K = transducer coefficient, g cm/mV s^2
K_{av} = average transducer coefficient, g cm/mV s^2
K_i = transducer coefficient for ith collision, g cm/mV s^2
$L_p(r)$ = local axial distance between particles, cm
$L_{pav}(r)$ = average local axial distance between particles, cm
m_p = mass of a single particle, g
m_{pav} = average mass of single particle, g
n = number of collisions
$N_p(r)$ = local flux of particles, number/cm^2 s
r = radial position, cm
R = radius of the tube, cm
t = time, s
t_e = time elapsed between two consecutive collisions, s
t_{eav} = average time elapsed between two consecutive collisions, s

$v_p(r)$ = local axial particle velocity, cm/s
$v_{pav}(r)$ = average local axial particle velocity, cm/s
W_p = total particle flow rate, number/s
γ = capture efficiency, dimensionless

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The Number of Roots in the Wilson Equation and Its Effect on Vapor–Liquid Equilibrium Calculations

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The number of roots in the Wilson equation that can be obtained from a set of binary activity coefficients (γ_i) is examined. It is concluded that only one set of roots exists for the case of $\gamma_i > 1$; however, as many as three sets of roots can exist for the case of $\gamma_i < 1$. The criteria with which to determine the number of such sets is presented. Best predictions of binary and multicomponent data appear to result from the set of roots that are smallest in absolute value.

Introduction

The Wilson equation has found extensive use in the correlation and prediction of vapor–liquid equilibrium (VLE) data (Wilson, 1964; Orye and Prausnitz, 1965). In predicting multicomponent equilibria from binary VLE data, one must first obtain the binary arameters. It is customary to regress all the available binary data; however, use of one binary point has also been suggested (Hudson and Van Winkle, 1970), especially if the data pair are the infinite dilution values (Hankinson et al., 1972; Schreiber and Eckert, 1971). The purpose of this study is to (i) discuss the number of sets of binary parameters (i.e., roots) obtained either from one data point (including the use of the infinite dilution activity coefficients) or from regressing all the binary data; and (ii) explore the effect of multiple sets of parameters, wherever they exist, on the accuracy of predicted data.

The Wilson Equation

For the ith component of an N-component system, the Wilson equation is

$$\ln \gamma_i = 1 - \ln \left[\sum_{j=1}^{N} \Lambda_{ij} x_j \right] - \sum_{k=1}^{N} \left[\frac{\Lambda_{ki} x_k}{\sum_{j=1}^{N} \Lambda_{kj} x_j} \right] \quad (1)$$

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where

$$\Lambda_{ij} \equiv \frac{v_j{}^L}{v_i{}^L} e^{-(\lambda_{ij} - \lambda_{ii})/RT} \quad (2)$$

For a binary system, the Wilson equation simplifies to

$$\ln (\gamma_1) = -\ln (x_1 + \Lambda_{12} x_2) + x_2 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{\Lambda_{21} x_1 + x_2} \right] \quad (3)$$

$$\ln (\gamma_2) = -\ln (\Lambda_{21} x_1 + x_2) - x_1 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{\Lambda_{21} x_1 + x_2} \right] \quad (4)$$

Given a set of experimentally derived binary activity coefficients, there are two methods that can be used to evaluate the Wilson parameters. First, use one set of activity coefficients (γ_1, γ_2) for a given composition, and solve a system of two equations (binary Wilson Equation) in two unknowns ($\Lambda_{12}, \Lambda_{21}$) to evaluate the Wilson parameters. Second, regress all the available binary VLE data to establish these parameters in a minimum error sense. These two methods can give distinctly different results (Hudson and Van Winkle, 1970). Table I presents some of their data.

These results should not, however, be interpreted as indicating the existence of a multiplicity of roots for the Wilson equation. It will be shown next that for a given set of binary activity coefficients, there is a unique set of Wilson parameters that best fit the data for positive deviations from Raoult's law.

Table I. Wilson Parameters (P = 760 mmHg)

Binary system (1-2)	All binary data $\lambda_{12} - \lambda_{11}$	$\lambda_{12} - \lambda_{22}$	One binary point $\lambda_{12} - \lambda_{11}$	$\lambda_{12} - \lambda_{22}$
Acetone–ethanol	38.2	418.9	856.9	10.1
Acetone–methanol	−215.0	664.3	46.4	444.9
Benzene–chloroform	148.4	−208.5	−783.1	1461.4
Benzene–methyl acetate	200.5	−10.2	−288.9	432.0
Cellosolve–ethylbenzene	747.4	129.8	1255.2	−280.2
Cyclohexane–toluene	−416.3	911.5	179.6	53.2
Heptane–toluene	−45.1	264.4	241.7	79.4
Methanol–2-propanol	85.7	−25.5	1448.6	−1047.2

$$\gamma_2 = \frac{(\gamma_1 t)^{-x_1/x_2}}{x_2^2}\left(x_2 \cdot x_1 \, \ell n \, (\gamma_1 t) \cdot x_1 \cdot \frac{x_1^2}{t}\right)$$
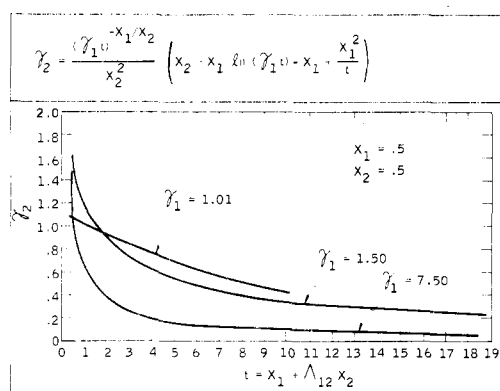
Figure 1. Positive deviations from ideality. Dependence of γ_2 on transformed parameter t.

For systems with negative deviations, on the other hand, three such sets may exist.

Parameter Values from One Binary Data Point

Following the suggestion of Aristovich et al. (1969), define a translation of coordinates as

$$t = x_1 + \Lambda_{12}x_2 \tag{5}$$

$$z = \Lambda_{21}x_1 + x_2 \tag{6}$$

Substitution of eq 5 into eq 3 will give

$$\Lambda_{21} = \frac{-\ln(\gamma_1 t) + \dfrac{t - x_1}{t}}{1 - \dfrac{x_1}{x_2}\left[-\ln(\gamma_1 t) + \dfrac{t - x_1}{t}\right]} \tag{7}$$

Further substitutions of eq 7 and 5 into eq 4 will yield an expression for γ_2 as a function of γ_1, t and x (i.e., γ_1, Λ_{12}, and x)

$$\gamma_2 = \frac{(\gamma_1 t)^{-x_1/x_2}}{x_2}\left[1 - \frac{x_1}{x_2}\left(-\ln\gamma_1 t + \frac{t - x_1}{t}\right)\right]$$
$$\equiv g_2(\gamma_1,t,x) \tag{8}$$

A similar manipulation will yield

$$\gamma_1 = \frac{(\gamma_2 z)^{-x_2/x_1}}{x_1}\left[1 - \frac{x_2}{x_1}\left(-\ln\gamma_2 z + \frac{z - x_2}{z}\right)\right]$$
$$\equiv g_1(\gamma_2,z,x) \tag{9}$$

which represents γ_1 as a function of γ_2, z, and x.

For a given composition (set of x_1, x_2 values) and the corresponding values for the activity coefficients (γ_1,γ_2), a plot of γ_2 as a function of γ_1 and $t(\Lambda_{12},x)$ can be made. Examples of these are presented in Figure 1 for $x_1 = x_2 = 0.5$ and for $\gamma_1 = 1.01, 1.5, 7.5$. From the known value of γ_2, one and only one
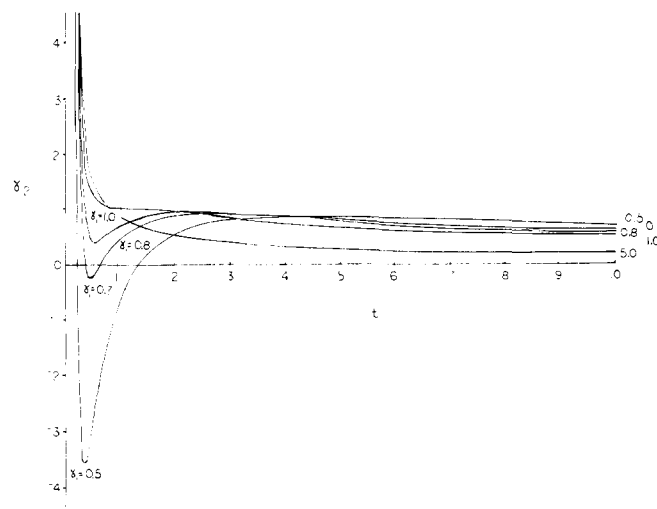
Figure 2. Negative deviations from ideality. Dependence of γ_2 on transformed parameter t. See eq 2, 5, and 8 in text at $x_1 = 0.5$.
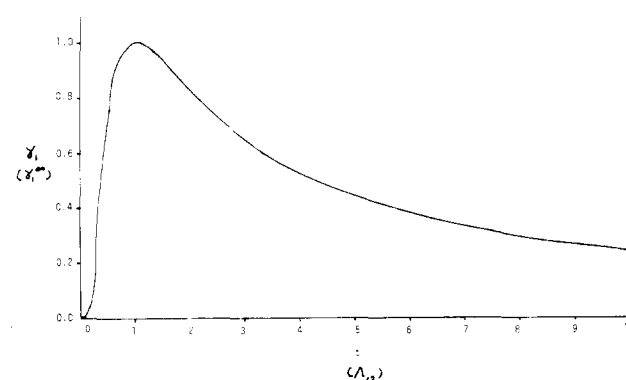
Figure 3. Negative deviations from ideality. Dependence of γ_1 on transformed parameter t with $F(\gamma_1,t) = 0$. Plot holds for γ_1^∞ as a function of Λ_{12} also; see eq 11 and 12 in text.

corresponding value of t; hence Λ_{12}, can be obtained. For example, let $\gamma_1 = 1.5$ and $\gamma_2 = 1.4$; then $t = 0.65$ and $\Lambda_{12} = 0.3$. This single value of Λ_{12} will yield a single value of Λ_{21} from eq 7. On the other hand, consider the case of negative deviations from Raoult's law as shown in Figure 2. Three values of t, hence Λ_{12}, can be found to correspond to a given γ_2.

These observations can be quantified and proven to be generally true. Consider the first derivative of γ_2 with respect to the transformed parameter t

$$\frac{\partial \gamma_2}{\partial t} = \frac{x_1^2(\gamma_1 t)^{-x_1/x_2}}{x_2^3 t}\left[1 - \frac{1}{t} - \ln(\gamma_1 t)\right]$$
$$\equiv g_2'(\gamma_1,t,x) \tag{10}$$

Define the quantity

$$F(\gamma_1,t) \equiv 1 - \frac{1}{t} - \ln(\gamma_1 t) \tag{11}$$

If $F(\gamma_1,t)$ never takes on the value of zero, then $g_2'(\gamma_1,t,x)$ can never be zero. Hence, γ_2 must be a monotonically changing function of t for given γ_1 and x. Clearly under these conditions there can only be unique solutions to the Wilson equation. If, on the other hand, $F(\gamma_1,t)$ is zero at some value of $t > 0$, then multiple roots may, in fact, exist. The implications of $F(\gamma_1,t)$ taking on zero values must be examined in some detail.

The values of γ_1 and t for which $F(\gamma_1,t)$ is zero define the points at which the uniqueness of solutions of the Wilson equation must be examined. Solving the equation $F(\gamma_1,t) = 0$ will define any restrictions on the possible values of γ_1 and
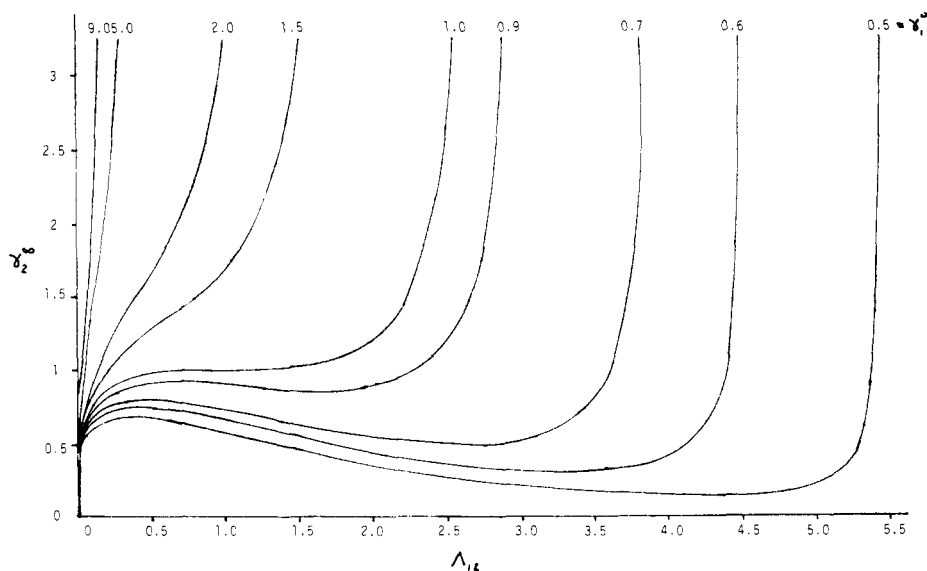
Figure 4. Negative deviations from ideality. Infinite dilution form. See eq 17 in text.

t that may exist. Solving for γ_1 gives

$$\gamma_1 = \frac{1}{t} e^{(t-1)/t} \equiv f_1(t) \tag{12}$$

To completely describe the values that γ_1 and t can take on for which $g_2{}'(\gamma_1,t,x)$ will be zero, the first and second derivatives are required

$$\frac{d\gamma_1}{dt} = \frac{1}{t^2}\left[\frac{1}{t} - 1\right] e^{(t-1)/t} \equiv f_1{}'(t) \tag{13}$$

$$\frac{d^2\gamma_1}{dt^2} = \frac{1}{t^4}\left[\frac{1}{t} + 2t - 4\right] e^{(t-1)/t} \equiv f_1{}''(t) \tag{14}$$

Equation 13 indicates that $f_1(t)$ attains a position of zero slope for only one value of t (call that value t_0) in the range $t > 0$, and that the value is unity. Equation 14 indicates that $f_1(t)$ attains a maximum value at t_0. Equation 12 indicates that this maximum value of γ_1 (attained at $t = t_0$) is unity. Thus $F(\gamma_1,t)$ is zero only for values of γ_1 less than unity, i.e., only for systems having negative deviations from ideality. Figure 3 depicts the relationship between γ_1 and t that must exist if $F(\gamma_1,t)$ is zero. Clearly for any given $\gamma_1 < 1$ there will be two values of t for which $F(\gamma_1,t)$ will be zero; these are $t_1 < 1$ and $t_2 > 1$.

While this defines the relationship that must exist between γ_1 and t, it does not completely describe the relationship between γ_2 and t. Consider the second derivative of γ_2 with respect to t

$$\frac{\partial^2 \gamma_2}{\partial t^2} = -\frac{x_1{}^2(\gamma_1 t)^{-x_1/x_2}}{x_2{}^3 t^2}$$

$$\times \left[\left(1 + \frac{x_1}{x_2}\right) F(\gamma_1,t) + \frac{t-1}{t}\right] \equiv g_2{}''(\gamma_1,t,x) \tag{15}$$

Clearly $F(\gamma_1,t)$ is zero at $t = t_1$ and $t = t_2$. Thus $g_2(\gamma_1,t,x)$ attains a minimum at $t = t_1$ and a maximum at $t = t_2$. There is a point of inflection at $t = t_0$ and at no other values of t. This describes the general shape of curves for γ_2 vs. t with γ_1 as a parameter (see Figure 2).

It is proven, therefore, that γ_2 is a monotonically decreasing function of t at given γ_1 and x for systems with positive deviations from ideality. This behavior is illustrated in Figure 1. For systems with negative deviations from ideality, however, γ_2 goes through a relative minimum at a $t_1 < 1$ and a relative maximum at a $t_2 > 1$. The actual values of t_1 and t_2 are those for which $F(\gamma_1,t) = 0$ (see Figure 3). In consequence, there can be three values of t (hence three pairs of Wilson parameters) that describe the given experimental conditions of x, γ_1, γ_2.

The necessary and sufficient condition for the existence of multiple roots is that the experimental value of γ_2 lie between the minima and maxima defined for γ_2 at t_1 and t_2. This behavior is illustrated in Figure 2. For example, if $x_1 = 0.5$ and $\gamma_1 = 0.7$, then any $\gamma_2 > 0.88$ will yield only a single set of values for the Wilson parameters. On the other hand, for $\gamma_2 < 0.88$ there will be three sets of Wilson parameters.

Parameter Values from a Pair of Infinite Dilution Activity Coefficients

For the case of infinite dilution activity coefficients, the Wilson equation can be transformed into the following expressions

$$\gamma_1{}^\infty = \frac{1}{1 - \ln \gamma_2{}^\infty \Lambda_{21}} e^{1 - \Lambda_{21}} \tag{16}$$

and

$$\gamma_2{}^\infty = \frac{1}{1 - \ln \gamma_1{}^\infty \Lambda_{12}} e^{1 - \Lambda_{12}} \tag{17}$$

An analysis similar to that performed above leads to analogous conclusions. For infinite dilution activity coefficients larger than unity, only a single set of Wilson parameters is obtained. The necessary condition for multiple parameter values is that the infinite dilution activity coefficients be less than unity. Furthermore, the necessary and sufficient condition is that $\gamma_2{}^\infty$ lie within the range defined by the relative maxima and minima for the given value of $\gamma_1{}^\infty$. This behavior is illustrated in Figure 4.

In addition, the values of the relative maxima and minima for $\gamma_2{}^\infty$ are defined as a function of $\gamma_1{}^\infty$ and Λ_{12} by the same expression used to define the relative maxima and minima of γ_2 as a function of γ_1 and t. Here $\gamma_1{}^\infty$ replaces γ_1, and Λ_{12} replaces t. Again Figure 3 is used.

As indicated in Figure 4, the curves for $\gamma_2{}^\infty(\gamma_1{}^\infty, \Lambda_{12})$ approach infinity at the values of $\Lambda_{12} = e/\gamma_1{}^\infty$. This is defined by the forms of eq 16 and 17.

Parameters from Regression of all Binary Data

In regressing a set of binary data, one is searching for a pair of parameter values $(\lambda_{12} - \lambda_{11})$ and $(\lambda_{12} - \lambda_{22})$ that minimize the function Q

$$Q \equiv \sum_{i=1}^{N} \left[\left(\frac{\gamma_{1,\exp} - \gamma_{1,\text{calc}}}{\gamma_{1,\exp}}\right)_i{}^2 + \left(\frac{\gamma_{2,\exp} - \gamma_{2,\text{calc}}}{\gamma_{2,\exp}}\right)_i{}^2\right] \tag{18}$$

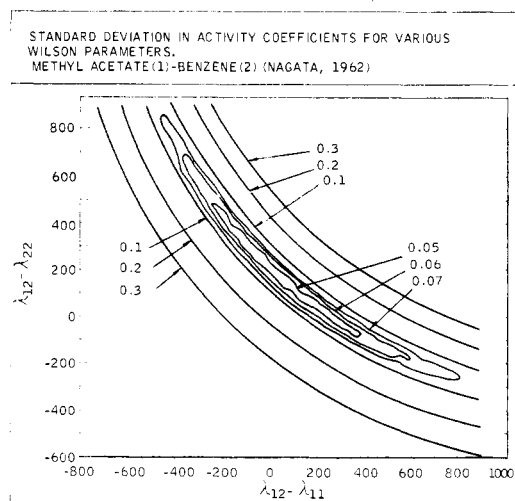Other minimization functions can be used. They have been

Figure 5. Typical contour plot. Standard deviation in activity coefficients for various Wilson parameters for the system methyl acetate (1)–benzene (2) (Nagata, 1962).

recently discussed by Silverman and Tassios (1973), but the approach is the same. Starting with a set of initial guesses to the parameter values, the regression subroutine varies them until Q assumes a minimum value.

Considering the complexities of eq 18, no parametric substitution can lead to meaningful conclusions about the number of sets of parameters that minimize Q. Instead two approaches have been considered.

The first approach is demonstrated in Figure 5 (Larson, 1971) for the system methyl acetate–benzene ($\gamma > 1$) where lines for constant values of S

$$S = \sqrt{\frac{Q}{2N - 1}} \qquad (19)$$

are plotted as functions of the corresponding values for ($\lambda_{12} - \lambda_{11}$) and ($\lambda_{12} - \lambda_{22}$). The plot suggests that only one pair of the Wilson parameters, lying inside the island characterized by $S = 0.05$, exists for which S assumes a minimum value. Finding this unique set of values by this method would require, of course, a very large number of ($\lambda_{12} - \lambda_{11}$) and ($\lambda_{12} - \lambda_{22}$) sets. The plot also explains why several sets of parameters, widely different, will give small values for the standard deviations.

In the second approach, the data were regressed through a nonlinear (simplex) regression subroutine (Gardner, 1960). A set of initial guesses for ($\lambda_{12} - \lambda_{11}$) and ($\lambda_{12} - \lambda_{22}$) is supplied to the subroutine which varies the parameter values until a minimum value for Q is obtained. If more than one set of roots exists, they can be obtained by using different values for the initial guesses provided, of course, that these roots do not lie too far away from the initial guesses. For this purpose, ten initial guesses covering the range -3000 to $+3000$ were used in this study. This represents the field of reasonable values for ($\lambda_{12} - \lambda_{11}$) and $\lambda_{12} - \lambda_{22}$). For systems with λ's larger than unity, all initial guesses lead to the same roots for a given system. For systems with γ's less than unity this is not the case. Eight such binary systems (Table II) were studied; each yielded three sets of parameters. The values of these parameters and the quality of the fit of the binary data obtained from their use are documented in Table III.

Table II. Binary Systems Exhibiting Negative Deviations from Ideality

System ID	Components	Conditions	Reference
007A	Acetone–chloroform	50 °C	Severns (1955)
007B	Acetone–chloroform	55 °C	Kudryautseva (1963)
035A	Chloroform–benzene	50 °C	Nagata (1970)
035B	Chloroform–benzene	760 mmHg	Nagata (1962)
036	Chloroform–ethyl acetate	760 mmHg	Nagata (1962)
038	Chloroform–methyl isobutyl ketone	760 mmHg	Karr (1951)
099A	Methyl acetate–chloroform	50 °C	Nagata (1970)
0.99B	Methyl acetate–chloroform	760 mmHg	Nagata (1962)

Table III. Parameter Values and Quality of Fit for Systems with γ's < 1

Binary system	Parameter values		Objective function	Pressure	Composition ×1000	Root code
007A	−34.85	−372.73	0.05722	5.66	5.61	A
	1877.86	−996.31	0.1657	3.73	7.51	B
	−875.84	1850.33	0.1844	10.29	14.47	C
007B	55.43	−475.76	0.009377	12.74	4.73	A
	5136.60	−1066.87	0.009636	7.86	4.74	B
	−912.30	2806.71	0.06993	8.95	17.14	C
035A	−213.15	91.51	0.02474	3.64	5.42	A
	1135.53	−728.32	0.02842	2.40	4.33	B
	−616.25	1103.12	0.02261	1.97	3.74	C
035B	−226.83	170.29	0.002266	3.68	1.72	A
	987.90	−681.27	0.002719	3.51	1.55	B
	−392.09	458.86	0.002402	3.91	3.91	C
036	−346.57	−104.25	0.007821	5.37	2.74	A
	−955.01	7166.10	0.009829	8.35	3.81	C
	2748.51	−1158.63	0.1341	26.90	15.70	B
038	−482.70	201.59	0.06379	29.74	6.94	A
	8970.31	−1484.86	0.7721	23.60	19.07	B
	−869.70	7234.66	0.1368	30.93	7.17	C
099A	30.60	−422.09	0.01362	2.67	4.14	A
	2127.15	−966.66	0.01999	3.82	4.00	B
	−949.86	2862.82	0.1899	10.93	18.44	C
099B	121.55	−460.33	0.01221	3.73	4.44	A
	−941.25	2025.03	0.09658	13.20	15.01	C
	2235.39	−971.20	0.002807	4.55	3.00	B

Table IV. Parameter Values and Quality of Fit from Infinite Dilution Coefficients in Systems with $\gamma^\infty < 1$

Binary system	Parameter values		Objective function	Mean absolute deviations in Pressure	Composition ×1000	Root code
007A	−52.70	−359.16	1.001×10^{-10}	5.96	5.71	A
	2146.26	−1090.22	5.478×10^{-11}	16.64	11.51	B
	−1077.04	2609.30	3.812×10^{-12}	36.72	35.93	C
007B	166.90	−565.33	4.732×10^{-10}	14.69	5.15	A
	1841.25	−1070.26	1.879×10^{-12}	22.52	10.01	B
	−1264.25	3795.72	2.484×10^{-10}	94.76	63.08	C
035A	−406.66	406.70	4.791×10^{-4}	4.89	6.58	B
	1596.51	−883.86	7.883×10^{-11}	13.62	14.30	A
035B	−344.52	363.46	7.548×10^{-5}	4.00	1.70	B
	1082.00	−732.05	9.743×10^{-11}	8.40	4.02	A
036	−439.56	79.14	4.864×10^{-12}	9.70	5.32	A
	−888.71	1588.66	2.078×10^{-12}	12.47	7.02	C
	3858.52	−1484.51	5.162×10^{-12}	74.55	54.56	B
038	−410.11	69.50	2.135×10^{-12}	26.02	7.35	A
	−811.88	1643.95	2.103×10^{-12}	34.87	6.64	C
	4502.51	−1828.73	1.170×10^{-11}	98.27	59.26	B
099A	41.09	−417.90	1.970×10^{-11}	3.00	4.66	A
	1787.19	−993.83	6.441×10^{-12}	7.33	7.47	B
	−1137.07	2823.44	2.088×10^{-11}	38.53	42.94	C
099B	320.58	−558.19	1.581×10^{-12}	7.07	7.16	A
	−1201.90	3219.19	7.524×10^{-11}	77.49	44.41	C
	1111.60	−843.05	4.379×10^{-11}	7.53	9.15	B
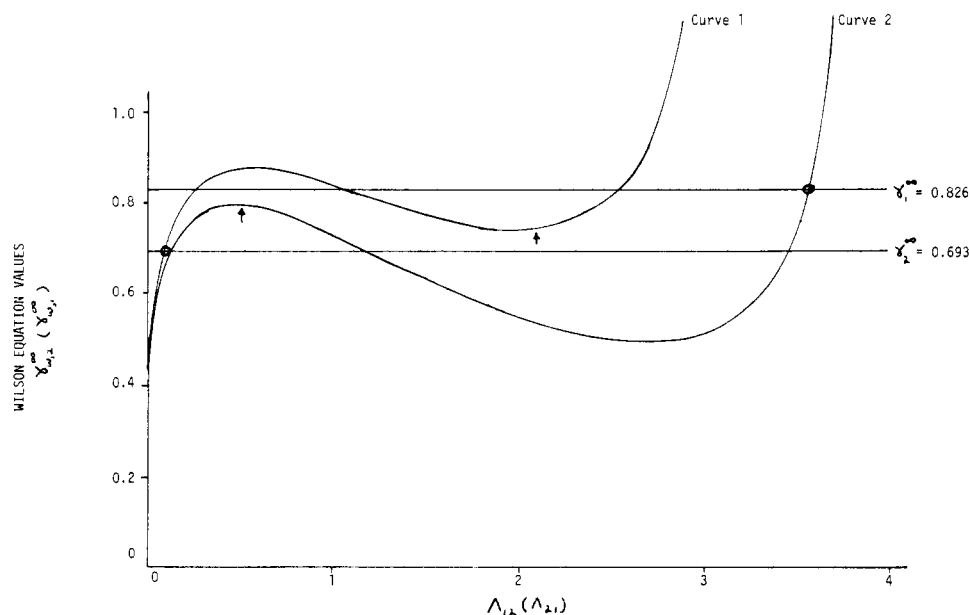
Figure 6. Infinite dilution activity coefficients. Chloroform (1)–benzene (2) (System 035A). Curve 1 depicts the locus of all values that the Wilson equation can predict for γ_2^∞ given that $\gamma_1^\infty = 0.826$; curve 2 depicts the locus of all values that $\gamma_{w,1}^\infty$ can assume given that $\gamma_2^\infty = 0.693$. There exists only one value of Λ_{12} for which $\gamma_{w,2}^\infty$ takes on the experimental value of 0.693. This location is circled and corresponds to $\Lambda_{12} = 0.092$ to give $\lambda_{12} - \lambda_{11} = 1596.5$ cal/g-mol. Similarly, only one root is found from curve 2 at $\Lambda_{21} = 3.575$ to give $\lambda_{21} - \lambda_{22} = -883.9$ cal/g-mol. The locations of the pseudo-roots are indicated by the arrows.

Parameters from Regression of Infinite Dilution Activity Coefficients

Direct solution of the Wilson equation from either one binary data point or from a pair of infinite dilution activity coefficients has already been described. A trial-and-error regression search for the parameter values has also been described. By suitably modifying the objective function, Q, whose value is to be minimized, the trial-and-error solution of the Wilson equation can be applied to the infinite dilution activity coefficients.

For this case Q has been defined as:

$$Q = (\gamma_{1,exp}^\infty - \gamma_{1,calc}^\infty)^2 + (\gamma_{2,exp}^\infty - \gamma_{2,calc}^\infty)^2 \quad (20)$$

and the searches performed as described previously. The results, including quality of fit of all the binary data, are documented in Table IV. In two of the eight systems, only two sets of parameter values were obtained. This was not the result of inexhaustive search. However, the analysis for a single binary point and for a pair of infinite dilution values both indicated that there must be either one or three sets of parameter values.

To explain this apparent discrepancy, consider the case where the observed value of γ_2^∞ lies either just above the relative maxima or just below the relative minima of the calculated function $\gamma_2^\infty(\gamma_1^\infty, \Lambda_{12})$. The latter case is illustrated for the binary system chloroform–benzene in Figure 6. If a

Table V. Prediction of Multicomponent Data: Number of Systems Where, to within 10%, the Regression Parameters Give Accuracy in Predicted y (within 10%)

Source	Type and number of systems	Better All data	One point	Equal
Hudson and	Quinary (1)	1	0	0
Van Winkle	Quaternary (3)	3	0	0
	Ternary (20)	8	2	10
Hankinson et al.	Quinary (1)	0	1	0
	Quaternary (3)	0	2	1
	Ternary (4)	0	2	2
Schreider and Eckert	Ternary (5)	3	1	1

Table VII. Distribution of Binaries with γ's < 1 in the Multicomponent Systems

Multicomponent system I.D.	Binary system I.D.			
001	035B	099B	007A	—	—
003	035B	099B	—	—	—
004	—	—	007A	—	—
009	—	—	007A	—	—
010	—	—	007A	—	—
026	—	—	—	036	—
061	035A	099A	—	—	—
062	035B	099B	—	—	—
066	—	—	007A	—	038
067	—	—	007B	—	—

Table VI. Multicomponent Systems of Interest

System ID	Components	Conditions	Reference
001	Benzene–chloroform–methanol–methyl acetate–acetone	760 mmHg	Hudson (1969)
003	Benzene–chloroform–methanol–methyl acetate	760 mmHg	Hudson (1969)
004	2,3-Dimethylbutane–methanol–acetone–chloroform	760 mmHg	Willock (1970)
009	Acetone–chloroform–2,3-Dimethylbutane	760 mmHg	Garrett (1969)
010	Acetone–methanol–chloroform	50 °C	Severns (1955)
026	Chloroform–methanol–ethyl acetate	760 mmHg	Nagata (1962)
061	Methyl acetate–chloroform–benzene	50 °C	Nagata (1970)
062	Methyl acetate–chloroform–benzene	760 mmHg	Nagata (1962)
066	Acetone–chloroform–methyl isobutyl ketone	760 mmHg	Karr (1951)
067	Ethanol–chloroform–acetone–hexane	55 °C	Vinichenko (1965)

nonlinear regression routine is utilized to obtain the best values of the Wilson parameters from a set of initial guesses in the neighborhood of the relative minima, then the program may converge to a set of pseudo-roots (i.e., false roots), at or near the relative minima. The resulting sets of real and pseudo-roots are also presented in Table IV. Notice that the values of the pseudo-roots are well within the normally accepted range of values for Wilson parameters. As a result, the existence of the pseudo-root is not obvious from inspection alone.

Prediction of Binary and Multicomponent Data

For systems with positive deviations from Raoult's law, where regression of all the binary data yields one set of parameters and use of one datum point yields, in general, another (with no multiple roots in either case), the question arises as to which set of parameters should be used for the prediction of binary and multicomponent data.

In the prediction of binary VLE data, Hudson and Van Winkle (1970) found that parameters obtained from one point (around $x = 0.5$ where experimental accuracy is best) or by regressing all available data gave equally good results. For the one system (benzene–methyl acetate, parameters presented in Table I) presented in their paper, however, the parameters obtained by regression seem to yield a lower maximum deviation in predicted y (about 2%) than the parameters obtained from one point (about 5%). On the other hand, Hankinson et al. (1972) indicated that for five systems studied, parameters obtained by regressing all the data and by using the two infinite dilution activity coefficients gave equally good results. In a similar comparison, Schreiber and Eckert (1971) report that for 31 binary systems parameters obtained by regression of all the data gave an average absolute error in y of 0.0075, while for the parameters obtained from the γ^∞ values the error was 0.0086.

Considering the prediction of multicomponent data, the accuracy of the predicted vapor phase compositions from parameters obtained (A) by regressing all binary data and (B) from one point—and this includes use of the two γ^∞ values—is compared for the two methods in Table V. The comparison indicates that on the average the two methods yield equally good results. However, the recent study of Silverman and Tassios (1973) found method B to the unreliable. Even though it generally gave comparable results to those obtained by regression of all binary data, it occasionally gave very poor results.

In the prediction of binary data for negative deviations from Raoult's law, Aristovich et al. (1968) indicated that for the two systems studied with γ's less than 1, all three sets of Wilson parameters gave very good fit of all data (within 2%) except for one set of roots where one of the values was negative. Such negative values are, however, unacceptable since the value of $(x_\infty + \Lambda_{ij}x_j)$ will be zero at some value of x_i and γ_i will become infinite. On the other hand, the study of Miyahara et al. (1970), using infinite dilution activity coefficients, shows that for the system acetone–chloroform only one set of parameters fit successfully all the data. The other gives a poor fit and the third an unacceptable one. All roots were positive. This is further supported by the results presented in Tables III and IV where it is clearly shown that not all parameters give good fit of the binary data.

Impact of the Presence of Multiple Roots on the Prediction of Multicomponent VLE

In order to gauge the impact that the presence of binary systems having multiple roots may have upon the prediction of multicomponent vapor–liquid equilibria, an extensive survey of such systems has been undertaken. Ten multicomponent systems (Table VI) comprising from three to five components and each containing from one to three binary systems with multiple roots (Table VII) have been studied. The results of this investigation are documented in Tables

Table VIII. Prediction of Multicomponent Vapor–Liquid Equilibria. One Binary with $\gamma < 1$

Multi-component system I.D.	Binary of interest I.D.	Root Code[a]	$\|\Delta Y\|_{av} \times 1000$ All binary data	Infinite dilution data
004	007A	A	6.9	4.2
		B	10.9	10.8
		C	14.0	21.4
009	007A	A	29.7	30.1
		B	30.6	34.9
		C	46.0	56.2
010	007A	A	25.4	24.9
		B	23.9	28.7
		C	29.0	40.7
026	036	A	26.8	27.1
		B	32.6	45.2
		C	25.5	28.4
067	007B	A	9.8	11.4
		B	12.1	13.1
		C	23.1	41.2

[a] Root codes defined in Tables III and IV.

Table IX. Prediction of Multicomponent VLE: Two or More Binaries with γ's < 1

Multi-component system I.D.	Binary of interest I.D.	Root code combination	$\|\Delta Y\|_{Av} \times 1000$ All binary data	Infinite dilution data
003	035B	A–A	5.6	11.3
	099B	B–B	11.7	5.8
		C–C	12.7	—
		B–A	7.5	6.2
		A–B	3.8	13.1
		A–C	—	20.8
		B–C	—	23.4
061	099A	A–A	4.6	29.9
	035A	B–B	28.8	14.7
		C–C	26.5	—
		A–C	5.0	—
		B–C	6.7	—
		A–B	13.9	14.8
		B–A	—	47.1
		C–A	—	29.5
		C–B	—	44.2
062	099B	A–A	4.9	22.8
	035B	B–B	23.5	14.7
		C–C	24.7	—
		A–B	11.5	14.5
		B–A	6.0	29.6
		C–A	—	33.1
		C–B	—	49.9
066	007A	A–A	23.6	29.9
	038	B–B	60.5	88.0
		C–C	38.5	56.0
		B–C	29.1	34.2
		A–C	—	32.4
		B–A	—	34.5
001	035B	A–A–A	7.1	8.5
	099B	A–B–B	—	13.2
	007A	A–C–C	—	14.5
		B–A–A	—	4.6
		B–B–B	11.4	6.6
		B–C–C	—	19.5
		C–C–C	14.5	—
		C–A–B	6.1	—
		C–B–A	8.3	—
		B–B–A	12.2	—
		B–A–B	32.3	—
		C–A–A	7.4	—

VIII and IX in terms of the degree of fit of the multicomponent data expressed as the mean absolute deviation in vapor phase composition.

Tables VIII and IX present the effect upon the quality of fit of multicomponent data for systems containing one binary with multiple roots and for systems containing more than one binary with multiple roots, respectively. Each table uses parameter values obtained from both the regression of all available binary data and from regression against the infinite dilution activity coefficients. The root code (see Tables III and IV) merely designates which one of the three possible roots for each binary of interest have been used in correlating the multicomponent data. For the systems documented in Table IX, unlike those of Table VIII, an extra complexity is added: that of combining the roots when more than one binary with multiple roots is present. The mixed cases were developed by allowing that a case be run with parameters of the same root code combined (i.e., A–A, B–B, C–C for the binaries of interest). The mixed code cases were developed by choosing those parameters that resulted in the best (and then second best) correlation of the binary data as measured by mean absolute deviation both in total pressure and in vapor phase composition.

Conclusions

With binary systems having positive deviations from Raoult's law, a single set of roots (i.e., parameter values) can be obtained by the direct solution of the Wilson equation for one data point (and this includes the infinite dilution activity coefficients). An unique set of parameters is also obtained by regressing all the available binary data, but its value is, in general, different from that obtained from only one data point. Correlation of binary data can be accomplished with about equally good accuracy by both approaches. For the correlation of multicomponent data, use of one binary point and regression of all binary data sometimes provides comparable accuracies. Regression of all binary data is recommended, however, as use of one point can lead to poor results.

From systems with negative deviations, three sets of parameter values can be obtained which may yield significantly different degrees of accuracy in the correlation of binary and multicomponent vapor–liquid equilibria. In the correlation of binary data, the best—or close to the best—degree of fit of binary vapor phase composition is achieved with the set of roots that are smallest in absolute value. With only one exception (system 007B), the same conclusion holds for the degree of fit of total pressure data. This observation applies to correlations based on the infinite dilution values or on regression of all data. With reference to Figures 2 and 4, this root set would correspond to the middle root of the three obtained by direct solution.

With respect to the correlation of multicomponent data, the situation is somewhat less clear. With parameter values derived from the regression of all available binary data, the same conclusion holds. With the parameter values derived from the infinite dilution activity coefficients, however, no generalization can be made. It should be noted that the degree of fit obtained from parameters derived from the infinite dilution points is at best only comparable, and often poorer, than that obtained from parameters derived from regression of all data. This observation, when coupled with the capability of choosing the roots smallest in absolute value and knowing good correlation is obtained, leads to the recommendation that the all-data parameter values be used in the prediction of multicomponent data.

Nomenclature

General

R = gas constant
T = absolute temperature, K
$v_i{}^L$ = molar volume of species i, cm³/g-mol
x_i = liquid mole fraction of species i
γ_i = activity coefficient of species i
$\gamma_i{}^\infty$ = infinite dilution activity coefficient of species i
Λ_{ij} = transformed Wilson parameter
$\lambda_{ij} - \lambda_{ii}$ = Wilson parameter, cal/g-mol

Specific

F = variable defining uniqueness of Wilson parameter
f_1 = values that γ_1 may assume when Wilson parameters are not unique
f_1' = first derivative of γ_1 with respect to t
f_1'' = second derivative of γ_1 with respect to t
g_1 = the Wilson activity coefficient for species 1
g_2 = the Wilson activity coefficient for species 2
g_2' = the first derivative of g_2 with respect to t
g_2'' = the second derivative of g_2 with respect to t
t = transformed coordinate
z = transformed coordinate

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Reactivity of Coal and Char. 1. In Carbon Dioxide Atmosphere

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Reactivities of a few raw coals and chars of these coals obtained from gasifiers operating under different conditions have been measured in CO_2 at temperatures of 840~1100 °C. The reactivities have been measured in a thermogravimetric analyzer up to complete conversions of the samples in most cases. Properties such as surface area, pore size distribution, porosity, and density have been determined for each sample. Actual pore structures of a few samples have been observed at different conversion levels by a scanning electron microscope. In order to compare the reactivities of different samples, the gasification process has been divided into two distinct stages: the first stage due to pyrolysis and the second stage due to char–CO_2 reaction. Reactivities due to the firs stage can be roughly related to volatile matter contents of the solids and the rate of heating. Through an Arrhenius type equation, an activation energy of about 2.5 kcal/mol is obtained for the first stage. The reactivity of a char in the second stage is found to depend more on its coal seam than on the gasification scheme in its production. Activation energy for the second stage reaction has been found to be about 59 kcal/mol. A rate equation has been proposed for the second stage that incorporates the effect of relative available pore surface area changing during reaction.

Introduction

A proper understanding of the coal/char gasification kinetics is essential for successful design of a gasifier. Effects of temperature, pressure, and gaseous environments on the rate of gasification of coal/char have been extensively studied by various investigators. In addition, the rate depends also on the nature and origin of the coal or char itself. The pore characteristics and hence the reactivity of a char have been found to vary not only with the maceral of its parent coal but also with the history of its genesis, i.e., the temperature, pressure,

rate of heating, and gaseous environments, etc., prevailing during its formation. The present study is devoted to determination of reactivities of a few coal and char samples which are produced in some pilot plant experiments conducted under different gasification schemes. This investigation will help us to find the relationship, if any, between the reactivities and the physical characteristics of the samples.

In the present investigation reactivities are measured in a flowing stream of pure CO_2 at atmospheric pressure. The rate of C–CO_2 reaction has been studied by various investigators (Gadsby et al., 1948; Gulbransen and Andrew, 1952; Walker