Kunzi, H. P., W. Krelle, and W. Oettli, *Non-Linear Programming*, Blaisdell, Waltham, Mass. (1966).

Ma, Y. H., and C. W. Shipman, "On the Computation of Complex Equilibria," *AIChE J.*, 18 (2), 299-303 (1972).

Naphtali, L. M., "Computing Complex Chemical Equilibria by Minimizing Free Energy," First Conference on Kinetics, Equilibria and Performance of High Temperature Systems, Butterworth, London (1959).

Null, H. R., *Phase Equilibrium in Process Design*, Wiley-Interscience, New York (1970).

Oliver, R. C., S. E. Stephanou, and R. W. Baier, "Calculating Free Energy Minimization," *Chem. Eng.*, 69, 4, 121 (1962).

Powell, M. J. D., "A New Algorithm for Unconstrained Optimization," in *Nonlinear Programming*, Academic Press, New York (1970).

Prigogine, I. and R. Defay, "On the Number of Independent Constituents and the Phase Rule," *J. Chem. Phys.*, 15, 614 (1947).

Sanderson, R. V. and H. H. Y. Chien, "Simultaneous Chemical and Phase Equilibrium Calculation," *Ind. Eng. Chem. Process. Des. Dev.*, 12 (1) (1973).

Schott, G. L., "Computation of Restricted Equilibria by General Methods," *J. Chem. Phys.*, 40, 2065 (1964).

Smith, W. R. and R. W. Missen, "Calculating Complex Chemical Equilibria by an Improved Reaction—Adjustment Method," *Can. J. Chem. Eng.*, 46, 269 (1968).

White, W. B., S. M. Johnson, and G. B. Dantzig, "Chemical Equilibrium in Complex Mixtures," *J. Chem. Phys.*, 28, 751 (1958).

Whitwell, J. C. and S. R. Dartt, "Independent Reactions in the Presence of Isomers," *AIChE J.*, 19 (6) (1973).

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Part II. Phase-splitting

A phase-splitting algorithm is coupled with the Rand method to improve its efficiency and reliability when the phase distribution is unknown at equilibrium. The coupled algorithm works well to give phase-splits in the metastable region where most stability tests fail. Exhaustive tests show fine performance in the region near liquid-liquid phase envelopes for systems with at least one partially miscible binary pair.

SCOPE

In Part I, we show that algorithms to calculate compositions in phase and chemical equilibrium can converge to local or constrained minima in Gibbs free energy. This paper is intended to present strategies that are more efficient and reliable for finding the global minimum.

One strategy is to assume the maximum number of phases given by the Gibbs Phase Rule:

$$P_{max} = C - R - f + 2$$

where $f = 2$, given specifications for temperature and pressure. Minimization algorithms, such as the Rand method and quadratic programming, eliminate extraneous phases, but may eliminate one or more phases improperly, given poor composition guesses. Further, these algorithms search the largest composition space and require large computation times.

The probability of reaching local or constrained minima increases with non-ideality and uncertainty in guessed compositions. This occurs particularly when processes involving non-ideal mixtures, with or without reaction, are analyzed using iterative procedures that produce large temperature and extent of reaction changes, increasing uncertainties in guessed compositions. Typical processes are:

1. Heterogeneous distillation towers, where two liquid phases may occur on one or more trays,
2. Methanation reactors, where carbon may or may not deposit on Ni catalyst,
3. Cryogenic separators, where CO_2 may or may not freeze out, and
4. Extraction trains, where one, two, or three liquid phases may occur in one or more units.

An alternative minimization strategy is to guess too few phases and to test for instability of phases during equilibrium calculations. Boston and Fournier (1978) illustrate this approach for splitting a nonideal liquid phase into two liquid phases. They use k-value algorithms to converge equilibrium calculations after splitting the liquid phase.

In this paper we introduce algorithms to split both vapor and liquid phases. Our algorithm permits very poor guesses for phase distribution; for example, all vapor or all liquid. Vapor or liquid phases are added as necessary during calculations to minimize Gibbs free energy. The search space is small and the phase-splitting algorithm has been successful in avoiding local and constrained minima for the systems tested.

CONCLUSIONS AND SIGNIFICANCE

The phase-splitting algorithm in this paper and the Rand algorithm (Newton's method) for minimization of Gibbs free energy have been tested for many systems. It is concluded that:

1. The phase-splitting algorithm improves the efficiency and reliability of the Rand algorithm (or any other minimization algorithm). Without the phase-splitting algorithm, random guesses for phase distribution led to no solution in 39 of 50 cases. With phase-splitting and very poor guesses (single liquid or vapor phase), the global

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minimum in Gibbs free energy was achieved in every case.

2. The phase-splitting algorithm increases the utility of algorithms to minimize Gibbs free energy. Coupled algorithms are strong candidates for process simulators where multiphase streams can exist and some streams approach chemical equilibrium. Often temperatures, pressures, and over-all compositions change greatly in iterative recycle calculations and it is important to have an efficient and reliable algorithm that can reach the global minimum in Gibbs free energy beginning with very poor guesses. Our coupled algorithm has been shown to satisfy this need.

3. The coupled algorithm is used in place of more rigorous methods to determine phase-stability. The algorithm works well to approximate phase-splits and has not been observed to fail in the metastable region—the case with most stability tests. However, it is limited to systems with at least one partially miscible binary pair, a property of most systems exhibiting multiple liquid phases.

Calculations for compositions at phase and chemical equilibrium require guesses for the moles of each species in each phase. If three liquid phases are expected at equilibrium, it can be difficult to provide guesses that do not lead to local and constrained minima in Gibbs free energy.

We have developed an algorithm that permits the assumption of one or more phases at equilibrium and adds phases, as necessary, during calculations to minimize Gibbs free energy.

Given guesses for phase distribution and compositions, where $P < P_{max}$, we initiate calculations using one of the minimization algorithms in Part I (e.g., Rand method, quadratic programming, etc.). Along the search trajectory, an additional phase is postulated by splitting one of the phases into two. If the Gibbs free energy is reduced, composition variables for these phases replace the composition variables for the parent phase, and the minimization algorithm is continued.

The identity of the source phase, s, and compositions of the trial phases, t_1 and t_2, must be determined. The source phase is selected as the phase which leads to the lowest Gibbs free energy after being split into two phases. To set the compositions of two liquid, trial phases, the nonidealities of the source phase are considered, and for vapor and liquid trial phases, liquid fugacities are also considered. Solid solutions are not considered in this paper, but would be created similarly given models for activity coefficients and solid fugacities. For pure solids in reacting systems, such as graphite or FeO, the method for determining whether the solid exists at equilibrium is described in Part I.

This approach is based upon the fact that a P phase solution, if it exists, has a lower Gibbs free energy than a P-1 phase solution.

PHASE-SPLITTING

Given guesses for phase distribution and composition at equilibrium, the surface of Gibbs free energy of mixing shows the stability or instability of any phase. Such a surface is illustrated for a binary mixture in Figure 1. BC is the region of intrinsic instability, where ΔG_m is concave, and two liquid phases exist. AB and CD are metastable regions, where ΔG_m is convex, but two liquid phases exist. RA and DS are regions of phase-stability, or a single phase. To check for concavity, the Hessian matrix of Equation (29) in Part I can be computed. If negative-definite (region BC), two phases occur. Otherwise, phase-instability may or may not occur. But, this procedure is time-consuming and costly for multicomponent mixtures and cannot identify instability in the metastable regions.

An alternate approach to determining instability was suggested by Boston and Shah (1976) and illustrated by Boston and Fournier (1978). This involves the creation of two liquid trial phases using an approximate solution model, followed by rigorous solution of the equations for equilibrium between two liquid phases.

Consider Figure 2 (Prausnitz 1969), which shows activities of four alcohols in binary mixtures with water. Over a wide range of compositions, butanol splits into two phases with compositions at A and B. Propanol is on the verge of instability while the other alcohols are stable. Between points A′ and B′ butanol satisfies the condition for instability of a liquid phase:

$$\left(\frac{\partial \ln a_j}{\partial x_j}\right)_{T,P} < 0 \qquad (1)$$

However, rather than compute derivatives, Boston and Shah (1976) and Boston and Fournier (1978) use the magnitude of the activity at infinite dilution in a mixture as a measure of nonideality. A better measure is activity at the composition of the mixture. This is justified, since at fixed composition binary activities of alcohols in water solutions increase with the nonideality of the alcohol-water solution (Figure 2).

To evaluate stability of a liquid or vapor mixture, vapor and liquid trial phases should be considered. In these cases, the magnitude of the activity in a mixture is a measure of the tendency to form two phases. Activities are large for supercritical or volatile chemicals in high

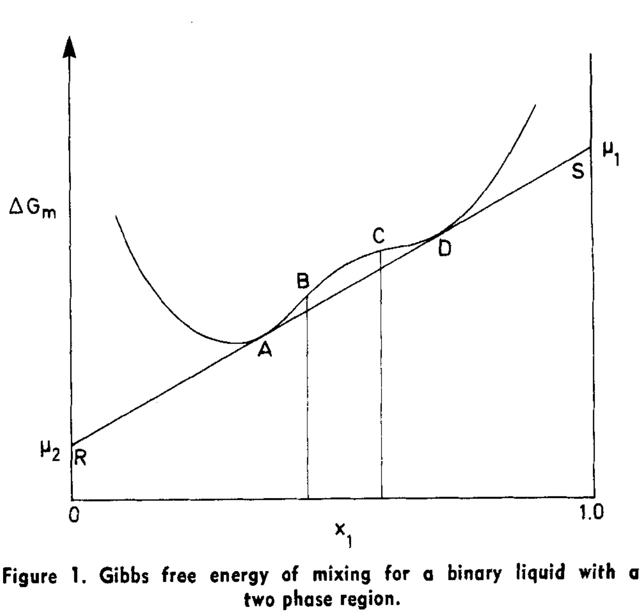

Figure 1. Gibbs free energy of mixing for a binary liquid with a two phase region.

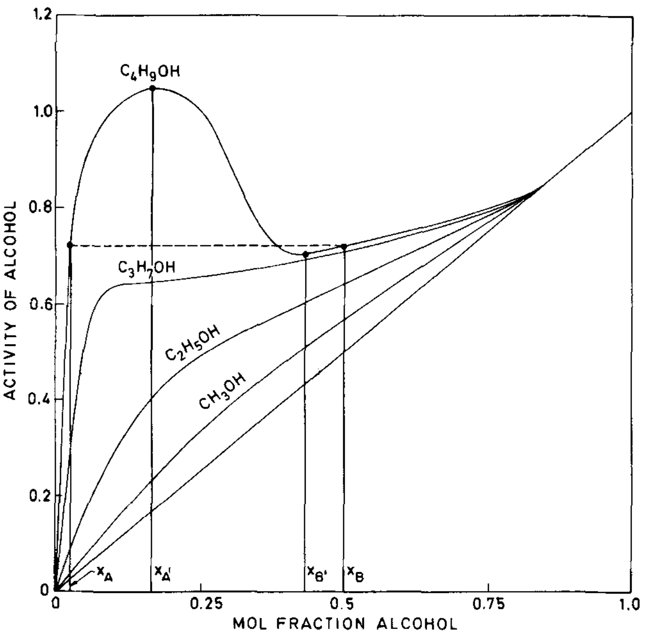

Figure 2. Activities of four alcohols in aqueous solutions at 298.2 K and 1.013 bar (1 atm).

concentration; these concentrate in a vapor phase when chemicals with smaller activities are present.

Phase-Splitting Algorithm

This leads to an algorithm for splitting a vapor or liquid phase into vapor and liquid trial phases ($V \rightarrow VL$ or $L \rightarrow VL$) or a liquid phase into two liquid trial phases ($L \rightarrow L_1L_2$). One algorithm was developed to handle the three combinations of source and trial phases. It is used separately for each possible combination.

The algorithm first locates the chemical m with highest activity in source phase, s

$$a_{ms} = \max_{j=1,\dots,C} a_{js} \tag{2}$$

where all species have the same standard state. The next chemical, m', is selected to have the highest binary activity with m, taking concentrations proportional to those in phase s,

$$a^b_{m's} = \max_{\substack{j=1,\dots,C \\ j\neq m}} a^b_{js} \tag{3}$$

where b indicates that activities are for binary mixtures of j and m. When forming a new liquid phase, if a chemical is present in large amounts in another liquid phase it is bypassed in the selection of chemicals m and m'. This assures that liquid trial phases are not similar in composition to existing liquid phases.

The compositions of m and m' in two trial, liquid phases are determined by solving the equations

$$\begin{aligned} \gamma_{mt_1}x_{mt_1} &= \gamma_{mt_2}x_{mt_2} \\ \gamma_{m't_1}x_{m't_1} &= \gamma_{m't_2}x_{m't_2} \end{aligned} \tag{4}$$

and for vapor and liquid trial phases

$$\begin{aligned} y_{mt_1}\phi_{mt_1}P &= x_{mt_2}\gamma_{mt_2}f_{mt_2} \\ y_{m't_1}\phi_{m't_1}P &= x_{m't_2}\gamma_{m't_2}f_{m't_2} \end{aligned} \tag{5}$$

where $x_{mt_i} = n_{mt_i}/(n_{mt_i} + n_{m't_i})$, $x_{m't_i} = n_{m't_i}/(n_{m't_i} + n_{mt_i})$, and y_{mt_i} and $y_{m't_i}$ are defined similarly. Equations (4) or (5) are two equations in two unknowns, since $n_{jt_1} = n_{js} - n_{jt_2}$. A Newton-Raphson procedure solves these equations with physical properties assumed constant over an iteration. The procedure, is relatively insensitive to guesses for compositions, n_{mt_i} and $n_{m't_i}$. Equation (4) is solved to give compositions of two phases at points A and D in Figure 1.

Table 1. Phase Equilibrium for a Mixture of IPA, IPE, and Water at 335 K and 1.013 Bar (1 atm). Activity Coefficients Using Margules Four-Suffix Equation

	Composition of single liquid	Composition after split		Composition at equilibrium	
		Phase 1	Phase 2	Phase 1	Phase 2
IPA	0.21	0.1092	0.1008	0.0186	0.1914
IPE	0.25	0.0018	0.2482	0.0021	0.2478
Water	0.54	0.5291	0.0109	0.3747	0.1653
G/RT	−1.29505	−1.28583		−1.37579	

In the case of a vapor source phase, chemicals m and m' are usually those present in largest amounts. A large amount of chemical m is placed in a trial vapor phase and a large amount of chemical m' is placed in a trial liquid phase. Ranking by activity accounts for volatility and nonideality effects and should be more reliable than ranking by pure liquid fugacity, f_j.

The remaining chemicals are ordered according to decreasing binary activity with chemical m. Let chemical r have the next highest binary activity, i.e.,

$$a^b_{rs} = \max_{\substack{j=1,\dots,C \\ j\neq m,m'}} a^b_{js} \tag{6}$$

Chemical r is distributed in phases t_1 and t_2 according to

$$\gamma_{rt_1}x_{rt_1} = \gamma_{rt_2}x_{rt_2} \tag{7}$$

for two trial, liquid phases, and

$$y_{rt_1}\phi_{rt_1}P = x_{rt_2}\gamma_{rt_2}f_{rt_2} \tag{8}$$

for vapor and liquid trial phases, where $x_{rt_i} = n_{rt_i}/(n_{mt_i} + n_{m't_i} + n_{rt_i})$ and y_{rt_i} is defined similarly for the vapor phase. Equations (7) and (8) have single unknowns, since $n_{rt_1} = n_{rs} - n_{rt_2}$. When forming a new liquid phase, if this chemical is present in large amounts in another liquid phase, it is distributed after the remaining chemicals, which are distributed similarly.

Each chemical is distributed holding the amounts of previously allocated species fixed. Thus, compositions given by Equations (7) or (8) are not at equilibrium, and the two trial phases may not have lower Gibbs free energy.

Table 1 summarizes calculations for splitting a liquid phase of isopropyl ether, isopropyl alcohol and water, into two liquid phases. As expected, IPE and water are species m' and m, respectively. A binary split of these two species is given by solving Equations (4) for the values shown in Table 1. IPE was allocated next by solving Equation (7) to yield the compositions shown. These compositions are guesses for any algorithm to minimize Gibbs free energy. Figure 3 shows dimensionless Gibbs free energy (G/RT) vs. iteration number using the Rand method. After splitting the liquid into two liquid phases, the Gibbs free energy increases from a value of −1.295 to −1.2858 (iteration 0). It decreases below the initial value after only one iteration of the Rand method. Convergence is achieved in 12 iterations.

Table 2 summarizes an attempt to separate liquid phase (2) into two phases. When these are used as guessed

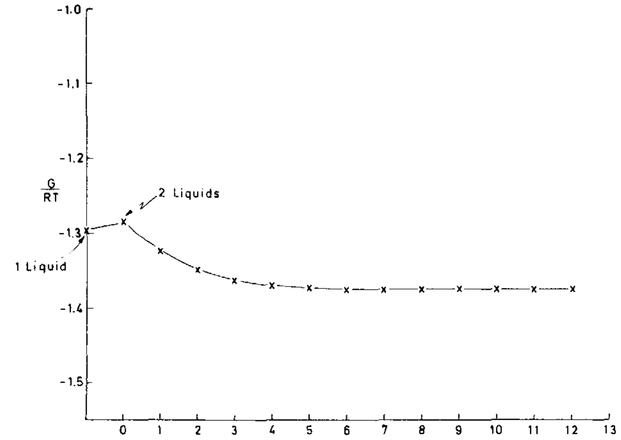

Figure 3. Gibbs free energy vs. iteration number for IPE, IPA, water system at 335 K and 1.013 bar (1 atm). Composition at iteration 0 is obtained from phase-splitting algorithm which gives two liquid phases.

Table 2. Unsuccessful Attempt to Split Stable Liquid Phase

	Composition of single liquid	Composition after split		Composition at G_{min}	
		Phase 1	Phase 2	Phase 1	Phase 2
IPA	0.1914	0.1241	0.0673	0.1914	—
IPE	0.2478	0.2473	0.0005	0.2478	—
Water	0.1653	0.0108	0.1545	0.1653	—
G/RT	−0.7586	−0.6566		−0.7586	

compositions in the minimization algorithm, one liquid phase is dropped. Figure 4 shows an increase in Gibbs free energy after the split, but the decrease in Gibbs free energy on minimization is slow until the extraneous liquid phase is dropped at iteration 11.

Table 3 summarizes similar calculations for a vapor-liquid split beginning with seven species in a vapor phase. Propylene and water are species m and m'. A decrease in Gibbs free energy from 260.61 to 256.07 is observed after phase-splitting. The Rand algorithm is started and the global minimum reached—vapor and liquid phases at equilibrium.

In summary, the phase-splitting portion of this algorithm is:

1. Chemical m has the highest activity in source phase s.
2. Chemical m' has the highest binary activity with m (concentrations proportional to those in s).
3. The chemicals m and m' are allocated to two trial phases t_1 and t_2 using Equations (4) or (5). When forming a new liquid phase, if a chemical is present in large quantities in another liquid phase it is bypassed.
4. The chemical with the next highest binary activity with m is allocated according to Equations (7) or (8).
5. The remaining chemicals are similarly allocated in order of decreasing binary activities with chemical m.

This algorithm is repeated for each feasible combination of source and trial phases. The two trial phases having the lowest Gibbs free energy are taken as candidates to replace their source phase.

Let $G^{(k)}$ be Gibbs free energy after iteration k prior to formation of trial phases, and let $G_{t_1t_2}^{(k)}$ be Gibbs free energy after formation of trial phases t_1 and t_2, with $G_{t_1t_2}^{(k)*}$ the lowest value. When an increase occurs ($G_{t_1t_2}^{(k)*} > G^{(k)}$), a few iterations of the minimization algorithm are carried-out to permit a decrease. If a decrease does not occur (that is, $G_{t_1t_2}^{(k+q)*} > G^{(k)}$, where q is the number of iterations), this experiment is repeated for the trial phases having the next lowest $G_{t_1t_2}^{(k)}$. Given no decrease after examining all combinations of source and trial phases, the phase-splits are termed "unsuccessful." Observations

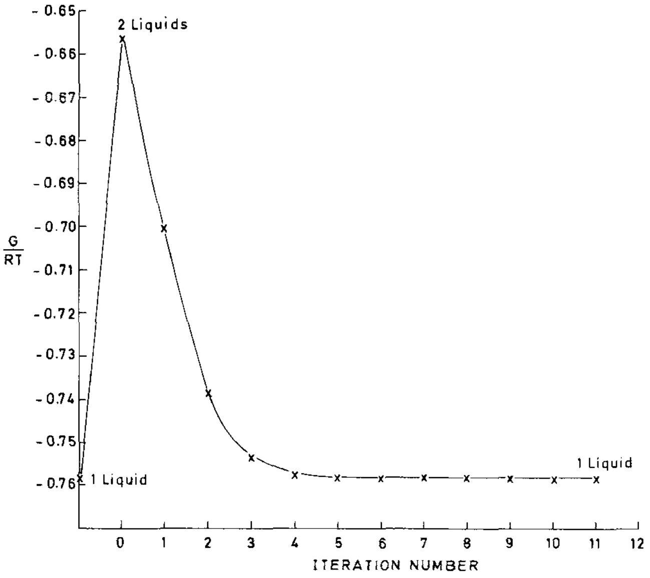

Figure 4. Gibbs free energy vs. iteration number for IPE, IPA, water system at 335 K and 1.013 bar (1 atm). Two liquid phases are obtained by the phase-splitting algorithm but one is eliminated as equilibrium is approached (iteration 11).

Table 3. Phase Equilibrium for a Seven Component Mixture at 388.5 K and 41.33 Bar (40.8 atm)

	Composition of vapor phase	Composition after split		Composition at equilibrium	
		Vapor	Liquid	Vapor	Liquid
Propylene	78.0	77.9863	0.01365	77.9805	0.0195
IPE	2.14	2.1383	0.0017	2.1384	0.0016
IPA	5.06	4.6382	0.4218	4.6773	0.3827
Water	11.90	3.7875	8.1125	4.0035	7.8965
Acetone	0.071	0.067	0.004	0.06714	0.0039
Hexene	2.80	2.79998	0.00001	2.79999	0.00001
n-Propanol	0.03	0.0283	0.0017	0.02835	0.00165
G/RT	260.60992	256.07624		256.06717	

Table 4. Phase Equilibrium for a Three Component Mixture at 395.2 K and 1.013 Bar (1 atm)

	Composition of liquid phase	Composition after split ($i = 0$)		Compositions prior to second split ($i = 6$)		Composition after second split ($i = 6$)			Composition at equilibrium ($i = 15$)		
		Liquid 1	Liquid 2	Liquid 1	Liquid 2	Liquid 1	Liquid 2	Liquid 3	Liquid 1	Liquid 2	Liquid 3
Glycol	0.4	0.0690	0.3340	0.0589	0.3411	0.0589	0.3399	0.0012	0.0723	0.3262	0.0014
Lauryl alcohol	0.3	0.2971	0.0029	0.2847	0.0153	0.2847	0.0145	0.0009	0.2825	0.0163	0.0012
Nitromethane	0.3	0.0233	0.2767	0.0467	0.2533	0.0467	0.1441	0.1092	0.0375	0.1283	0.1341
G/RT	−3.3127	−3.5588		−3.5351		−3.5616			−3.5617		

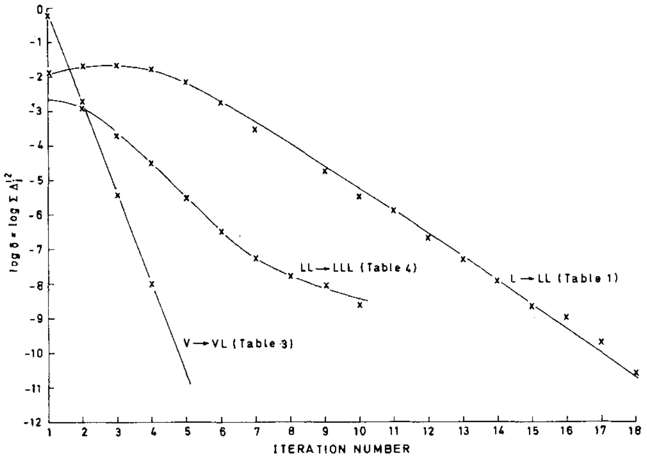

Figure 5. Degree of convergence as a function of iteration number.

for many systems show that decreases occur in two or less iterations and, otherwise, do not occur.

Even when Gibbs free energy decreases (that is, $G_{t_1t_2}^{(k)*} < G^{(k)}$), q iterations of the minimization algorithm are carried out, because the phase-split may not lead to addition of a new phase. Two trial phases may coalesce after several iterations of the minimization algorithm.

Coalescence usually occurs if the new phase (vapor in a $L \rightarrow VL$ split, liquid in a $V \rightarrow VL$ split, or either phase in a $L \rightarrow L_1L_2$ split) is small in quantity. When $\Delta G_{t_1t_2}^{(k+q)*}$ $(= G^{(k)} - G_{t_1t_2}^{(k+q)*})$ is greater than $10^{-5}G^{(k)}$, the new phase is normally present in larger than trace quantities, and the phase-split is accepted as "successful."

If this condition is not satisfied, or the new phase is dropped, this experiment is repeated for the trial phases having the next lowest $G_{t_1t_2}^{(k)}$. Should no combination satisfy this condition, the trial phases leading to the lowest Gibbs free energy are accepted. This algorithm works well, with $q = 4$, to keep trace phases from being accepted without consideration of other pairs of trial phases.

Note that for systems of one phase, no reaction, and feasible guesses for compositions (satisfy mass balances), when Gibbs free energy decreases in formation of two trial phases, these phases cannot coalesce during subsequent iterations of the minimization algorithm.

PHASE-SPLITTING IN SEARCH FOR GLOBAL MINIMA AT EQUILIBRIUM

This procedure can improve initial guesses before starting a minimization procedure. It can also expand the phase-space between iterations of a minimization procedure. Here a criterion is required to decide when to attempt addition of a phase along the search trajectory traced by the minimization procedure. In the initial stages of a search, compositions change rapidly and may be too random to attempt a meaningful phase-addition. Later in a search, attempts to add a phase should be less frequent when the rate of convergence is slow than when it is rapid. Further, as the global minimum (equilibrium) is approached, attempts should become more infrequent.

It was decided to use $\delta = \Sigma\Delta_j'^2$, where $\Delta_j' = N_j' - n_j$, as a measure of the degree of convergence. Figure 5 is a plot of ln δ vs. iteration number for the following representative systems:

1. Vapor-liquid system: A vapor phase consisting of propylene, IPE, IPA, water, acetone, hexene and propanol at 388.5K and 41.33 bar (40.8 atm) was split into vapor and liquid phases (see Table 3) by the phase-splitting algorithm and the Gibbs free energy minimized using the Rand method.

2. Liquid-Liquid-Liquid system: The phase-splitting algorithm was used to add a third liquid phase to a two liquid phase system of nitromethane, lauryl alcohol and glycol at 295.2K and 1.013 bar (1 atm). Compositions of the two liquid phases are given in Table 4. The Gibbs free energy of the resulting three phase solution is minimized.

3. Liquid-Liquid system: A single liquid mixture of IPE, IPA and water at 335K and 1.013 bar (1 atm) is split into two liquid phases (see Table 1), by the phase-splitting algorithm and Gibbs free energy minimized.

Given the curves in Figure 5 a function was developed to compute the number of iterations, IT, between attempts to add a phase. IT is computed after every iteration of the minimization algorithm except after the q iterations immediately following phase-splits. When the number of iterations since the last attempt at phase-splitting equals or exceeds IT, another attempt is made to add a phase. IT is given by

$$IT = \frac{-ak^b}{s} + 0.5 \tag{9}$$

where

$$s = \frac{\sum_{i=1}^{k} i(\ln \delta_i - \ln \delta_{i-1})}{\sum_{i=1}^{k} i} \tag{10}$$

i is iteration counter, k is the number of the most recent iteration, and s is a weighted average of slopes of the ln δ vs. i curve with increased weighting for more recent iterations. The constants a and b are determined by experimentation. In this work, $a = 3$, and $b = 0.5$ were found to give good performance (see the performance of algorithm, later in the text).

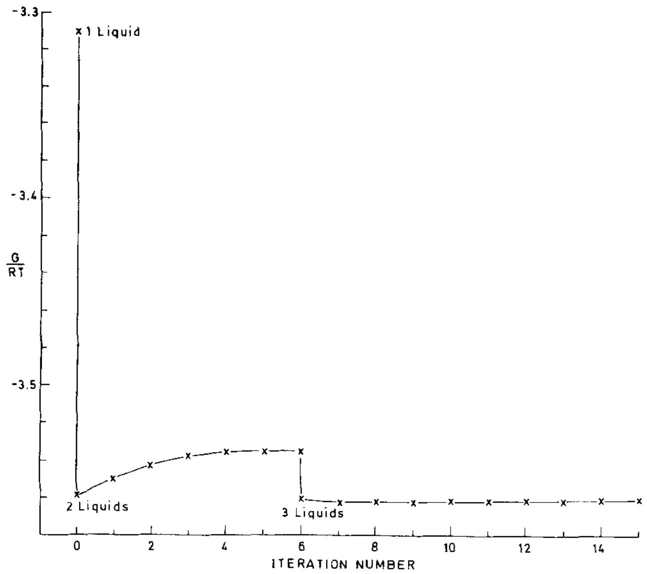

Figure 6. Gibbs free energy as a function of iteration for the system glycol-lauryl alcohol-nitromethane at 295.2 K and 1.013 bar (1 atm).

This strategy was used to calculate compositions at equilibrium for the system of glycol, lauryl alcohol and nitromethane at 295.2K and 1.013 bar (1 atm). A single liquid phase is assumed at equilibrium. This is split into two liquid phases with compositions and Gibbs free energies, shown in Table 4. Gibbs free energy decreases and $\Delta G_{L_1L_2}^{(4)} > 10^{-5}G^{(0)}$; hence, the trial phases replace the source phase. After five iterations of the minimization algorithm ($k = IT = 6$), Phase 2 is split into Phases 2 and 3 and the Gibbs free energy is reduced and $\Delta G_{L_2L_3}^{(10)} > 10^{-5}G^{(6)}$.

A closer look at Gibbs free energy as a function of iteration (Figure 6) reveals that from iterations 1-6, G/RT *increases* and appears to be converging to a local maximum point. This is permissible, since Newton's method locates extremum in close proximity of guess values, either maximum or minimum points. After the phase-split, G/RT reaches a new low and decreases to a minimum after iteration 7, prior to a small increase and convergence. The compositions at convergence agree to four significant figures with those computed by Null (1970) using a k-value algorithm. Compositions after iteration 7 differ by approximately 2% and are further removed from experi-

TABLE 5. PHASE AND CHEMICAL EQUILIBRIUM IN ESTERIFICATION AT 358.2 K AND 1.013 BAR (1 ATM); K = 31.75 (GEORGE ET AL. 1976); ANTOINE VAPOR PRESSURES AND WILSON ACTIVITY COEFFICIENTS (SANDERSON AND CHIEN 1973)

	G_f^0 J/Kg mol	Inlet moles	Guess liquid moles	After $i = 4$	Composition after split ($i = 4$)		Liquid phase dropped, $i = 8$	Compositions at equilibrium, $i = 13$
				Liquid	Vapor	Liquid	Vapor	Vapor
ETOH	1.029593×10^7	50	49	14.681	10.3475	4.3335	11.4311	7.5361
HAC	0	50	49	14.681	9.9075	4.7736	11.4311	7.5361
ETAC	0	0	1	35.319	35.2836	0.0353	38.5689	42.4639
H_2O	0	0	1	35.319	31.3329	3.9861	38.5689	42.4639
G/RT			47.2163	−59.6469	−75.5626		−83.5478	−85.6516

TABLE 6. EXECUTION TIMES FOR MINIMIZATION CALCULATIONS (UNIVAC

System	Phase-split algorithm†							Minimization calc. (sec)
	Phase-splits							
	$L \rightarrow LL$ No.	Sec.	$L \rightarrow VL$ No.	Sec.	$V \rightarrow VL$ No.	Sec.	Tot. time	
1. $L \rightarrow LL$ (IPA, IPE, water—335 K, 1.013 bar (1 atm))	3	1.22	3	0.7			1.92	2.7
2. $V \rightarrow VL$ (C_3H_6, IPE, IPA water, acetone, C_6H_{12}, *n*-propanol—388.5 K, 41.33 bar (40.8 atm))	1	2.25			2	12.3	14.55	4.1
3. $L \rightarrow LL$ (Glycol, lauryl alcohol, nitromethane—295.2 K, 1.013 bar (1 atm))	3	0.63	3	0.75			1.38	2.49
4. $V \rightarrow VLL$ (C_3H_6, IPE, IPA, water—378 K, 41.33 bar (40.8 atm))	3	3.75			3	1.56	5.31	2.34
5. $L \rightarrow VL \rightarrow V$ (Ethanol, acetic acid, ethyl acetate, water—358.2 K and 1.013 bar (1 atm))	1	0.10	1	0.12	1	0.11	0.33	1.81

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* Average time for successful solutions.
In all trials the correct phase distribution was assumed.
† Solution obtained in *every* case.

mental values. This increase in Gibbs free energy was observed in this case only. It may be associated with the modified van Laar equation and its inability to represent experimental data uniformly well.

Table 5 presents results for the esterification of ethanol and acetic acid at 358.2K and 1.013 bar (1 atm). The free energies of formation are adjusted to correspond to $K = 31.75$ in the vapor phase (George et al. 1976) and Antoine coefficients and interaction coefficients for the Wilson equation are those of Sanderson and Chien (1973). A liquid phase is assumed containing principally reactants and the phase-splitting algorithm forms a vapor phase after four iterations of the minimization algorithm. Ethyl acetate and water products build in subsequent iterations until the liquid phase is dropped at iteration 8.

PERFORMANCE OF ALGORITHM

This algorithm has been tested for several systems with execution times reported in Table 6. For each system, only a single phase was assumed to be present at equilibrium. The left-most columns show the number of attempts to split phases and execution times. For system 1, three attempts were made to split a liquid into two liquid phases in 1.22 sec, with one success, and vapor and liquid phases, with no successes in 0.7 sec. The next columns show the time for minimization calculations using the Rand method and the total time to reach the global minimum in Gibbs free energy. The right-most columns show average times for successful solutions, beginning with random guesses for compositions, but the correct phase distribution.

In 50 trials, only 11 were successful—beginning with compositions close to those at equilibrium. In unsuccessful trials, the moles of species in one phase approached zero and those variables were eliminated from the search space. Execution times for the few successful solutions were comparable to those using the phase-splitting algorithm. The phase-splitting algorithm, beginning with compositions of a single phase reached the correct solution in every case and, hence, adds greatly to reliability at comparable execution times.

The times for phase-splits in Table 6 depend upon several factors including the number of chemicals, degree of nonideality, and the success or lack of success in achieving trial phases. Lack of success occurs when the solution of Equations (4) or (5) place chemicals m and m' in a single phase; this causes the Jacobian to become singular.

To measure reliability of the phase-splitting algorithm, an hypothetical ternary system was postulated with miscible pairs 1-2 and 1-3 and the partially miscible pair 2-3. The three-suffix Wohl equation was used to model solution behavior:

$$\ln \gamma_1 = A_{12}x_2^2 + A_{13}x_3^2 + (A_{12} + A_{13} - A_{23})x_2x_3$$
$$\ln \gamma_2 = A_{12}x_1^2 + A_{23}x_3^2 + (A_{12} + A_{23} - A_{13})x_1x_3$$
$$\ln \gamma_3 = A_{13}x_1^2 + A_{23}x_2^2 + (A_{13} + A_{23} - A_{12})x_1x_2 \tag{11}$$

with $A_{12} = A_{13} = 0$ and $A_{23} > 2$ (for partial miscibility). Three values of A_{23} were used and two-phase envelopes plotted in Figure 7 as solid lines. For compositions tested below the dashed lines, two liquid phases were calculated by the phase-splitting algorithm and compositions on the two-phase envelopes computed using the minimization algorithm. When $A_{23} = 3$ and 6, the region between solid and dashed lines is due to the small amount of one phase. When below a prespecified amount, the phase is deleted from the search space. As the prespecified amount is reduced, the dashed curves approach the two-phase envelopes, but singularity in the coefficient matrix is encountered.

Larger values of A_{23} (e.g., equal 10) broaden the two-phase envelope to include a region high in concentration of species 1. Above $x_1 = 0.7$, for $A_{23} = 10$, a_{1s} is largest, $m = 1$, and the phase-splitting algorithm fails. Such regions are uncommon, as large concentrations of species 1 usually preclude the formation of two liquid phases. In these cases, it may be desirable to select species

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Total time to equilibrium (sec)	Random guesses: No. successful solutions	Random guesses: Average time* (sec)	Random guesses: No. of unsuccessful solutions
4.62	3	5.33	7
16.65	2	20.3	8
3.87	1	5.5	9
7.65	1	7.5	9
2.14	4	4.1	6

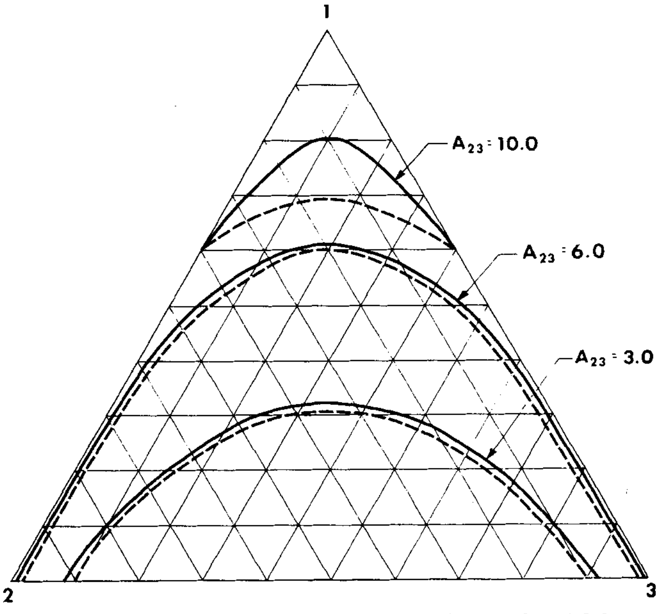

Figure 7. Hypothetical ternary phase diagram: Pairs 1-2 and 1-3 are ideal. Pair 2-3 is partially miscible. The three-suffix Wohl equation (11) is used with $A_{12} = A_{13} = 0$ and $A_{23} > 2$. The solid lines bound regions including two liquid phases. The dashed lines bound regions for which the phase-splitting algorithm gives two liquid phases.

m as having the largest activity coefficient rather than activity. But this alternative cannot be used with dilute solutes having high activity coefficients or vapor trial phases.

In the region of a plait point, the phase-splitting algorithm predicts two similar trial phases and four iterations of the minimization algorithm are often not sufficient to reduce Gibbs free energy. Occasionally 6 or 7 iterations are necessary.

Similar tests of the phase-splitting algorithm should be successful for phase diagrams with at least one partially miscible pair. For a design study, it is important to identify regions where the algorithm fails, and either modify or avoid using the algorithm in these regions. Systems must contain at least one partially miscible pair for the phase-splitting algorithm to apply.

The decision to accept the first trial phases that satisfy $\Delta G_{t_1t_2}^{(k+q)*} > 10^{-5}G^{(k)}$, rather than examine all combinations of source and trial phases, saves much computer time. But, it gives rise to the possibility that the same two trial phases are accepted repeatedly, with one rejected after q iterations of the minimization algorithm, preventing other trial phases from being considered. As an example, for a VL_1L_2 system at equilibrium, with initial guesses for two liquids L_1L_2, it might be possible for the sequence $L_1L_2 \rightarrow L_1L_2L_3 \rightarrow L_1L_2$ to be repeated, preventing examination of the trial phases L_2V. This is highly unlikely, as the composition of phases L_1L_2 would be closer to a constrained minimum in Gibbs free energy prior to the next split and the criteria, $\Delta G_{t_1t_2}^{(k+q)*} > 10^{-5}G^{(k)}$, would not likely be satisfied.

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NOTATION

a, b = coefficients in Equation (9)
a_j = activity of species j in a multicomponent phase
$a^b{}_{js}$ = activity of species j in a binary mixture with species m; compositions in the binary mixture are proportional to those in phase s
A_{ij} = interaction coefficients for three-suffix Wohl equation—binary pair i-j
C = number of chemical species
f_{jl} = fugacity of pure species j in phase l at the temperature and pressure of the system
G = Gibbs free energy
$G^{(k)}$ = Gibbs free energy after iteration k prior to formation of trial phases
$G_{t_1t_2}^{(k)}$ = Gibbs free energy after formation of trial phases t_1 and t_2
k = number of most recent iteration of optimization algorithm
n_{jl} = moles of species j in phase l
P = number of phases, pressure
$P_{\max}$ = maximum number of phases
R = universal gas constant
s = weighted average slope of degree of convergence curve (see Equation 10)
T = absolute temperature
x_{jl} = mole fraction of species j in liquid phase l
y_{jl} = mole fraction of species j in vapor phase l

Greek Symbols

δ_i = $\Sigma\Delta_j'^2$ after iteration i
Δ_j' = $N_j' - n_j$
γ_{jl} = activity coefficient of species j in phase l
ϕ_{jl} = fugacity coefficient of species j in vapor phase l

Subscripts

m = species in source phase with highest activity
m' = species in source phase with highest $a^b{}_{js}$
s = source phase
t = trial phase

LITERATURE CITED

Boston, J. F. and R. Fournier, "A Quasi-Newton Algorithm for Solving Multiphase Equilibrium Flash Problems," presented at 71st Annual AIChE Meeting, Miami (Nov., 1978).

Boston, J. F. and V. Shah, personal communication (1976).

George, B., L. P. Brown, C. H. Farmer, P. Buthod, and F. S. Manning, "Computation of Multicomponent Multiphase Equilibrium," *Ind. Eng. Chem. Process Des. Devel.*, **15**, 3 (1976).

Null, H. R., *Phase Equilibrium in Process Design*, Wiley-Interscience, New York (1970).

Prausnitz, J. M., *Molecular Thermodynamics of Fluid-Phase Equilibria*, Prentice-Hall, New Jersey (1969).

Sanderson, R. V. and H. H. Y. Chien, "Simultaneous Chemical and Phase Equilibrium Calculation," *Ind. Eng. Chem. Process Des. Devel.*, **12**, 1 (1973).

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Part III. Electrolytic Solutions

Methods for estimating the properties of electrolytic solutions are reviewed, with emphasis on molecule-molecule, molecule-ion, and ion-ion interactions. The algorithms of Parts I and II, to search for global minimum in Gibbs free energy, are extended to handle electrolytes and compared with an algorithm using k-values. Results are presented for SO_2-H_2O and H_2S-NH_3-H_2O systems and agree with experimental values.

SCOPE

In recent years, extensive work has been done to develop methods for estimating the properties of organic compounds that do not dissociate (Reid et al. 1977). But, many chemical processes involve aqueous solutions of inorganic compounds that dissociate into ionic species. These include salt crystallizers, acid gas scrubbers, and sour water strippers.
