

Activity coefficient Correlations and Uses.

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الخلاصة :

يتطلب تصميم المعدات الصناعية بيانات توازن الطور لربط مراحل بخار السائل بدقة متناهية. معاملات التلاشي ومعامل النشاط هي العوامل المستخدمة في الصناعات البتروكيمياوية للحد من الانحرافات عن السلوك المثالي في مزيج من المواد الكيميائية. في مزيج مثالي، تكون التفاعلات المجهريّة بين كل زوج من الأنواع الكيميائية هي نفسها، وترتبط بالديناميكا الحرارية من خلال علاقات معقدة المرتبطة بالانتروبيا (القصور الحراري) وارتباطات طاقة جيبس الحرة. ونتيجة لذلك، يمكن التعبير عن خصائص المخاليط مباشرة من حيث التركيزات البسيطة أو الضغوط الجزئية للمواد الموجودة على سبيل المثال. قانون راؤول. يتم استيعاب الانحرافات عن المثالية (الحالة المثالية) عن طريق تعديل التركيز من خلال معامل النشاط. تقدم ورقة المراجعة هذه، مقارنة بين الاساليب الرائدة التي تتناول تقدير معاملات النشاط في المطبوعات (المؤلفات). يتفاوت الانحراف من مركبات متنوعة إلى أخرى بناءً على التركيب الجزيئي للمركبات والمكونات الجزيئية. حسابات توازن طور البخار السائل هي متطلبات أساسية في التصميم الصناعي. كما تلعب حسابات معامل النشاط ومعامل التلاشي دورًا مهمًا في الحسابات الديناميكية الحرارية.

Abstract:

Design of industrial equipment requires phase equilibrium data to correlate liquid vapor phases with accurate precision. Fugacity coefficients and activity coefficient are factors used in petrochemical industries to minimize the deviations from ideal behavior in a mixture of chemical substances. In an ideal mixture, the microscopic interactions between each pair of chemical species are the same and, are correlated thermodynamically through complex relations associated with entropy and Gibbs free energy correlations. As a result, properties of the mixtures can be expressed directly in terms of simple concentrations or partial pressures of the substances present e.g. Raoult's law. Deviations from ideality are accommodated by modifying the concentration by an activity

coefficient. This review paper present a comparison between leading methods dealing with estimation of activity coefficients in literature. Deviation varies from different structure to another based on molecular structure of the compounds and molecular constituents. Liquid vapor phase equilibria calculations are essential requirements in industrial design. The calculations of activity coefficient and fugacity coefficient play an important role in thermodynamic calculations.

Introduction:

The liquid phase activity coefficient, γ_i , is a function of pressure, temperature and liquid composition. At conditions remote from the critical conditions it is virtually independent of pressure and, in the range of temperature normally encountered in distillation, can be taken as independent of temperature.

Correlations for liquid phase activity coefficients:

Several equations have been developed to represent the dependence of activity coefficients on liquid composition.^(1,2,3,4)

1. Margules activity equation:

The Margules activity model is a simple thermodynamic model for the excess Gibbs free energy of a liquid mixture introduced in 1895 by Max Margules.

In chemical engineering the Margules Gibbs free energy model for liquid mixtures is better known as the Margules activity or activity coefficient model.

Margules expressed the excess Gibbs free energy of a binary liquid mixture as a power series of the mole fractions x_i :

$$\frac{G^{ex}}{RT} = X_1 X_2 (A_{21} X_1 + A_{12} X_2) + X_1^2 X_2^2 (B_{21} X_1 + B_{12} X_2) + \dots + X_1^m X_2^m (M_{21} X_1 + M_{12} X_2)$$

A, B are constants, which are derived from regressing experimental phase equilibria data.

- **One-parameter margules equation :**

The simplest expression for Gibbs excess energy function:

$$\frac{G^E}{RT} = Ax_1x_2$$

Parameter A is a constant which is not associated with the other uses of the variable (equation of state parameters, Helmholtz energy, Antoine coefficients).

Derive the expressions for the activity coefficients from this expression.

$$\frac{G^E}{RT} = An_2 \frac{n_1}{n}$$
$$\frac{1}{RT} \left(\frac{\partial G^E}{\partial n_i} \right)_{T, P, n_{j \neq i}} = An_2 \left[\frac{1}{n} - \frac{n_1}{n^2} \right] = A \frac{n_2}{n} \left[1 - \frac{n_1}{n} \right] = Ax_2(1 - x_1)$$

$$\ln y_1 = Ax_2^2 \quad \ln y_2 = Ax_1^2$$

- **Two-parameters margules equation:**

$$\ln y_1 = x_2^2 [A_{12} + 2(A_{21} - A_{12})x_1]$$

$$\ln y_2 = x_1^2 [A_{21} + 2(A_{12} - A_{21})x_2]$$

2. Van Laar's Equation:

Originally the van Laar(1910) development was based on the van der Waals EOS but since the fit of activity coefficient data with van der

Waals parameters is poor, the van Laar equation now is regarded as a purely empirical one.

Expressions for the activity coefficients,

$$\ln \gamma_1 = \frac{A_{12}}{\left[1 + \frac{A_{12}x_1}{A_{21}x_2}\right]^2}; \quad \ln \gamma_2 = \frac{A_{21}}{\left[1 + \frac{A_{21}x_2}{A_{12}x_1}\right]^2}$$

The point of van Laar theory is to use experimental data for mixtures to estimate the values of A_{12} and A_{21} . These equations can be rearranged to obtain A_{12} and A_{21} from γ_1 and γ_2 given any one VLE point.

$$A_{12} = \ln \gamma_1 \left[1 + \frac{x_2 \ln \gamma_2}{x_1 \ln \gamma_1}\right]^2 \quad A_{21} = \ln \gamma_2 \left[1 + \frac{x_1 \ln \gamma_1}{x_2 \ln \gamma_2}\right]^2$$

3. Regular Solution (RS) Model :

This activity coefficient model is derived for solutions that show moderate deviations from ideal solution behavior, and for which V^E and S^E are both zero. The model was proposed by Scatchard and Hildebrand (J. H. Hildebrand & R. L. Scott. The Solubility of Non-electrolytes, Dover, 1964) and constitutes one of few models that are derived from theory. Known as the Regular Solution Model, the molar excess Gibbs free energy function is given by:

$$G^E / RT = (x_1V_1 + x_2V_2) \Phi_1\Phi_2 (\delta_1 - \delta_2)^2$$

$$\ln \gamma_1 = V_1\Phi_2^2 (\delta_1 - \delta_2)^2$$

$$\ln \gamma_2 = V_2\Phi_1^2 (\delta_1 - \delta_2)^2$$

where, $\Phi_i =$ volume fraction $= \frac{x_iV_i}{V_m}$; $V_i =$ molar volume of pure i^{th} species, and $V_m = \sum_i x_iV_i$

Further: $\delta_i =$ solubility parameter for i^{th} species, which is given by:

$$\delta_i = \sqrt{\frac{(\Delta U_i^{vap})}{V_i}} \cong \sqrt{\frac{(\Delta H_i^{vap} - RT)}{V_i}}$$

Where ΔU_i^{vap} , ΔH_i^{vap} are molar internal energy, and enthalpy of vaporization of i^{th} species at the temperature of interest.

The above relations may be extended to multi-component mixtures for which:

$$RT \ln \gamma_i = V_i (\delta_i - \bar{\delta})^2$$

$$\bar{\delta} = \sum_j \Phi_j \delta_j$$

$$\Phi_j = \frac{x_j V_j}{\sum_j x_j V_j}$$

(where, j R runs over all the species) .

4. Free volume and Flory-Huggins Theory:

The volume occupied by one molecule is not accessible to the other molecules. When we mix two components, each component's entropy increases according to how much more space it has:

$$\Delta S_i = N_i k \ln(V_{fm} / V_{fi})$$

Where V_{fm} = the free volume of the mixture.

V_{fi} = the free volume in the i th pure component.

It is customary to assume that the fraction of free volume in any component is the same.

$$V_{fi} = N_i v_i v_f$$

Where v_i = volume of the i species.

v_f = universal fraction of free volume.

The entropy may be taken as that of a perfect gas composed of the same number of molecules confined to a volume equal to the free volume.

$$\frac{\Delta S}{Nk} = x_1 \ln\left(\frac{V_{f_m}}{V_{f_1}}\right) + x_2 \ln\left(\frac{V_{f_m}}{V_{f_2}}\right)$$

$$\frac{\Delta S}{Nk} = x_1 \ln\left(\frac{n_1 v_1 + n_2 v_2}{n_1 v_1}\right) + x_2 \ln\left(\frac{n_1 v_1 + n_2 v_2}{n_2 v_2}\right) = -\sum x_i \ln \Phi_i$$

$$\frac{\Delta S^E}{Nk} = -\sum x_i \ln \Phi_i + \sum x_i \ln x_i = -\sum x_i \ln(\Phi_i / x_i)$$

For a binary solution,

$$\frac{\Delta G^E}{NkT} = \frac{H^E}{NkT} - \frac{\Delta S^E}{Nk} = x_1 \ln \frac{\Phi_1}{x_1} + x_2 \ln \frac{\Phi_2}{x_2} + \Phi_1 \Phi_2 \frac{(\delta_1 - \delta_2)^2}{RT} (x_1 v_1 + x_2 v_2)$$

$$\ln \gamma_1 = \ln(\Phi_1 / x_1) + (1 - \Phi_1 / x_1) + \frac{v_1}{RT} \Phi_2^2 (\delta_1 - \delta_2)^2$$

$$\ln \gamma_2 = \ln(\Phi_2 / x_2) + (1 - \Phi_2 / x_2) + \frac{v_2}{RT} \Phi_1^2 (\delta_1 - \delta_2)^2$$

5. Wilson equation:

The equation developed by Wilson (1964) is convenient to use in process design:

$$\ln \gamma_k = 1.0 - \ln \left[\sum_{j=1}^n (x_j A_{kj}) \right] - \sum_{i=1}^n \left[\frac{x_i A_{ik}}{\sum_{j=1}^n (x_j A_{ij})} \right]$$

Where γ_k = activity coefficient for component k,

A_{ij}, A_{ji} = Wilson coefficients (A values) for the binary pair i, j,
 n = number of components.

The Wilson equation is for systems that are severely non-ideal; but, like other equations, it cannot be used to represent systems that form two phases in the concentration range of interest.

A significant advantage of the Wilson equation is that it can be used to calculate the equilibrium compositions for multicomponent systems using only the Wilson coefficients obtained for the binary pairs that comprise the multicomponent mixture. The Wilson coefficients for several hundred binary systems are given in the DECHEMA vapor-liquid data collection, DECHEMA (1977), and by Hirata (1975). Hirata gives methods for calculating the Wilson coefficients from vapor liquid equilibrium experimental data.

6. Non-random two liquid equation (NRTL) equation:

The NRTL equation developed by Renon and Prausnitz overcomes the disadvantage of the Wilson equation in that it is applicable to immiscible systems. It can be used to predict phase compositions for vapor-liquid and liquid-liquid systems.

$$\frac{G^E}{x_1 x_2 RT} = \frac{G_{21} \tau_{21}}{x_1 + x_2 G_{21}} + \frac{G_{12} \tau_{12}}{x_2 + x_1 G_{12}}$$

$$\ln y_1 = x_2^2 \left[\tau_{21} \left(\frac{G_{21}}{x_1 + x_2 G_{21}} \right)^2 + \frac{G_{12} \tau_{12}}{(x_2 + x_1 G_{12})^2} \right]$$

$$\ln y_2 = x_1^2 \left[\tau_{12} \left(\frac{G_{12}}{x_2 + x_1 G_{12}} \right)^2 + \frac{G_{21} \tau_{21}}{(x_1 + x_2 G_{21})^2} \right]$$

$$G_{12} = \exp(-\alpha \tau_{12}) \quad G_{21} = \exp(-\alpha \tau_{21})$$

$$\tau_{12} = \frac{b_{12}}{RT} \quad \tau_{21} = \frac{b_{21}}{RT}$$

α , b_{12} , and b_{21} are parameters specific to a particular pair of species, and are independent of composition and temperature.

7. Universal quasi-chemical (UNIQUAC) equation:

The UNIQUAC equation developed by Abrams and Prausnitz (1975) is usually preferred to the NRTL equation in the computer aided design of separation processes. It is suitable for miscible and immiscible systems, and so can be used for vapor-liquid and liquid-liquid systems. As with the Wilson and NRTL equations, the equilibrium compositions for a multicomponent mixture can be predicted from experimental data for the binary pairs that comprise the mixture. Also, in the absence of experimental data for the binary pairs, the coefficients for use in the UNIQUAC equation can be predicted by a group contribution method: UNIFAC.

The best source of data for the UNIQUAC constants for binary pairs is the ECHEMA vapor-liquid and liquid-liquid data collection, DECHEMA (1977).

For multicomponent solution:

$$\frac{G^E}{RT} = \sum_j x_j \ln(\Phi_j/x_j) - 5 \sum_j q_j x_j \ln(\Phi_j/\theta_j) - \sum_j q_j x_j \ln\left(\sum_i \theta_i \tau_{ij}\right)$$

$$\ln y_k = \ln y_k^{COMB} + \ln y_k^{RES}$$

$$\ln y_k^{COMB} = \ln(\Phi_k/x_k) + (1 - \Phi_k/x_k) - 5q_k [\ln(\Phi_k/\theta_k) + (1 - \Phi_k/\theta_k)]$$

$$\ln y_k^{RES} = q_k \left[1 - \ln\left(\sum_i \theta_i \tau_{ik}\right) - \sum_j \frac{\theta_j \tau_{kj}}{\sum_i \theta_i \tau_{ij}} \right]$$

UNIQUAC equation requires two adjustable parameters characterized from experimental data for each binary system.

$$\ln \gamma_1 = \ln \left(\frac{\Phi_1}{x_1} \right) + \left(1 - \frac{\Phi_1}{x_1} \right) - 5q_1 \left[\ln \left(\frac{\Phi_1}{\theta_1} \right) + \left(1 - \frac{\Phi_1}{\theta_1} \right) \right]$$

$$+ q_1 \left[1 - \ln (\theta_1 + \theta_2 \tau_{21}) - \frac{\theta_1}{\theta_1 + \theta_2 \tau_{21}} - \theta_2 \frac{\tau_{12}}{\theta_1 \tau_{12} + \theta_2} \right]$$

$$\ln \gamma_2 = \ln \left(\frac{\Phi_2}{x_2} \right) + \left(1 - \frac{\Phi_2}{x_2} \right) - 5q_2 \left[\ln \left(\frac{\Phi_2}{\theta_2} \right) + \left(1 - \frac{\Phi_2}{\theta_2} \right) \right]$$

$$+ q_2 \left[1 - \ln (\theta_1 \tau_{12} + \theta_2) - \frac{\theta_1 \tau_{21}}{\theta_1 + \theta_2 \tau_{21}} - \frac{\theta_2}{\theta_1 \tau_{12} + \theta_2} \right]$$

Where:

$$\Phi_j \equiv \frac{x_j r_j}{\sum_i x_i r_i} \quad \theta_j \equiv \frac{x_j q_j}{\sum_i x_i q_i}$$

$$r_j = \sum_k \nu_k^{(j)} R_k; \quad q_j = \sum_k \nu_k^{(j)} Q_k$$

R_k parameter => group volume.

Q_k parameter => group surface area.

Molecule size (r_j) and molecule shape (q_j) may be calculated by multiplying the group parameters by the number of times each group appears in the molecule, and summing all the groups in the molecule.

$\nu_k^{(j)}$ is the number of groups of the k type in the j molecule.

8. Modified separation of cohesive energy density

model(MOSCED):

It is Thermodynamic model for the estimation of limiting activity coefficients (also known as activity coefficient at infinite dilution).

$$\ln \gamma_2^\infty = \frac{\nu_2}{RT} \left[(\lambda_1 - \lambda_2)^2 + \frac{q_1^2 q_2^2 (\tau_1^T - \tau_2^T)^2}{\psi_1} + \frac{(\alpha_1^T - \alpha_2^T) (\beta_1^T - \beta_2^T)}{\xi_1} \right] + d_{12}$$

$$d_{12} = \ln \left(\frac{\nu_2}{\nu_1} \right)^{aa} + 1 + \left(\frac{\nu_2}{\nu_1} \right)^{aa}$$

$$aa = 0.953 - 0.002314 \left((\tau_2^T)^2 + \alpha_2^T \beta_2^T \right)$$

$$\alpha^T = \alpha \left(\frac{293K}{T} \right)^{0.8}, \beta^T = \beta \left(\frac{293K}{T} \right)^{0.8}, \tau^T = \tau \left(\frac{293K}{T} \right)^{0.4}$$

$$\psi_1 = POL + 0.002629 \alpha_1^T \beta_1^T$$

$$\xi_1 = 0.68 (POL - 1) + \left[3.4 - 2.4 \exp \left(-0.002687 (\alpha_1 \beta_1)^{1.5} \right) \right]^{(293K/T)^2}$$

$$POL = q_1^4 \left[1.15 - 1.15 \exp \left(-0.002337 (\tau_1^T)^3 \right) \right] + 1$$

Where :

- v Molar liquid volume
- λ Dispersion parameter
- q Induction parameter
- τ Polarity parameter
- α Hydrogen-bond acidity parameter
- β Hydrogen-bond basicity parameter
- ξ and ψ Asymmetry factors
- d_{12} Combinatorial term (modified Flory-Huggins)
- Index 1 Solvent
- Index 2 Solute

The activity coefficient of the solute and solvent can be extended to other concentrations by applying the principle of the Margules equation. This gives:

$$\ln \gamma_2 = (\ln \gamma_2^\infty + 2 (\ln \gamma_1^\infty - \ln \gamma_2^\infty) \Phi_2) \Phi_1^2$$

$$\ln \gamma_1 = (\ln \gamma_1^\infty + 2 (\ln \gamma_2^\infty - \ln \gamma_1^\infty) \Phi_1) \Phi_2^2$$

where

$$\Phi_i = \frac{x_i \nu_i}{\sum_j \nu_j x_j}$$

9. Debye–Hückel equation:

The Debye–Hückel limiting law enables one to determine the activity coefficient of an ion in a dilute solution of known ionic strength.

$$\ln(\gamma_i) = -\frac{z_i^2 q^2 \kappa}{8\pi\epsilon_r \epsilon_0 k_B T} = -\frac{z_i^2 q^3 N_A^{1/2}}{4\pi(\epsilon_r \epsilon_0 k_B T)^{3/2}} \sqrt{\frac{I}{2}} = -Az_i^2 \sqrt{I}$$

z_i is the charge number of ion species i

q is the elementary charge

κ is the inverse of the Debye screening length,

ϵ_r is the relative permittivity of the solvent

ϵ_0 is the permittivity of free space

k_B is Boltzmann's constant

T is the temperature of the solution

N_A is Avogadro's number

I is the ionic strength of the solution,

A is a constant that depends on temperature.

Extensions of the theory ;

Extended Debye–Hückel equation is given by:

$$-\log_{10}(\gamma) = \frac{A|z_+ z_-| \sqrt{I}}{1 + Ba\sqrt{I}}$$

The Debye–Hückel equation cannot be used in the solutions of surfactants where the presence of micelles influences on the electrochemical properties of the system.

• Relation between the model parameters and infinite dilute activity coefficients :

A common feature of all the models are that the parameters are basically related to the infinite dilute activity coefficients for each binary.⁽⁵⁾ Table (1) shows the relation between the model parameters and infinite dilute activity coefficients.

Table (1) shows the relation between the model parameters and infinite dilute activity coefficients.

Model	Relation between the model parameters and infinite dilute activity coefficients
Two-suffix Margules	$\ln \gamma_1^\infty = \ln \gamma_2^\infty = A$
Three-suffix Margules	$\ln \gamma_1^\infty = A_{12}$; $\ln \gamma_2^\infty = A_{21}$
Van Laar	$\ln \gamma_1^\infty = A_{12}$; $\ln \gamma_2^\infty = A_{21}$
Wilson	$\ln \gamma_1^\infty = 1 - \Lambda_{21} - \ln \Lambda_{12}$; $\ln \gamma_2^\infty = 1 - \Lambda_{12} - \ln \Lambda_{21}$
NRTL	$\ln \gamma_1^\infty = \tau_{21} + \tau_{12} \exp(-\alpha\tau_{12})$; $\ln \gamma_2^\infty = \tau_{12} + \tau_{21} \exp(-\alpha\tau_{21})$

• **Comparison of Equations.**

The merits of the individual activity-coefficient correlation methods have been cited locally, and a comparison of a sort is in table (2) . Those conclusions may be summarized.

Table (2) Frequencies of best fits of fine activity coefficient correlations of the DECHEMA vapor-liquid equilibrium data collection

Part of Collection	Number of Data	Margules	van Laar	Wilson	NRTL	UNIQUAC
1 Aqueous organics	504	0.143	0.071	0.240	0.403*	0.143
2A Alcohols	574	0.166	0.085	0.395*	0.223	0.131
2B Alcohols and phenols	480	0.213	0.119	0.342*	0.225	0.102
3/4 Alcohols, ketones, ethers	490	0.280*	0.167	0.243	0.155	0.155
6A C ₄ -C ₆ hydrocarbons	587	0.172	0.133	0.365*	0.232	0.099
6B C ₇ -C ₁₈ hydrocarbons	435	0.225	0.170	0.260*	0.209	0.136
7 Aromatics	493	0.260*	0.187	0.225	0.160	0.172
Total of 7 parts	3563	0.206	0.131	0.300*	0.230	0.133

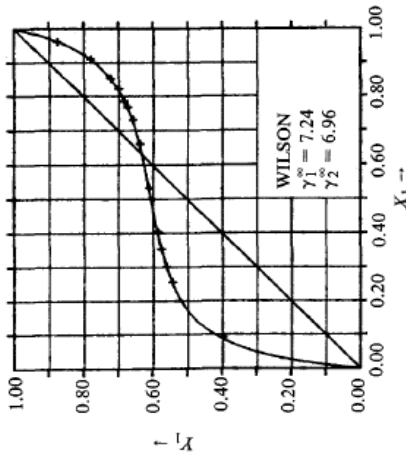
*Identifies the most frequent best fit in each category.

1. The Margules, van Laar, and related algebraic forms have the merit of mathematical simplicity, ease of evaluation of the parameters from activity-coefficient data, and often adequate representation of even fairly non-ideal binary mixtures, including partially miscible liquid systems. They are not applicable to multicomponent systems without ternary or higher interaction parameters.
2. The Wilson equation represents vapor-liquid equilibria of binary and multicomponent mixtures very well with only binary parameters. Because of its greater simplicity it may be preferable to the NRTL and UNIQUAC equations for this purpose. Although it is not directly applicable to liquid-liquid equilibria.
3. The NRTL equation represents vapor-liquid and liquid-liquid equilibria of binary and multicomponent systems quite well, and is often superior to the others for aqueous systems. It is simpler in form than the UNIQUAC method but has the disadvantage of involving three parameters for each pair of constituents. The third parameter α_{12} often can be estimated from the chemical natures of the components, and a strong claim has been made for a universal value $\alpha_{12} = -1$. The value $\alpha_{12} = 0.2$ has been adopted for all mixtures in the DECHEMA LLE Data Collection.
4. Although it employs only two parameters per pair of components, the UNIQUAC equation is algebraically the most complex one. It utilizes knowledge of molecular surfaces and volumes of the pure components, which can be estimated from structural contributions, and for this reason the method may be particularly applicable to mixtures of widely different molecular sizes. It is applicable to vapor-liquid and liquid-liquid equilibria of multicomponent mixtures with binary parameters and pure component data only.

Sample page from the DECHEMA Collection.

Sample Page from the DECHEMA Collection of Vapor-Liquid Equilibrium Data (1979, Vol I/3&4 p. 228)

(1) ACETONE		C3H6O		(2) HEXANE		C6H14					
***** ANTOINE CONSTANTS		REGION *****		CONSISTENCY							
(1)	7.11714	1210.595	229.664	-13-	55 C	METHOD 1	*				
(2)	6.91058	1189.640	226.280	-30-	170 C	METHOD 2	*				
TEMPERATURE= 20.00 DEGREE C											
LIT: RALL W.,SCHAEFER K.,Z.ELECTROCHEM.63,1019(1959).											
CONSTANTS:		A12	A21	ALPHA12							
MARGULES	1.7448	1.8012									
VAN LAAR	1.7416	1.8044									
WILSON	1077.8013	375.5248									
NRTL	632.4249	583.8331	0.2913								
UNIQUAC	-41.9959	512.3937									
EXPERIMENTAL DATA											
P	MMHG	X1	Y1	MARGULES	VAN LAAR	WILSON	NRTL	UNIQUAC			
				DIFF P	DIFF Y1	DIFF P	DIFF Y1	DIFF P	DIFF Y1		
119.60	0.0	0.0	0.0	-0.67	0.0	-0.67	0.0	-0.67	0.0		
187.20	0.0913	0.3966	4.24	0.0024	0.0028	-1.26	-0.0110	2.90	-0.0011		
226.70	0.2563	0.5421	-0.19	-0.0166	-0.0166	1.32	-0.0023	0.07	-0.0137		
232.30	0.3019	0.5595	0.85	-0.0161	0.89	3.13	-0.0007	1.28	-0.0128		
232.40	0.3543	0.5737	-2.36	-0.0154	-2.33	-0.02	-0.0009	-1.89	-0.0121		
237.00	0.4035	0.5827	0.37	-0.0153	0.38	2.40	-0.0032	0.76	-0.0125		
238.80	0.5325	0.6092	-0.02	-0.0043	-0.0046	0.92	-0.0020	0.10	-0.0039		
237.70	0.6609	0.6362	-1.47	0.0045	-1.49	-0.89	-0.0028	-1.44	0.0027		
239.30	0.7309	0.6564	1.22	0.0065	1.20	1.76	-0.0033	1.24	0.0042		
237.90	0.7679	0.6722	1.21	0.0081	1.19	1.62	-0.0017	1.20	0.0060		
234.30	0.7862	0.6825	-1.38	0.0097	-1.41	-1.10	0.0004	-1.43	0.0078		
234.10	0.8219	0.6975	1.18	0.0038	1.14	1.08	-0.0037	1.02	0.0024		
230.30	0.8528	0.7202	0.88	0.0028	0.83	0.29	-0.0021	0.60	0.0021		
220.60	0.9105	0.7778	1.70	-0.0051	1.64	-0.07	-0.0026	1.18	-0.0041		
202.90	0.9619	0.8739	-0.14	-0.0071	-0.18	-2.24	0.0009	-0.66	-0.0050		
181.50	1.0000	1.0000	-3.96	0.0	-3.96	-3.96	0.0	-3.96	-0.44		
MEAN DEVIATION:				1.23	0.0084	1.31	0.0027	1.13	0.0064	1.17	0.0073
MAX. DEVIATION:				4.24	0.0166	3.13	0.0110	2.90	0.0137	3.60	0.0151



Application of Activity Coefficient Models;

- Activity coefficients are used in phase equilibria calculation for modeling equilibrium properties.^{(6),(7)} As shown in the following table.

$$y_i P = x_i \gamma_i P_i^{sat}$$

System Type	Models
Species similar in size and shape	One-constant Margules
Moderately non-ideal mixtures	Two-constant Margules, Van Laar, Regular Solution
Strongly non-ideal mixtures (for example Alcohols +Hydrocarbons)	Wilson, NRTL, UNIQUAC
Solutions with miscibility gap	NRTL, UNIQUAC

▪ Calculation of solubility :

Experimental determination of solubility is time consuming and costly, therefore it is effective to use activity coefficient models to predict solubility

In Equilibrium:

$$a^{solid} = a^{solute} = x^{sat} \gamma^{sat}$$

Solubility can be calculated as follow

$$x = \frac{a^{solid}}{\gamma}$$

a^{solid} is activity of solid which is function of physical properties of solid like melting temperature, heat of fusion and heat capacity γ is activity coefficient.

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