virial equation permits very simple composition differentiation. In the virial equation fugacity coefficients are given by

$$\ln \phi_i = 2\sum_k b_{ik} y_k - b^* \tag{18}$$

where

$$b^* = \sum_i \sum_j b_{ij} y_i y_j, \quad b_{ij} = \frac{B_{ij}(T)P}{RT} \tag{19}$$

Table 1. Execution Time to Calculate Coefficients and Derivatives*

Model Equation	No. of Components	Time, ms Activity or Fugacity Coeff.	Temperature Derivatives	Composition Derivatives
Wilson	5	2.4	0.9 (0.4)**	1.6 (0.65)**
	15	20.0	9.0 (0.45)	32.0 (1.6)
NRTL	5	3.0	1.3 (0.45)	2.6 (0.90)
	15	24.0	10.0 (0.40)	43.0 (1.8)
SRK	5	2.0	0.9 (0.45)	1.2 (0.60)
	15	7.1	4.4 (0.60)	8.4 (1.2)
Random/nonrandom	5	12.0	2.5 (0.20)	5.4 (0.45)
	15	75.0	19.0 (0.25)	60.0 (0.80)

*Calculation by IBM 3081, WATFIV compiler.

**Numbers in parentheses give time for evaluation of derivatives relative to that for activity/fugacity coefficients only.

The composition derivatives are

$$n_T\left(\frac{\partial \ln \phi_i}{\partial n_j}\right)_{T,P} = 2b_{ij} - \ln \phi_i - \ln \phi_j \qquad (20)$$

Results

Table 1 gives computation times for activity coefficients and their derivatives for the Wilson equation and the NRTL equation, and, similarly, fugacity coefficients and derivatives for the SRK equation and, as an example of a more complex model, the random/nonrandom equation of state. The UNIQUAC equation and the UNIFAC equation have also been tested. For UNIQUAC, results are almost identical to those with the Wilson equation, while times for UNIFAC are comparable to those for NRTL.

Conclusion

The results given here indicate that analytic derivatives of fugacity and activity coefficients can be evaluated for a fraction of the cost required for numerical evaluation. The relative expense of evaluating derivatives does not vary greatly with the complexity of the model, although it seems that this relative expense is smallest for the more complex model.

When new simulation algorithms are evaluated relative to Newton's method or other second-order methods, a comparison where one Newton step is equated to $N + 1$ calls of a simple physical properties routine is unfair and unrealistic. A more appropriate cost factor to associate with evaluation of derivatives seems to be 1.5–2.5, depending on the number of components in the mixture.

Notation

A^* = reduced residual Helmholz energy, Eq. 14
b_{ij}, B_{ij} = coefficients of the virial equation, Eq. 19
E_k = defined in Eq. 4
g^E = molar excess Gibbs energy
G^* = defined in Eq. 5
i, j, k = component or summation indices
$\underline{n}$ = vector of molar amounts in mixture
n_i = molar amount of component i
n_t = total amount of moles in mixture
N = number of components in mixture
P = pressure
R = gas constant
T = absolute temperature
υ = parameter of Wilson equation
V = total volume of mixture
x_i, y_i = mole fraction of component i

Greek letters

γ_i = activity coefficient, component i
ϵ_{ik} = defined in Eq. 8
$\Delta\lambda_{kj}$ = parameter of Wilson equation
Λ_{kj} = defined in Eq. 3
η_i = defined in Eq. 8
ϕ_i = fugacity coefficient, component i

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