LETTERS TO THE EDITOR

To the Editor:

I would like to comment on the R&D Note entitled, "On Apparent Second-Order Kinetics" (**33**(6), June, 1987, p. 1050) concerning the tendency of systems with a large number of parallel reactions to approximate simple second-order kinetics. The article presents some very interesting results, especially those dealing with nonfirst-order intrinsic kinetics. I would like to point out, however, that in contrast to the authors' statement, apparent reaction orders greater than 2 <u>are</u> possible in the case of first-order intrinsic kinetics for appropriate initial reaction rate distributions. The discrepancy arises from the authors' assumption in Eq. 1 that $\alpha > 1$.

$$c(k,0)dk = \frac{\alpha^\alpha}{\Gamma(\alpha)} \cdot \left(\frac{k}{\hat{k}}\right)^{\alpha-1} \frac{\exp(-\alpha k/\hat{k})}{\hat{k}}\, dk \qquad (1)$$

This restriction is not necessary since Eq. 1 is integrable as long as $\alpha > 0$. Eq. 2 then gives apparent reaction orders, β, greater than 2.

$$\beta = (\alpha + 1)/\alpha \qquad (2)$$

This also applies to the asymptotic behavior of these systems, which has been discussed previously (Krambeck, 1984). Thus, based on the well-known limit theorem for Laplace transforms,

$$c(k,0) \sim k^{\alpha-1} \quad \text{as} \quad k \rightarrow 0 \text{ iff} \qquad (3)$$

$$C(t) \sim t^{-\alpha} \quad \text{as} \quad t \rightarrow \infty \qquad (4)$$

Eq. 4 implies the same asymptotic behavior as a reaction of order β.

The second order case, $\beta = 2$, occurs when $\alpha = 1$. By Eq. 3 this is true whenever $c(k, 0)$ has a finite nonzero value at $k = 0$. However, one could clearly postulate distributions with $\alpha < 1$ in Eq. 3, so that higher asymptotic orders are possible. This could occur when refractory (unreactive) materials are even more prevalent than in the apparent second-order case. In actuality, however, the second-order approximation is quite accurate in many cases.

I believe that the other result in the note concerning extension to nonlinear kinetics is also quite interesting. The problem alluded to in the authors' Eq. 18 could be eliminated by restricting the form of $r(c)$ to avoid its nasty behavior for narrow cuts [e.g., $c(k,0) = \delta(k - \hat{k})$]. For example, it could be restricted to the form

$$r[c(k,t)] = h\left[\frac{c(k,t)}{c(k,0)}\right] c(k,t) \qquad (5)$$

where h is an arbitrary function. In this case $g[kt, c(k,0)]$ will be linear in $c(k, 0)$ but arbitrary kinetics can be specified for an individual lump.

Literature Cited

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Krambeck, F. J., "Computers and Modern Analysis in Reactor Design," *Int. Chem. E. Symp. Ser.*, **87** (ISCRE 8) 733 (1984).

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To the Editor:

A recent paper by Lucia (Nov., 1986, p. 1761) provides an interesting new result: flash calculations at specified pressure and vapor fraction are shown to have a unique solution for mixtures described by stable Gibbs energy models (homogeneous mixtures in the terminology of Lucia). In our opinion the proof is incomplete.

The uniqueness result would rule out certain retrograde phenomena and Lucia therefore states that "specifications must be chosen well below the critical state of the mixture (to avoid retrograde effects)." However, we miss a quantitative indication of how much the specification must be below the critical state, and strangely, the proof makes no use of this restriction.

In particular, two essential parts of the proof seem to be based on assumptions that are not presented in the paper. These will be discussed in the following.

Nonnegative Inverse. Lucia states that the matrix $(\nabla^2 G^L + \nabla^2 G^V)^{-1}$ has only positive elements whenever G^L and G^V are stable Gibbs free energy models. ($\nabla^2 G^L$ and $\nabla^2 G^V$ are Hessian matrices in the mole numbers of the respective phases). It is not hard to find a counterexample provided at least three components are present in the mixture.

To guarantee stable phase models we select the Wilson equation for the liquid phase and the ideal gas law for the vapor phase. Assume that the parameter matrix for the Wilson equation is

$$\Lambda = \begin{pmatrix} 1. & 10. & 10. \\ 0.1 & 1. & 0.1 \\ 0.1 & 0.1 & 1. \end{pmatrix}$$

and that equilibrium compositions of the liquid and vapor phases are $x = (0.70, 0.15, 0.15)$ and $y = (0.25, 0.50, 0.25)$. The reduced Hessian matrices of the Gibbs energy for the liquid and vapor phases are

$$n_L \frac{\nabla^2 G^L}{RT} = \begin{pmatrix} 0.9935 & -2.3181 & -2.3181 \\ -2.3181 & 6.0126 & 4.8054 \\ -2.3181 & 4.8054 & 6.0126 \end{pmatrix},$$

$$n_V \frac{\nabla^2 G^V}{RT} = \begin{pmatrix} 3.0 & -1.0 & -1.0 \\ -1.0 & 1.0 & -1.0 \\ -1.0 & -1.0 & 3.0 \end{pmatrix}$$

and it is readily verified that the (2, 3) and (3, 2) elements of the inverse Hessian are negative whenever the vapor fraction $\beta = n_V/(n_V + n_L)$ is in the range $0.32 < \beta < 0.93$.

Lucia states without proof that a specific split of the Hessian is possible: "Such a split, while not unique, is guaranteed by the form of the excess parts of $\nabla^2 G^L$ and $\nabla^2 G^V$, the Gibbs-Duhem equation for each phase and the positive definiteness of $(\nabla^2 G^L + \nabla^2 G^V)$". The counterexample satisfies all the formal thermodynamic requirements. Our first question to Lucia therefore is whether additional assumptions are hidden in phrase "the form of the excess parts," and whether a mathematical proof of the properties of the split, rather than the guarantee, can be given.

Negative $H^L - H^V$. The partial molar enthalpy of a component in a liquid phase is assumed by Lucia to be less than its partial molar enthalpy in the equilibrium vapor phase. This is certainly not always true.

As a counterexample, consider Henry's Law to describe the solubility of an ideal gas component. The liquid phase chemical potential is

$$\mu_i = \mu_i^0 + RT \ln K_i x_i$$

where μ_i^0 is the pure ideal gas chemical potential and K_i is Henry's constant. The partial molar enthalpy difference is

$$(\bar{H}_i^L - \bar{H}_i^V) = -RT^2 d \ln K_i/dT$$

and will be positive whenever the Henry's constant decreases with increasing temperature.

Above roughly 100°C, the Henry's constants for N_2, H_2, CO,CH_4, etc. in H_2O decrease with increasing temperature. In these cases, at least, Lucia's assumption is wrong.

Retrograde phenomena are the rule in mixtures at high pressures. While they are no doubt rare in low pressure applications, where a near-ideal vapor is in equilibrium with a stable liquid, examples can be constructed.

Consider substance one with Henry's constant

$$\ln K = +2{,}500/T + 2.7$$

when dissolved in substance two. The vapor pressure of substance two is

$$\ln P_s = -4{,}600/T + 10$$

If the pressure units are MPa, these equations (very roughly) approximate hydrogen dissolved in water at about 150°C.

A mixture with 99 moles of substance two per mole of substance one has lines of constant quality that show minima in pressure as temperature increases. As a consequence, VP flash problems can have more than one solution. For instance at 5 MPa, the vapor fraction is 0.0098 both at 364.2 K and at 392.0 K. Nonuniqueness for this example certainly occurs much below the critical state of the mixture, which is close to the critical point of water. Our second question to Lucia is: What is the thermodynamical basis for assuming a negative enthalpy difference, and what are the precise conditions that guarantee a negative difference.

In addition, the connection between uniqueness of calculated equilibria and the stability of the phase models was made at least 65 years ago. A uniqueness proof can be found in the classical paper by Jouguet (1921), but Jouguet cites publications by Duhem from the turn of the century.

Jouguet's (1921) proof is for uniqueness of equilibrium in a closed system at fixed temperature and pressure. The case considered is more complex than the comparable TP flash development in Lucia's (1986) manuscript since Jouguet postulates any number of phases with chemically reacting species.

The QP flash problem discussed by Lucia (1986) can be posed as a maximization of the entropy in a closed system at fixed enthalpy and pressure. Convexity of the phase models therefore excludes the possibility of multiple two-phase solutions (i.e. the behavior shown in Lucia's fig. 2b violates the Second Law of Thermodynamics).

Literature cited

Jouguet, M. E., "Observations sur les Principes et les Théorémes Généraux de la Statique Chimique," *J. de L'Ecole Polytechnique*, 2me Ser., **21,** 62 (1921).

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Reply:

The issues of inverse nonnegativity and negative $(\bar{H}^L - \bar{H}^v)$ raised by Drs. Michelsen and Heidemann are relevant.

With inverse nonnegativity, it is true that the example given by Michelsen and Heidemann satisfies the stability and Gibbs-Duhem conditions for each phase. It also exhibits strong negative deviations from Raoult's Law in the liquid phase. I am unable to feret out either a flaw in my proof or in their arguments, and, as a result, must for now accept their criticism. I do not agree, however, that counterexamples are easy to find and I would be convinced if a realistic example (such as a multicomponent electrolyte or polymer system that has been fit to experimental data) was presented.

Regarding negative $(\bar{H}^L - \bar{H}^v)$, the behavior illustrated does not occur if near or supercritical components are not present in the mixture. Here the temperature is 3 to 5 times the critical temperature of hydrogen, which constitutes the bulk of the vapor phase. Drs. Michelsen and Heidemann give a reasonable condition in the form of the Gibbs-Helmholtz equation. There may be other more useful criteria.

In addition, the work of Duhem, Jouget etc. is well known. The proof of the TP case is included for completeness because it is used in conjunction with the mappings used to show uniqueness in the other cases. Furthermore, there are often many ways to prove a given fact. In the case of the QP flash problem, one way is, as Michelsen and Heidemann state, to maximize the entropy. Another way to do it is the way I did, by constructing a one-to-one, onto mapping which clearly shows the relationship between convexity and uniqueness in this case and which has definite computational value in the context of a continuation procedure. The result I obtained is consistent with the Second Law of Thermodynamics. Extrema of any thermodynamic potential function are a consequence of the Second Law of Thermodynamics so I do not understand the point here.

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