Thermochimica Acta, 23 (1978) 41–55

LIMITS ON THE SIMULTANEOUS CORRELATION OF g^E AND h^E DATA BY THE NRTL, LEMF AND WILSON's EQUATIONS*

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(Received 23 March 1977)

ABSTRACT

Three currently popular excess free energy models (Wilson's equation, the NRTL equation, and the LEMF equation) were subjected to a theoretical parametric analysis to determine limits to their ability to correlate experimental g^E and h^E data simultaneously. The LEMF equation was found to be distinctly superior in its ability to predict VLE data from h^E data. Both Wilson's equation and the NRTL equation were shown to break down to ideal solution models in the limit of large intermolecular interactions ($|h^E|_{max.} > 200$ cal gmol^{-1}) whereas the LEMF equation does not. For mixtures whose h^E data exhibit maxima less than 100 cal gmol^{-1} and which have positive s^E the LEMF equation coupled with the method of Hanks, Gupta, and Christensen can predict reliable VLE data from h^E data. For $|h^E|_{max.} > 200$ cal gmol^{-1}, the LEMF equation/Hanks–Gupta–Christensen method is accurate to within 10–15% where the other two equations generate errors in excess of 40%.

INTRODUCTION

The ability to predict vapor–liquid equilibrium (VLE) data accurately and quickly for non-ideal multicomponent mixtures is of great industrial importance and interest. Most early attempts[1] at correlation of VLE data based on Van der Waals interactions tended to follow the general pattern of Wohl[2] which involves a sequence of terms of increasing complexity representing interactions between larger and larger numbers of molecules. Each higher order interaction term in turn introduced one or more adjustable parameters the evaluation of which required VLE data of that order. That is, ternary interaction parameters require ternary VLE data for their evaluation, etc. Thus, excess free energy models such as these are only correlative in nature, but not predictive.

Wilson[3] introduced a new concept, that of "local compositions," which Orye and Prausnitz[4] showed allowed the generalization of binary correlation parameters

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to multicomponent systems without the need for higher order interaction terms of the Wohl type. This introduced a predictive capability into multicomponent VLE correlation which was most desirable. Since its introduction, Wilson's equation has been used, modified, analyzed, and finally accepted as a useful, practical and generally accurate model by numerous investigators. Wilson's local composition concept has also served as the basis for the development of other useful models. Renon and Prausnitz[5] used this concept to develop their now widely used NRTL equation. More recently, Marina and Tassios[6] have modified the NRTL equation to produce the LEMF equation.

All of these equations, Wilson's, the NRTL, and the LEMF, have in common the ability to generalize binary VLE correlation parameters to multicomponent systems without the need of obtaining multicomponent VLE data.

Hanks et al.[7] proposed a new technique in which excess free energy models such as those mentioned above are used in the integration of the Gibbs–Helmholtz relation

$$h^E = \frac{\partial(g^E/T)}{\partial(1/T)} \tag{1}$$

thus permitting the prediction of g^E (excess free energy) and hence VLE data from h^E (heat of mixing) data. They demonstrated the applicability of this technique to isothermal binary systems. This technique, coupled with the ability to generalize to multicomponent VLE using one of the above g^E models, opens a whole new field of VLE prediction. The present authors recently demonstrated the ability of this technique to predict isothermal[8] ternary VLE data and isobaric[9] binary and ternary VLE data.

Vonka et al.[10] recently pointed out a limitation to Wilson's equation. They analyzed the case for an equimolar mixture ($x_1 = x_2 = 0.5$) with the two Wilson parameters $A_1 = A_2 = A$. For this condition they observed that the following expression for H^* derived from Wilson's equation

$$H^* = \frac{-A \ln A}{1 + A} \tag{2}$$

leads to the physically unrealistic result $H^* = 0$ as A approaches zero (corresponding to infinitely large molecular interactions). In eqn (2) H^* is the value of H for $x_1 = x_2 = 0.5$, where $H = h^E/RT$. Furthermore, the function given by eqn (2) possesses a maximum value $H^*_{max} = 0.278$ at the point $A = 0.278$. This means that for conditions leading to eqn (2) ($x_1 = x_2 = 0.5$, $A_1 = A_2 = A$) Wilson's equation is capable of simultaneously predicting g^E and h^E only so long as $H^* \leq 0.278$. For 25°C this corresponds to $|h^E| \leq 165$ cal gmol^{-1}. The implication of this observation is that for those systems where $|h^E| > 165$ cal gmol^{-1}, Wilson's equation is inappropriate to use in the Hanks–Gupta–Christensen[7] method. Vonka et al.[10], on the basis of the above observation, concluded that "... attempts to fit simultaneously g^E and h^E cannot be successful. The recent approach (e.g., Hanks et al.[7]) to determine g^E in terms of the measured values of h^E seems, therefore, illusory and the procedure is of limited importance." This conclusion is entirely unwarranted and irrelevant to the results which they obtained. All that they showed was the inappropriateness of using Wilson's equation beyond the limits observed. The Hanks–Gupta–Christensen method[7] is fundamentally sound, since it involves only the integration of the Gibbs–Helmholtz relation. Any limitations to this method are occasioned only by limitations inherent in the g^E–h^E models used.

It is the purpose of the present paper to examine three currently popular g^E models — Wilson's equation, the NRTL equation and the LEMF equation — and establish limits to their applicability. These limits will be examined both theoretically and experimentally.

THEORETICAL ANALYSIS

The Hanks–Gupta–Christensen method[7] involves the integration of eqn (1). The necessity of having a set of g^E data at the base temperature to evaluate integration constants is obviated by the use of a semi-empirical g^E model. Three models seem to offer considerable promise in their ability to represent real systems and to be generalized to multicomponent systems. These are the Wilson equation[3], the NRTL equation of Renon and Prausnitz[5], and the LEMF equation of Marina and Tassios[6]. We shall consider each of these equations separately.

The Wilson equation

In terms of the function $Q = g^E/RT$, Wilson's equation may be written as

$$Q = -x_1 \ln(x_1 + \tau_2 x_2) - x_2 \ln(x_1 \tau_1 + x_2) \qquad (3)$$

where

$$\tau_1 = \frac{v_1}{v_2} \exp(-G_1/RT) \qquad (4)$$

$$\tau_2 = \frac{v_2}{v_1} \exp(-G_2/RT) \qquad (5)$$

where $G_1 = (g_{12} - g_{22})$ and $G_2 = (g_{12} - g_{11})$ are intermolecular energy interaction parameters. Application of eqn (1) to eqns (3) and (5) produces the following expression for H

$$H = \frac{x_1 x_2}{RT}\left[\frac{\tau_1 G_1}{x_2 + \tau_1 x_1} + \frac{\tau_2 G_2}{x_1 + \tau_2 x_2}\right] \qquad (6)$$

for the case where $\partial G_1/\partial T = \partial G_2/\partial T = 0$. If one sets $x_1 = x_2$, $v_2/v_1 = \rho$, $\tau_2 = \rho k \tau$, and $\tau_1 = \tau/\rho$, eqn (6) becomes

$$H^* = -\frac{1}{2}\left\{\frac{\tau \ln \tau}{\rho + \tau} + \frac{\rho k \tau \ln(k\tau)}{1 + \rho k \tau}\right\} \qquad (7)$$

In eqn (7), the value of k determines the degree of asymmetry in the curve of H^* vs. τ while the value of ρ reflects the effects of molecular size disparity.

As Vonka et al.[10] showed, when G_1 becomes very large, corresponding to extremely nonideal intermolecular interactions, $\tau \to 0$ and $H^* \to 0$. This may easily be seen to be true from eqn (7) for any fixed values of k, ρ. Also, for the completely symmetrical case $k = \rho = 1$, they showed that eqn (7) again has the limit zero when $G_1 \to 0$ ($\tau \to 1$). They further showed that for the case $k = \rho = 1$, H^* possesses a maximum value $H^*_{\max} = 0.278$ at $\tau = 0.278$. If one more closely examines the behavior of eqn (7) as a function of its three parameters τ_1, k, ρ, one finds a different behavior from that intimated by Vonka et al.[10]. The partial derivatives of eqn (7) with respect to τ, k, and ρ are respectively

$$\left(\frac{\partial H^*}{\partial \tau}\right)_{k,\rho} = \frac{-\frac{1}{2}(\rho + \tau + \rho \ln \tau)}{(\rho + \tau)^2} + \frac{k}{\tau}\left(\frac{\partial H^*}{\partial k}\right)_{\rho,\tau} \tag{8}$$

$$\left(\frac{\partial H^*}{\partial k}\right)_{\tau,\rho} = \frac{-\frac{1}{2}\rho\tau[1 + \rho k\tau + \ln(k\tau)]}{(1 + \rho k\tau)^2} \tag{9}$$

$$\left(\frac{\partial H^*}{\partial \rho}\right)_{k,\tau} = -\frac{1}{2}\left\{-\frac{\tau \ln \tau}{(\rho + \tau)^2} + \frac{k\tau \ln(k\tau)}{(1 + \rho k\tau)^2}\right\} \tag{10}$$

It may easily be seen that setting $\rho = 1$, $k = 1$, $\tau = 0.278$K causes eqns (8)–(10) to vanish simultaneously; the conditions for an extreme value of H^*. This is the case

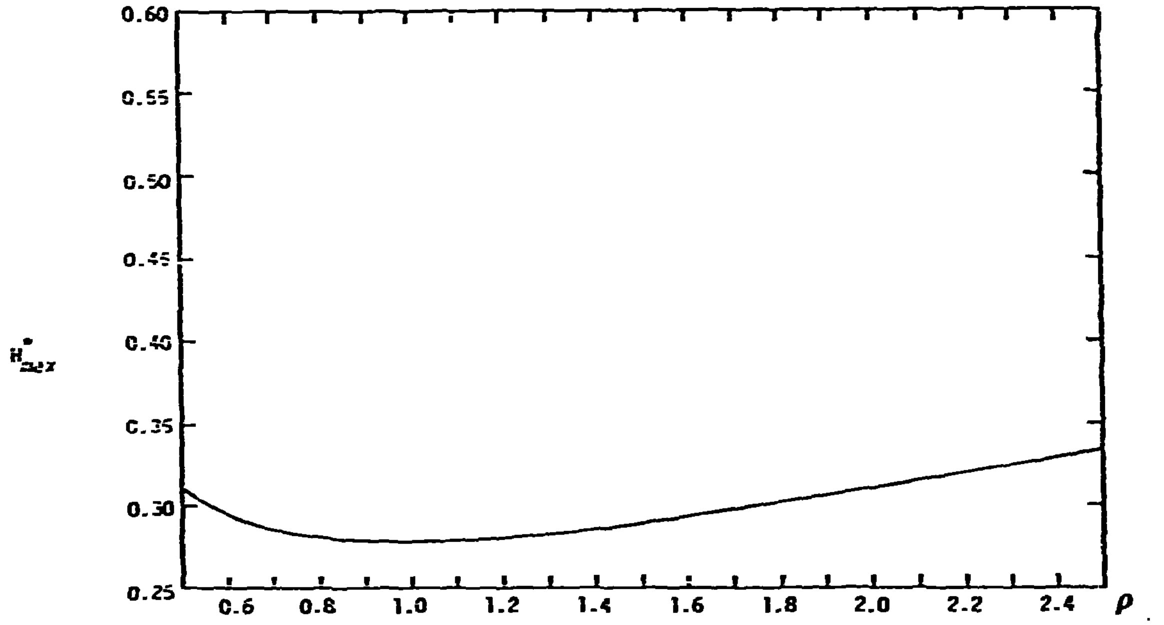

Fig. 1. Variation of $H^*_{\max}$ with ρ for Wilson's equation.

observed by Vonka et al.[10]. Figure 1 shows how the maximum value of H^* varies with ρ in the physically meaningful range $0.5 \leq \rho \leq 2.5$. As ρ approaches either 0 or ∞, this curve increases without bound. From Fig. 1, it can be seen that $H^*(0.5) = 0.3101$ ($\tau = 0.2315$, $k = 1.3578$) and $H^*(2.5) = 0.3333$ ($\tau = 0.3233$, $k = 0.6649$). This corresponds to $|h^E|_{\max.} = 184$ cal gmol^{-1} ($T = 25$°C) when $\rho = 0.5$ and $|h^E|_{\max.} = 197$ cal gmol^{-1} ($T = 25$°C) when $\rho = 2.5$.

The consequence of the above parametric analysis is that when Wilson's equation is used as a two-parameter model, defined as where ρ is fixed at its physically real value, there will be a maximum value of H^*, given by Fig. 1, above which it is impossible for Wilson's equation to represent both g^E and h^E simultaneously. This means, that if a binary mixture exhibits a h^E–x_1 curve which has H^* greater than the values of $H^*_{\max.}$ given by Fig. 1, Wilson's equation cannot be used in the method of Hanks, Gupta, and Christensen[7] to predict VLE data with any degree of confidence. If one were to ignore the physical significance of ρ and merely treat it as a third parameter, the above results indicate that the limiting value of H^* may be increased indefinitely and Wilson's equation might be expected to perform better. However, because of the well-known limitation of Wilson's equation when liquid phase separation occurs, it is doubtful whether this extension of the range of ρ would have any practical utility.

The NRTL equation

In terms of the quantities $Q = g^E/RT$ and $H = h^E/RT$, the NRTL equation may be expressed as

$$Q = x_1 x_2 \left[\frac{\tau_1^\alpha G_1}{x_2 + x_1 \tau_1^\alpha} + \frac{\tau_2^\alpha G_2}{x_1 + x_2 \tau_2^\alpha}\right] \tag{11}$$

$$H = Q - \alpha x_1 x_2 \left[\frac{x_1 \tau_2^\alpha G_2^2}{(x_1 + x_2 \tau_2^\alpha)^2} + \frac{x_2 \tau_1^\alpha G_1^2}{(x_2 + x_1 \tau_1^\alpha)^2}\right] \tag{12}$$

where $\tau_1 = \exp(-G_1)$, $\tau_2 = \exp(-G_2)$, $G_1 = (g_{12} - g_{11})/RT$, $G_2 = (g_{12} - g_{22})/RT$, and α, $(g_{12} - g_{11})$, and $(g_{12} - g_{22})$ are three adjustable parameters which are assumed to be independent of temperature.

If, in eqns (11, 12), one introduces $\tau_1 = k' \tau_2$, recognizes that $G_1 = -\ln \tau_1$ and $G_2 = -\ln \tau_2$, and sets $x_1 = x_2 = 0.5$, one obtains

$$Q^* = -\frac{1}{2\alpha}\left[\frac{\tau \ln \tau}{1 + \tau} + \frac{k\tau \ln (k\tau)}{1 + k\tau}\right] \tag{13}$$

$$H^* = -\frac{1}{2\alpha}\left\{\frac{\tau \ln \tau}{1 + \tau}\left[1 + \frac{\ln \tau}{1 + \tau}\right] + \frac{k\tau \ln (k\tau)}{1 + k\tau}\left[1 + \frac{\ln (k\tau)}{1 + k\tau}\right]\right\} \tag{14}$$

where $\tau = \tau_2^\alpha$, $k = (k')^\alpha$.

From the definition of τ_2, it follows that for $\alpha > 0$ as $\tau_2 \to 0$, $\tau \to 0$ corresponding to $G_2 \rightarrow \infty$. This represents the cases of very large intermolecular interaction parameters, and hence highly non-ideal solutions. In this limit eqns (13) and (14) reveal an interesting difference between the NRTL equation and Wilson's equation. Comparing eqn (13) and eqn (7), it is evident that Q^* for the NRTL equation depends on k, τ in exactly the same formal sense as does H^* for Wilson's equation for the case $\rho = 1$. Thus, it is evident that in the present case $Q^* \rightarrow 0$ as $\tau \rightarrow 0$. That is, the NRTL equation suffers from a more serious limitation in the case of highly non-ideal solutions than does Wilson's equation because the g^E expression for the NRTL equation degenerates to an ideal solution model when G_2 becomes large. Q^* from eqn (12) possesses a maximum value $Q^*_{\max} = 0.2785/\alpha$ at $\tau = 0.2785$ for the case $k = 1$. This means that in the symmetrical case ($k = 1$), the NRTL equation is limited at 25°C to data for which $|g^E| \leq 165/\alpha$ cal gmol^{-1}. For many binary mixtures, Renon and Prausnitz[5] recommend $\alpha = 0.3$–0.4 which for the above limit means that $|g^E| \leq 550$ cal gmol^{-1} ($\alpha = 0.3$) or 413 cal gmol^{-1} ($\alpha = 0.4$).

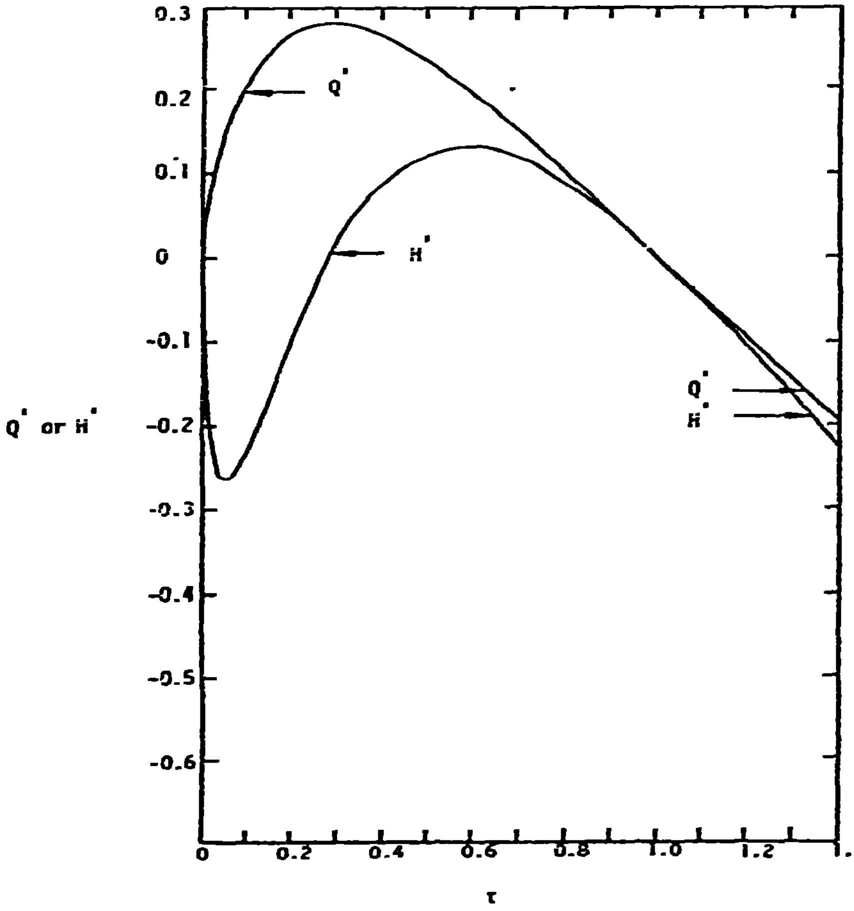

Fig. 2. Variation of $Q' = -\alpha Q^*$ and $H' = -\alpha H^*$ with the parameter $\tau = \tau_2^\alpha$ for the NRTL equation. For this case $k = 1$, $\alpha > 0$.

We now consider the H^* function. For the special symmetrical case ($k = 1$), eqn (14) reduces to

$$H^*(k = 1) = -\frac{1}{\alpha}\left[\frac{\tau \ln \tau}{1 + \tau} + \frac{\tau(\ln \tau)^2}{(1 + \tau)^2}\right] \qquad (15)$$

Again, as $\tau \rightarrow 0(\alpha > 0)$, we find $H^*(k = 1) \rightarrow 0$. Figure 2 shows how $Q^*(k = 1)$ and $H^*(k = 1)$ vary with τ. It is evident that H^* possesses two extreme values, one of opposite sign to Q^* and one of the same sign as Q^* showing that the NRTL equation has a greater degree of flexibility for simultaneous representation of g^E and h^E than does Wilson's equation.

The two extremes in the H^* curve in Fig. 2 occur at $\tau^{(1)} = 0.05$ ($H^* = 0.264/\alpha$) and $\tau^{(2)} = 0.575$ ($H^* = -0.131/\alpha$). For $\alpha = 0.3$ this means if h^E is of opposite sign to g^E, simultaneous representation of h^E and g^E is possible only if $|h^E| < 521$ cal gmol^{-1} (at $T = 25$°C). Again for $\alpha = 0.3$, if h^E is of the same sign as g^E, simultaneous representation of h^E and g^E is possible only if $|h^E| < 259$ cal gmol^{-1} (at $T = 25$°C). These limits are a little larger than the one found above for Wilson's equation. Vonka et al.[10], also showed that the NRTL equation is incapable of representing h^E and g^E simultaneously whenever s^E changes sign in the interval $0 < x_1 < 1$.

The effect of k on the extrema in Q^* and H^* is illustrated in Fig. 3 from which it is seen clearly that the maximum limits of Q^* and H^* are achieved when $k = 1$. Figure 3 also shows that, if $k < 0.25$, the NRTL equation loses entirely its ability to represent h^E and g^E data of the same sign.

The effect of the parameter α on Q^* and H^* is monatonic as may be seen if one considers eqns (13) and (14). This follows since for any given $\alpha > 0$, there will exist a $\tau_2 = \tau^{1/\alpha}$ and $a\ k' = k^{1/\alpha}$ which make the previously discussed results valid. Thus,

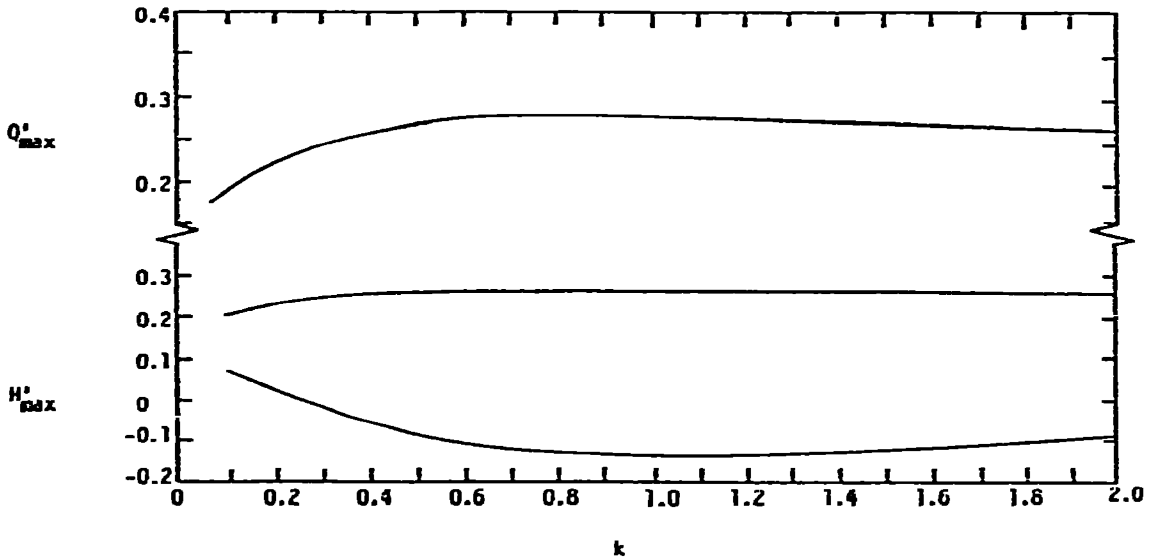

Fig. 3. Variation of maximum values of $Q' = -\alpha Q^*$ and $H' = -\alpha H^*$ with k for the NRTL equation.

both Q^* and H^* vary inversely with α as already discussed. The larger the value of α that is required, the more limited is the range of h^E for which simultaneous representation of g^E and h^E is possible with the NRTL equation.

The NRTL equation is not restricted to one liquid phase system as is Wilson's equation and hence, is more versatile. In view of this greater flexibility, it is not surprising that the NRTL equation has been found[7] to be more versatile in predicting VLE data from h^E data.

The LEMF equation

If the parameter α is allowed to be freely adjustable rather than set at 0.3-0.4 as suggested by Renon and Prausnitz[5], it is often observed to have negative values[6, 8]. Marina and Tassios[6] performed an analysis of the NRTL equation's ability to fit VLE data as a function of the parameter α. They observed that $\alpha = 0.3$ and $\alpha = -1$ were two values which consistently produced minimum values of standard deviations of VLE data fits, with the lowest values corresponding to $\alpha = -1$. They named the NRTL equation with $\alpha = -1$ the LEMF equation[6].

For this model the quantities $Q = g^E/RT$ and $H = h^E/RT$ are given by

$$Q = x_1x_2\left[\frac{G_1}{x_1 + x_2\tau_1} + \frac{G_2}{x_2 + x_1\tau_2}\right] \tag{16}$$

$$H = Q + x_1x_2\left[\frac{x_1\tau_2G_2^2}{(x_2 + x_1\tau_2)^2} + \frac{x_2\tau_1G_1^2}{(x_1 + x_2\tau_1)^2}\right] \tag{17}$$

where $G_1 = (g_{12} - g_{11})/RT$, $G_2 = (g_{12} - g_{22})/RT$, $\tau_1 = \exp(-G_1)$, and $\tau_2 = \exp(-G_2)$. Again $(g_{12} - g_{11})$ and $(g_{12} - g_{22})$ are assumed to be independent of temperature.

Recognizing that $G_1 = -\ln\tau_1$, $G_2 = -\ln\tau_2$ and setting $\tau_2 = k\,\tau_1$, $x_1 = x_2 = 0.5$, one can rewrite eqns (16, 17) as

$$Q^* = -\frac{1}{2}\left[\frac{\ln\tau_1}{1 + \tau_1} + \frac{\ln(k\tau_1)}{1 + k\tau_1}\right] \tag{18}$$

$$H^* = -\frac{1}{2}\left\{\frac{\ln\tau_1}{1 + \tau_1}\left[1 - \frac{\tau_1\ln\tau_1}{1 + \tau_1}\right] + \frac{\ln(k\tau_1)}{1 + k\tau_1}\left[1 - \frac{k\tau_1\ln(k\tau_1)}{1 + k\tau_1}\right]\right\} \tag{19}$$

From eqns (18, 19), it can be shown that as $\tau_1 \to 0$ ($G_1 \to \infty$) both Q^* and H^* become unbounded. Also, as τ_1 becomes small, Q^* and H^* approach one another. This means that in this limit $S^* \to 0$ ($S^* = s^E/R$ for $x_i = 1/2$). Since $Q - H = -s^E/R$, it follows from eqns (16, 17) that

$$\frac{s^E}{R} = x_1x_2\left[\frac{x_1\tau_2G_2^2}{(x_2 + x_1\tau_2)^2} + \frac{x_2\tau_1G_1^2}{(x_1 + x_2\tau_1)^2}\right] \tag{20}$$

Equation (20) shows that the LEMF equation always predicts positive excess entropies. Thus, regardless of the values of k or τ_1, the LEMF equation cannot simultaneously represent h^E and g^E when $|h^E| < |g^E|$. This means the whole class of fluids having negative s^E is excluded as is the class for which s^E changes sign in the interval $0 \leq x_1 \leq 1$. This exculsion is similar to that observed by Vonka et al.[10], for the NRTL equation with $\alpha = 0.3$. It is more severe, however, in that s^E/R for the NRTL equation is given by eqn (20) multiplied by $-\alpha$. Thus, depending upon the sign of α, the NRTL equation can predict either positive or negative s^E/R whereas the LEMF equation is restricted to $s^E/R > 0$.

Since eqns (18, 19) become unbounded as $\tau_1 \rightarrow 0$, it follows that the maxima exhibited by both Wilson's equation and the NRTL equation do not exist here. Thus, provided s^E is positive, the LEMF equation is not restricted to some low range of h^E values. Since there are no maxima, the effects of k are of no concern and need not be investigated.

EXPERIMENTAL COMPARISONS

The preceding analysis has revealed several theoretical limitations to the capability of these excess free energy models to represent g^E and h^E simultaneously. In this section of the paper, several aspects of the present method will be examined in comparison with actual data.

When utilizing experimental data taken from a variety of sources in the literature, one is constantly faced with variability of quality and experimental error. Since the method of Hanks et al.[7] relies heavily upon such data, it is limited by the intrinsic quality of the data. One can thus raise two questions in relation to the actual data themselves: (1) What is the intrinsic level of accuracy to be expected from the literature data? (2) How do errors in the h^E data propagate into the predictions of VLE data.

The first question is important in establishing a background "noise level" against which the reliability of the basic method may be judged and the effects of model limitations such as those described above assessed. In order to evaluate the basic h^E data, two systems were considered which had been studied by different investigators under the same conditions. They are: (I) n-Heptane(1)–toluene(2); and (II) acetonitrile(1)-benzene(2).

Both systems were treated as follows. One set of h^E data was arbitrarily selected as a reference set and treated as being correct. The second set of h^E data was compared to the first statistically and a standard deviation computed. In this way, an estimate of the variability of h^E data due to different investigators is obtained. To obtain an estimate of how errors in the h^E data propagate into the VLE data, each of the sets of NRTL parameters (one set was obtained for $\alpha = 0.3$, one for α freely floating) obtained from the two different authors' sets of h^E data were used in the NRTL equation to compute VLE data. One set of VLE data thus computed was arbitrarily chosen as a reference and the other compared with it statistically. In this manner the standard deviation in the VLE data caused by a certain standard deviation in the h^E data could be assessed. The results of these calculations are shown in Table 1. From these results, it can be seen that the errors in h^E are decreased by approximately a

TABLE 1

EVALUATION OF EFFECTS OF EXPERIMENTAL ERRORS IN h^E DATA ON PREDICTED VLE DATA

System	*Temp. (°C)*	$^{\sigma}h$(%)	$^{\sigma}$VLE(%)	*a*	*Ref.*
I[a]	25	—	—	—	11[c]
I	25	19.84	5.61	0.3	12
I	25	19.84	9.29	0.5711	12
II[b]	45	—	—	—	13[c]
II	45	6.63	1.35	0.3	14
II	45	6.63	3.87	−2.366	14

[a] n-Heptane(1)-toluene(2). [b] Acetonitrile(1)-benzene(2). [c] These data were arbitrarily selected as the reference for comparison purposes.

TABLE 2

DETERMINATION OF VARIABILITY OF EXPERIMENTAL VLE DATA

System No.	*Temp. (°C)*	σ_{y_1}(%)	*Ref.*
III[a]	70	—	16
III	70	4.34	17
III	70	1.96	18
IV[b]	60	—	19
IV	60	2.08	20
V[c]	40	—	21
V	40	3.23	22
V	60	—	21
V	60	2.87	22
VI[d]	45	—	23
VI	45	1.49	24

[a] Benzene(1)-cyclohexane(2). [b] Benzene(1)-n-heptane(2). [c] Cyclohexane(1)-n-heptane(2). [d] Benzene (1)-n-hexane(2).

factor of three in the VLE data. Thus, a 20% error in h^E produced an average error of about 7.5% in the VLE for system I while a 7% error in h^E produced an average error of about 2.6% in VLE for system II. These results are consistent with the error-smoothing feature inherent in the integration processes employed in the method. It appears that errors of as much as 20% in h^E are possible when using literature data sources. One may thus conclude that uncertainties of 3–7% due to variability of to h^E data might be anticipated. Thus, VLE predictions which agree within 3–7% with observed data should be considered to be acceptable to within the intrinsic accuracy of the data.

Another potential source of uncertainty in the predicted data are experimental inaccuracies of the VLE data themselves. In order to evaluate this source of errors four systems (one at two different temperatures) were studied. They are: (III) Benzene

TABLE 3

PARAMETERS FOR TESTING LIMITS OF THE WILSON, NRTL, AND LEMF EQUATIONS

System	*Ref.*	$\lvert h^E \rvert_{max}^a$	*Wilson's equation*			*NRTL equation*							*LEMF equation*		
						$\alpha = 0.3$			α = *Free*						
			$g_{12}-g_{11}$	$g_{12}-g_{22}$	S_0^a	$g_{12}-g_{11}$	$g_{12}-g_{22}$	S_0^a	$g_{12}-g_{11}$	$g_{12}-g_{22}$	α	S_0^a	$g_{12}-g_{11}$	$g_{12}-g_{22}$	S_0^a
VII[b]	26	44	18.65	273.0	0.2	300.2	− 79.12	33.3	− 252.8	202.1	−1.321	32.1	− 19.74	175.7	1.3
VIII[c]	25	90	262.4	193.6	47.8	203.8	211.5	33.8	204.4	211.6	0.290	66.0	141.4	154.3	49.0
III[d]	16	194	753.9	759.4	2770	564.7	473.5	29.6	273.8	326.0	−0.570	40.6	250.2	280.0	99.4
VI[e]	23	205	731.7	843.7	7470	896.2	391.4	22.1	200.8	350.6	−0.993	47.5	200.0	350.0	47.9
IX[f]	25	414	886.5	743.2	3.76 (10^5)	1602	1756	2703	1027	509.4	−0.078	2608	450.9	447.0	1836

[a] Cal gmol^{-1} — All h^E data are at 25°C. [b] Cyclohexane(1)-n-hexane(2). [c] Methylacetate(1)-benzene(2). [d] Benzene(1)-cyclohexane(2). [e] Benzene(1)-n-hexane(2). [f] Methylacetate(1)-cyclohexane(2).

(1)–cyclohexane(2); (IV) benzene(1)–n-heptane(2); (V) cyclohexane(1)–n-heptane(2); (VI) benzene(1)–n-hexane(2). As with the h^E data, one set of data was arbitrarily chosen as a reference and a standard deviation of the other authors' data in comparison was calculated. The results of these calculations are shown in Table 2, from which it appears that most investigators agree with one another to within about 2–3%.

Based upon the above analysis of h^E and VLE data, it appears that one can reasonably anticipate an uncertainty of from 5–10% in VLE data predicted from h^E data in comparison with experimental values due just to the average uncertainities in experimental data and exclusive of any modeling effects. Therefore, predictions of VLE data made from h^E data which compare with experimental data within 5–10% may be considered acceptable.

The final effect to be explored experimentally is the influence of h^E values which are increasingly larger than the theoretical limiting values predicted in the first part of this paper. In order to do this, five binary systems were chosen which have $|h^E|_{\max.}$ values ranging from 44 to 414 cal gmol^{-1}. The five binary systems are (in order of increasing $|h^E|_{\max.}$): (VII) Cyclohexane(1)–n-hexane(2); (VIII) methylacetate(1)–benzene(2); (III) benzene(1)–cyclohexane(2); (VI) benzene(1)–n-hexane(2); (IX) methylacetate(1)–cyclohexane(2).

Each of these five systems was analyzed by the method of Hanks et al.[7] using Wilson's equation, the NRTL equation, and the LEMF equation. Table 3 contains a listing of the parameters obtained and the quantity S_c^2, which is a statistical measure of the fit of the h^E data and is the function minimized by the curve-fitting routine[15] used. The quantity S_c^2 is defined by

$$S_c^2 = \frac{1}{N-2}\sum_j [h^E_{\text{calc}} - h^E_{\text{expt}}]_j^2 \qquad (21)$$

From the values of S_c^2 in Table 3, it is clear that Wilson's equation provided pro-

TABLE 4

EFFECT OF $|h^E|_{\max.}$ ON VLE FITS FOR THE WILSON, NRTL, AND LEMF EQUATIONS

System	*T(°C)*	*Ref.*	*σ_y*[a]				*$|h^E|_{\max.}$(cal gmol^{-1})*
			Wilson	*NRTL*[b]	*NRTL*[c]	*LEMF*	
VII[d]	70	17	24.6	6.63	1.46	5.75	44
VIII[e]	30	25	17.0	13.3	13.4	9.19	90
III[f]	40	26	47.2	35.7	21.4	19.0	194
VI[g]	25	26	45.9	42.7	18.1	18.1	205
IX[h]	35	25	—[i]	102.6	41.2	20.1	414

[a] $\sigma_y = (\sigma_{y1} + \sigma_{y2})/2$ = average % standard deviation of fit of VLE data. [b] $\alpha = 0.3$; 2-parameter NRTL equation. [c] α = Free; 3-parameter NRTL equation. [d] Cyclohexane(1)–n-hexane(2). [e] Methylacetate(1)–benzene(2). [f] Benzene(1)–cyclohexane(2). [g] Benzene(1)–n-hexane(2). [h] Methylacetate(1)–cyclohexane(2). [i] Wilson's equation not applicable here. See text.

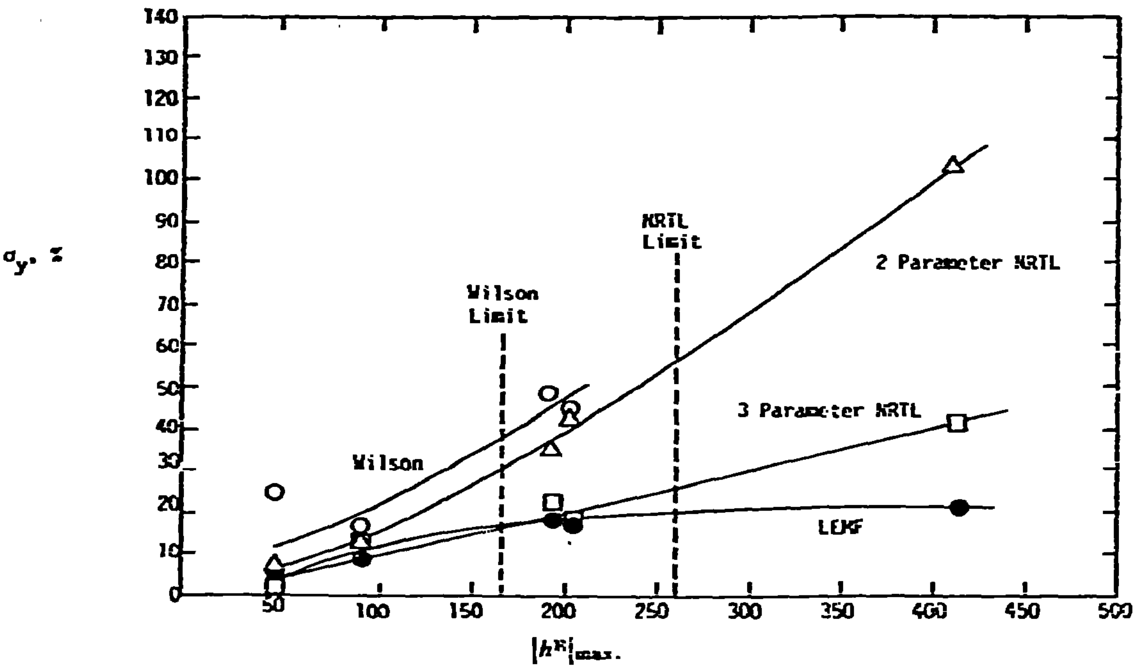

Fig. 4. Variation of σ_y with $|h^E|_{max.}$ for Wilson's equation, the 2-parameter NRTL and 3-parameter NRTL equations, and the LEMF equation for five different systems.

gressively worse fits as $|h^E|_{max.}$ increased. The other equations retained roughly equivalent fits for $|h^E|_{max.} \leq 200$ cal gmol^{-1}, becoming worse for $|h^E|_{max.} > 400$. For system (IX), the LEMF equation was best able to fit the h^L data.

Each of the sets of parameters in Table 3 was used to compute VLE values which were then compared with experimental data for each of the five systems. The results are shown in Table 4 and also displayed graphically in Fig. 4. Also shown in Fig. 4 are the theoretical limits estimated above for Wilson's equation and the two-parameter NRTL equation. The very large value of S_e^2 given for system (IX) with Wilson's equation in Table 3 shows that for this system Wilson's equation was incapable of fitting the h^E data. For this reason, no point for σ_y is included in Fig. 4 for system (IX). The curve in Fig. 4 for Wilson's equation is not defined above about 250 cal gmol^{-1}.

From these results, several things are clear. As $|h^E|_{max.}$ increases, there exists a definite increase in the deviation between predicted and actual VLE data. This is as anticipated based on the theoretical analyses given earlier. Figure 4 shows that both Wilson's equation and the two-parameter NRTL equation begin to develop unacceptably large errors in the predicted VLE data at $|h^E|_{max.}$ values significantly lower than the theoretical limits. Figure 4 also shows that the order of effectiveness for predicting VLE data from h^E data in order from best to worst is LEMF–3-parameter NRTL–2-parameter NRTL–Wilson.

Figure 4 further shows that for $|h^E|_{max.} < 200$ cal gmol^{-1}, the LEMF equation is of equal accuracy with the 3-parameter NRTL equation but for $|h^E|_{max.} >$

200 cal gmol^{-1}, the LEMF equation is distinctly superior to any of the others. Of particular interest, is the fact that the LEMF equation appears to reach an asymptotic limit of $\sigma_y = 20\%$ for large $|h^E|_{max}$ values while all the others appear to produce σ_y values which increase indefinitely as $|h^E|_{max}$ increases.

CONCLUSIONS

A combined theoretical and experimental analysis of the parametric behavior of three currently popular g^E models has revealed a number of significant limitations to these models when they are used to correlate g^E and h^E simultaneously. The existence of these limitations is of importance in determining the successfulness of the Hanks–Gupta–Christensen method of predicting VLE data from h^E data. The conclusions which may be drawn from the present analysis are as follows.

(1) The LEMF equation is distinctly superior to either the Wilson or the NRTL equations in its ability to predict VLE data from h^E data for systems having positive s^E.

(2) Both Wilson's equation and the NRTL equation (either two- or three-parameter versions) approach ideal solution behavior in the limit of large intermolecular interactions. This behavior means that as the values of h^E increase, both equations will provide increasingly poor simultaneous representations of g^E and h^E.

(3) The LEMF equation does not approach ideal solution behavior in the limit of large intermolecular interactions. Consequently, it is capable of maintaining some degree of success in simultaneously representing g^E and h^E as h^E becomes large.

(4) For $|h^E|_{max} < 100$ cal gmol^{-1}, both the NRTL and LEMF equations are reliable predictors of VLE data from h^E data. However, if $|h^E|_{max}$ exceeds 200 cal gmol^{-1}, only the LEMF equation produces reliable results.

(5) For $|h^E|_{max} > 200$ cal gmol^{-1}, the LEMF equation produces VLE data with a maximum of σ_y of 20%, while the other two equations produce σ_y values which appear to increase indefinitely as $|h^E|_{max}$ increases.

(6) There is an inherent uncertainty in VLE data predicted from h^E data of from 5–10% which is independent of g^E models.

(7) The LEMF equation, coupled with the Hanks–Gupta–Christensen method, can produce VLE data which are fully reliable (that is, $\sigma_y < 10\%$) whenever $|h^E|_{max} \leq 100$ cal gmol^{-1} and which are at most 10–15% in error (that is, $\sigma_y < 20\%$) if $|h^E|_{max} > 200$ cal gmol^{-1} and $s^E > 0$.

(7) The LEMF equation is not capable of representing g^E and h^E simultaneously, if s^E changes sign in the composition interval $0 \leq x_1 \leq 1$, or if $s^E < 0$.

It would appear from the present analysis that a fruitful field of endeavor would be to develop an excess property model which retains the desirable qualities of the LEMF model but which also accounts for more realistic variations of s^E with composition.

ACKNOWLEDGEMENT

This work was partially supported by a grant from the Union Carbide Corporation, South Charleston, West Virginia.

REFERENCES

1 J. M. Prausnitz, *Molecular Thermodynamics of Fluid-Phase Equilibria*, Prentice-Hall, Englewood Cliffs, NJ, 1969.
2 K. Wohl, *Trans. A.I.Ch.E.*, 42 (1946) 215.
3 G. M. Wilson, *J. Am. Chem. Soc.*, 86 (1964) 127.
4 R. V. Orye and J. M. Prausnitz, *Ind. Eng. Chem.*, 57 (1965) 18.
5 H. Renon and J. M. Prausnitz, *A.I.Ch.E. J.*, 14 (1968) 135.
6 J. M. Marina and D. P. Tassios, *I/EC Process Des. Devel.*, 12 (1973) 67.
7 R. W. Hanks, A. C. Gupta and J. J. Christensen, *I/EC Fundam.*, 10 (1971) 504.
8 R. L. Tan, R. W. Hanks and J. J. Christensen, *Thermochim. Acta*, 21 (1977) 157.
9 R. L. Tan, R. W. Hanks and J. J. Christensen, *Thermochim. Acta*, 23 (1978) 29.
10 P. Vonka, J. P. Novak, J. Suska and J. Pick, *Chem. Eng. Commun.*, 2 (1975) 51.
11 H. W. Schnaible, *Ph. D. Dissertation*, Purdue University, (1955).
12 G. W. Lundberg, *J. Chem. Eng. Data*, 9 (1964) 193.
13 D. A. Palmer and B. C. Smith, *J. Chem. Eng. Data*, 17 (1972) 71.
14 I. Brown and F. Smith, *Aust. J. Chem.*, 8 (1955) 62.
15 R. L. Tan, *M.S. Thesis*, Brigham Young University, (1977).
16 G. Scatchard, S. E. Wood and J. M. Mochel, *J. Phys. Chem.*, 43 (1939) 119.
17 M. P. Susarev and S. T. Chien, *Russ. J. Phys. Chem.*, 37–8 (1963) 1739.
18 M. Diaz Pena and D. R. Cheda, *Ann. Quim.*, 66 (1970) 721.
19 I. Brown and A. H. Ewald, *Aust. J. Sci. Res.*, A4 (1951) 198.
20 D. O. Hanson, *Ph. D. Dissertation*, University of Texas, (1966).
21 J. L. Crutzen, R. Haase and L. Sieg, *Z. Naturforsch.*, 59 (1950) 600.
22 R. Rothe, *Ph. D. Dissertation*, Göttingen, 1958.
23 V. C. Smith and R. L. Robinson, Jr., *J. Chem. Eng. Data*, 15 (1970) 391.
24 K. R. Harris and P. J. Dunlop, *J. Chem. Thermodyn.*, 2 (1970) 805.
25 I. Nagata, T. Ohta, T. Takahashi and K. Gotoh, *Jpn. J. ChE.*, 6 (1973) 129.
26 K. Ridgway and P. A. Butler, *J. Chem. Eng. Data*, 12 (1967) 509.