Correlation of Vapor-Liquid Equilibrium for non ideal systems using infinite pressure mixing rules

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Abstract

Isothermal vapor-liquid equilibrium data of five groups, which are polar-polar at low and high pressure, polar-non polar at low and high pressure, and non polar-non polar at high pressure were investigated. Each group of these contains four binary mixtures with 334 overall data points. By using PRSV-EOS with WS and HVOS mixing rules at infinite pressure where $G_E{}^\infty$ obtained by adopting UNIQUAC and Wilson models. These mixing rules have many advantages and can handle all the systems with good accuracy. Noting that WS mixing rules have one adjustable parameter and HVOS mixing rules without adjustable parameter. Many efforts to modify the results were made. The best modification which gives the more accurate results for all groups is the introduction of a new constant value 'C' which is specified for each system in HVOS mixing rules with quadratic mixing rules with one adjustable parameter h_{ij}.

Key word: Vapor-Liquid Equilibrium, Equation of State, Mixing Rules, Adjustable Parameter

1. Introduction

Vapor-Liquid Equilibrium (VLE) refers to a system in which a single liquid phase is in equilibrium with its vapor [1]. The accurate design and operation of separation process units requires reliable knowledge of phase equilibrium behavior. Many experiments are necessary to obtain such equilibrium data, at least for binary systems, where non-idealities in both phases must be determined. Therefore further improvement to theoretical models for describing and predicting these non-idealities are indispensable [2]. Most of the vapor-liquid equilibrium data published up to date are obtained under atmospheric pressure, while under different pressures are still limited in number. Accordingly it is especially convenient for engineering purposes to find the methods for predicting the x-y correlation at every different pressure on the basis of the known data at a given pressure. This problem in principle may be solved by means of the thermodynamic relationships. One of these relationships is the cubic equations of state (EOS) which is widely used for phase equilibrium calculations. There are many advantages in using EOS for phase equilibrium calculations. EOS can be used to calculate vapor-liquid, liquid-liquid and supercritical fluid phase equilibrium of homogeneous fluids at normal conditions without any conceptual difficulties. To improve the VLE results, much efforts in recent years have been devoted toward developing multiparameter mixing rules, especially those incorporate the excess free energy (G^E) to extend the cubic equation of state for the phase equilibrium calculations of asymmetric and strongly non-ideal mixtures[3,4]. **Wong and Sandler, in 1992**[5] equated the excess free energy at infinite pressure from a cubic EOS to that from an activity coefficient model and also constrained the equation of state parameters 'a' and 'b' to satisfy the second virial coefficient condition, these excess free energy mixing rules have been successfully applied to strongly polar systems. The aim of this work is to investigate the use of infinite dilution activity coefficients in cubic EOS mixing rules, and trying to modify the obtained VLE calculated results by modifying the $G_E{}^\infty$ mixing rules in this path.

2. PRSV-EOS

The Peng-Robinson Stryjek-Vera (PRSV-EOS), in 1986 [6] is modification of the PR-EOS that extends the application of the original PR method for moderately non-ideal systems. It has been shown to match vapor pressures curves of pure components and

mixtures more accurately than the PR method, especially at low vapor pressures.

The modifications to the PR-EOS by Stryjek and Vera was an expanded alpha, α term that became a function of acentricity and an empirical parameter, K, used for fitting pure component vapor pressures.

$$\alpha = \left[1 + K\left(1 - \sqrt{Tr}\right)\right]^2$$

$$K = K_0 + K_1\left(1 - \sqrt{Tr}\right)\left(0.7 - \sqrt{Tr}\right)$$

$$K_0 = 0.378893 + 1.4897\omega - 0.17138\omega^2 + 0.019655\omega^3$$

Where:

K_0= constant characteristic of each substance correlated against acentric factors

K_1 = characteristic pure component parameter

2.1. Applying Different Mixing Rules on the EOS

Two mixing and combining rules are applied to 5 different groups each group contain 4 binary mixtures with 334 overall data points, to investigate the ability of these mixing and combining rules to correlate the VLE data to find the most suitable one for each group. These forms of mixing and combining rules are:

2.1.1. Wong and Sandler mixing rules

Wong and Sandler (WS), in 1992[5] derived a general form of mixing rules first by combining the quadratic dependence of the second virial coefficient on composition and the relation between the second virial coefficient and the parameters in a cubic EOS. The second equation in their mixing rules was derived by taking the limit of the excess Helmholtz free energy for a cubic EOS mixture at infinite pressure. Helmholtz free energy is less pressure dependent, and can be approximated by excess Gibbs energy at low pressure where most experimental data are collected. The resultant mixing rules are pressure independent and satisfy the quadratic requirement [7,8] :

$$b = \frac{\sum_{i=1}^{N}\sum_{j=1}^{N} x_i x_j (b - a/RT)_{ij}}{1 - \frac{1}{RT}\left(\sum_{i=1}^{N} x_i \frac{a_i}{b_i} + \frac{G^E}{C}\right)}$$

$$a = b\left[\frac{G^E}{C} + \sum_{i=1}^{N} x_i \frac{a_i}{b_i}\right]$$

$$\left(b - \frac{a}{RT}\right)_{ij} = \frac{1}{2}(b_i + b_j) - \frac{\sqrt{a_i a_j}}{RT}(1 - k_{ij})$$

$$C = -0.623$$

In equation above K_{ij} is a second virial coefficient binary interaction parameter, it has to be obtained experimentally near the conditions of interests.

2.1.2. Modified Huron-Vidal Model (HVOS)

The EOS- G_E^{∞} models that are based on the zero pressure limit are mathematically approximate because of the lack of liquid density root of the EOS at zero pressure and some temperature. To approximate the molar volume of liquid at high pressures and high temperatures, **Orbey and Sandler, in 1995** [6]assumed that there is an universal linear algebraic core volume as $V = ub$, where u is a positive constant greater than unity. By matching the Helmholtz free energy at infinite pressure and assuming $u = 1$, they generated a new set of mixing rules, or the HVOS model in short, that involves parameter a in the following form [7,8]:

$$a = bRT\left[\sum_{i=1}^{N} x_i \frac{a_i}{b_i RT} + \frac{1}{C}\left[\frac{G^E}{RT} + \sum_{i=1}^{N} x_i \ln\left(\frac{b}{b_i}\right)\right]\right]$$

$$b = \sum_i x_i b_i \qquad, C = -0.623$$

A modified procedure of using WS and HVOS mixing rules based on UNIQUAC and Wilson activity coefficient at infinite dilution is tried in order to get more accurate VLE results for all groups, these modification are:

1- Trying to find a new value substituted in place of the constant 'C' in both WS and HVOS mixing rules (each mixture has it's own value) instead of using a constant number for all systems, since this constant has no physical meaning. The new constant value is varied from system to another as shown in table 2.

2- The second modification is trying to reduce the error associated with the covolume term by the introduction of h_{ij} adjustable parameter in the quadratic mixing rules which is substituted in HVOS mixing rule, which has the form:

$$b = \sum_i \sum_j x_i x_j b_{ij}$$

$$b_{ij} = \frac{b_i + b_j}{2}(1 - h_{ij})$$

The results can be shown in table 3.

3- The last modification tried to improve the results by the use of quadratic mixing rules with the new constant in the HVOS mixing rules; this modification gives very good results for all systems at different conditions. h_{ij} and the new constant values with VLE calculated results are shown in table 4.

3. Results and Discussion

The **Wong Sandlar** and **Orbey Sandler (HVOS)** mixing rules were used sharing with **PRSV-EOS** since it gives the lowest deviation from the experimental data. By linking the EOS parameters '*a*' and '*b*' with excess Gibbs free energy at infinite dilution derived from UNIQUAC and Wilson models. These mixing rules had been applied successfully in several ways. First, when combined with cubic EOS and an appropriate activity coefficient model for the excess Gibbs free energy term, it showed very good correlations of vapor-liquid equilibria data. Second, because low pressure Gibbs free energy information had been used in developing this mixing rule. Wong, Orbey and Sandler found that activity coefficient parameters reported in data banks could be used directly and with good accuracy in these mixing rules without need of refitting any experimental data. But in WS mixing rule there is one point about the binary interaction parameter K_{ij} which should be chosen so that the excess Gibbs free energy value is reproduced as closely as possible at the pressure at which the activity coefficient model parameters are reported. The correlative capabilities of the WS and HVOS mixing rules are shown in table 1 for all groups used in this work. This table shows that for polar-polar group at low and high pressures which contain symmetric polar mixtures, WS mixing rules with one adjustable parameter with Wilson and UNIQUAC models considered to be better mixing rule for these groups. For polar-non polar group at low and high pressures, HVOS mixing rules without adjustable parameter with Wilson and UNIQUAC models give good results. For non polar-non polar group at high pressures both WS and HVOS mixing rules give good results. The stated modification on WS and HVOS mixing rules based on UNIQUAC and Wilson activity coefficients at infinite dilution at low and high pressures were tried. The first modification was to find the

more accurate constant 'C' in the original WS and HVOS mixing rules constant based on the hypothetical aspects assumption during the derivation of these mixing rules. But this modification showed little improvement with WS mixing rule as can be seen in table 2 for UNIQUAC and Wilson models. When this modification is applied to HVOS mixing rules with UNIQUAC and Wilson models better results are obtained than these obtained with the only one constant value as can be seen in table 2. The second modification which applied to HVOS mixing rules only, showed a little improvement in the results obtained as shown in table 3 for UNIQUAC and Wilson models. The final modified approach (third modification) showed very accurate results when compared with all mixing rules used in this work for all five groups as shown in table 4 for UNIQUAC and Wilson models. The results are expressed as absolute average deviations in vapor phase composition $|\Delta y|\%$ where:

$$|\Delta y| = \frac{1}{N} \sum_{i=1}^{N} |y_{exp} - y_{cal}|$$

$y_{exp}=$ represent the value of y obtained by experimental data

$y_{cal}=$ = represent the value of y calculated by using the different methods

4. Conclusion

the correlation of VLE data were made using WS and HVOS mixing rules which are based on the excess Gibbs free energy at infinite dilution, and were calculated using UNIQUAC and Wilson models which are suitable for infinite pressure conditions. This is coupled with CEOS. Infinite pressure activity coefficients at infinite dilution were obtained from available low pressure activity coefficient at several temperatures. The parameters of UNIQUAC and Wilson models at low pressure which are available in data bank were used in calculation, since WS and HVOS mixing rules were derived at infinite pressure. Several efforts to modify these results were made. The most fruitful modification was when the constant 'C' was taken as variable change and where its value changes for each binary mixture with quadratic mixing rules and one adjustable parameter h_{ij}. This approach was applied to HVOS mixing rule and this modification gave least deviation of the absolute from experimental values

Table 1: The absolute average deviation when using PRSV- EOS with WS, HVOS mixing rules and G_E^∞ from UNIQUAC and Wilson models for all groups								
System	*No. Pts.*	*T (K)*	*P range (atm)*	|Δy| *with WS mixing rules*		|Δy| *with HVOS mixing rules*		*Ref.*
				UNIQUAC	*Wilson*	*UNIQUAC*	*Wilson*	
Methanol_2-Propanol	21	328.15	0.299-0.678	0.01592	0.01050	0.03293	0.00540	10
Methanol-Water	21	338.15	0.246-1.02	0.00668	0.00670	0.04411	0.01322	10
Ethanol-Water	21	363.16	0.691-1.57	0.02453	0.02423	0.06247	0.03221	10
Acetone-Methanol	28	328.15	0.713-0.997	0.01038	0.01041	0.01146	0.01098	11
overall average absolute deviation				0.01305	0.01296	0.03774	0.01535	
2-Propanol_Water	21	423.15	4.706-9.035	0.02276	0.02277	0.04145	0.04061	10
Ethanol-Water	17	423.15	5.511-9.730	0.02075	0.02079	0.05776	0.04223	12
Methanol-Water	21	413.15	3.571-10.67	0.00728	0.00726	0.04866	0.01626	10
Methanol-Acetone	12	422.6	11.06-13.48	0.00515	0.00515	0.01812	0.00621	13
overall average absolute deviation				0.01398	0.01399	0.04149	0.02633	
Acetone-Hexane	21	318.15	0.444-0.844	0.04154	0.04003	0.04465	0.03826	10
Acetone-Heptane	21	338.15	0.574-1.353	0.05486	0.05378	0.03666	0.03782	10
Ethanol-Hexane	21	333.15	0.462-1.07	0.08309	0.07650	0.02728	0.04865	10
Ethanol-Heptane	21	348.15	0.475-1.175	0.08922	0.08973	0.02944	0.06432	10
overall average absolute deviation				0.06718	0.06501	0.03451	0.04726	
Methanol-Ethane	5	298.15	4.741-38.85	0.08794	0.58610	0.10271	0.07019	14
Acetone-Ethane	8	298.15	2.14-50.90	0.09665	0.96901	0.06923	0.05130	14
Methanol-Butane	27	368.51	8.614-14.219	0.05989	0.06026	0.08178	0.09819	15
2-Propanol_Butane	23	364.51	8.364-12.674	0.02842	0.02863	0.06391	0.07366	15
overall average absolute deviation				0.05530	0.05323	0.07532	0.08106	
Ethane-Propane	4	260.95	6.805-17.01	0.00237	0.00239	0.00760	0.00781	16
Ethane-Butane	11	363.40	15.23-52.56	0.07896	0.07860	0.01707	0.02566	17
Propane-Butane	8	363.38	13.63-33.68	0.00429	0.00435	0.01701	0.01013	18
Ethane-Hexane	7	298.15	5.012-35.03	0.01586	0.01616	0.06103	0.07325	14
overall average absolute deviation				0.03411	0.03407	0.02605	0.03024	

System	No. Pts.	T (K)	P range (atm)	|Δy| with WS mixing rules				|Δy| with HVOS mixing rules			
				UNIQUAC		Wilson		UNIQUAC		Wilson	
				C	|Δy|	C	|Δy|	C	|Δy|	C	|Δy|
Methanol_2-Propanol	21	328.15	0.299-0.678	-1	0.0105	-0.258	0.0104	-1	0.0294	-0.541	0.0013
Methanol-Water	21	338.15	0.246-1.02	-0.378	0.0067	-0.85	0.0066	-0.378	0.0127	-0.584	0.0190
Ethanol-Water	21	363.16	0.691-1.57	-0.623	0.0245	-0.01	0.0235	-0.5	0.0255	-0.548	0.0051
Acetone-Methanol	28	328.15	0.713-0.997	-0.1	0.0103	-0.987	0.0104	-0.684	0.0041	-0.548	0.0047
overall average absolute deviation					0.0128		0.0126		0.0169		0.0054
2-Propanol_Water	21	423.15	4.706-9.035	-0.754	0.0227	-0.05	0.0227	-0.682	0.0216	-0.563	0.0310
Ethanol-Water	17	423.15	5.511-9.730	-0.59	0.0207	-0.953	0.0207	-0.466	0.0080	-0.497	0.0152
Methanol-Water	21	413.15	3.571-10.67	-0.959	0.0072	-0.114	0.0072	-0.333	0.0095	-0.555	0.0116
Methanol-Acetone	12	422.6	11.06-13.48	-0.623	0.0051	-0.153	0.0051	-0.921	0.0056	-0.688	0.0060
overall average absolute deviation					0.0147		0.0147		0.0121		0.0172
Acetone-Hexane	21	318.15	0.444-0.844	-0.256	0.0414	-0.42	0.0396	-0.698	0.0306	-0.655	0.0356
Acetone-Heptane	21	338.15	0.574-1.353	-0.362	0.0548	-0.41	0.0537	-0.688	0.0260	-0.59	0.0322
Ethanol-Hexane	21	333.15	0.462-1.07	-0.01	0.0829	-0.24	0.0697	-0.665	0.0034	-0.54	0.0026
Ethanol-Heptane	21	348.15	0.475-1.175	-1	0.0892	-0.632	0.0897	-0.651	0.0222	-0.52	0.0063
overall average absolute deviation					0.0671		0.0632		0.0206		0.0192
Methanol-Ethane	5	298.15	4.741-38.85	-0.05	0.0697	-0.05	0.0574	-0.252	0.0646	-0.289	0.0639
Acetone-Ethane	8	298.15	2.14-50.90	-0.05	0.0966	-0.05	0.0965	-0.743	0.0691	-0.623	0.0206
Methanol-Butane	27	368.51	8.614-14.219	-0.05	0.0598	-0.05	0.0602	-0.73	0.0537	-0.54	0.0035
2-Propanol_Butane	23	364.51	8.364-12.674	-0.05	0.0283	-0.05	0.0284	-0.38	0.0087	-0.581	0.0047
overall average absolute deviation					0.0537		0.0530		0.0401		0.0109
Ethane-Propane	4	260.95	6.805-17.01	-0.125	0.0023	-0.849	0.0023	-0.967	0.0055	-1.25	0.0047
Ethane-Butane	11	363.40	15.23-52.56	-0.623	0.0789	-0.55	0.0786	-0.586	0.0170	-1.47	0.0243
Propane-Butane	8	363.38	13.63-33.68	-0.623	0.0042	-0.623	0.0043	-1.55	0.0094	-1.12	0.0065
Ethane-Hexane	7	298.15	5.012-35.03	-0.08	0.0157	-0.75	0.0158	-0.988	0.0092	-1.12	0.0084
overall average absolute deviation					0.0294		0.0294		0.0139		0.0119

Table 2: The absolute average deviation and "C" values when applying UNIQUAC and Wilson model in PRSV-EOS with WS, HVOS mixing rules for all groups

Table 3: Second modification applied to HVOS with the share of UNIQUAC and Wilson models for all groups							
System	No. Pts.	T (K)	P range (atm)	HVOS with quadratic mixing rules			
				UNIQUAC		Wilson	
				h_{ij}	$|\Delta y|$	h_{ij}	$|\Delta y|$
Methanol_2-Propanol	21	328.15	0.299-0.678	-1.48	0.03133	0.615	0.00366
Methanol-Water	21	338.15	0.246-1.02	-1.22	0.04055	-1.788	0.00939
Ethanol-Water	21	363.16	0.691-1.57	-1.15	0.05675	-1.2	0.02529
Acetone-Methanol	28	328.15	0.713-0.997	0.658	0.00601	-0.652	0.00964
overall average absolute deviation					0.03153		0.01181
2-Propanol_Water	21	423.15	4.706-9.035	0.421	0.31225	-1.757	0.30406
Ethanol-Water	17	423.15	5.511-9.730	-0.954	0.05178	-1.17	0.03533
Methanol-Water	21	413.15	3.571-10.67	-0.7	0.04493	-0.581	0.01317
Methanol-Acetone	12	422.6	11.06-13.48	-0.826	0.01212	0.041	0.00619
overall average absolute deviation					0.03697		0.02239
Acetone-Hexane	21	318.15	0.444-0.844	0.978	0.01586	0.875	0.01712
Acetone-Heptane	21	338.15	0.574-1.353	-1.23	0.03252	0.552	0.03509
Ethanol-Hexane	21	333.15	0.462-1.07	0.772	0.00894	-0.721	0.04585
Ethanol-Heptane	21	348.15	0.475-1.175	0.136	0.02941	0.786	0.05855
overall average absolute deviation					0.02168		0.03915
Methanol-Ethane	5	298.15	4.741-38.85	-0.45	0.09094	-0.36	0.08780
Acetone-Ethane	8	298.15	2.14-50.90	0.28	0.09250	-0.8	0.01674
Methanol-Butane	27	368.51	8.614-14.219	-1.35	0.03231	-0.23	0.05493
2-Propanol_Butane	23	364.51	8.364-12.674	0.055	0.06387	0.028	0.02078
overall average absolute deviation					0.05613		0.04022
Ethane-Propane	4	260.95	6.805-17.01	-0.466	0.00335	-0.624	0.00662
Ethane-Butane	11	363.40	15.23-52.56	0.017	0.01699	0.12	0.02110
Propane-Butane	8	363.38	13.63-33.68	-0.455	0.00601	0.489	0.00815
Ethane-Hexane	7	298.15	5.012-35.03	-1.826	0.01645	1.527	0.01762
overall average absolute deviation					0.01212		0.01490

System	No. Pts.	T (K)	P range (atm)	HVOS with quadratic mixing rules and C value					
				UNIQUAC			Wilson		
				h_{ij}	C	$|\Delta y|$	h_{ij}	C	$|\Delta y|$
Methanol_2-Propanol	21	328.15	0.299-0.678	-1	0.852	0.02249	-0.541	-1.26	0.00110
Methanol-Water	21	338.15	0.246-1.02	-0.378	-0.006	0.01240	-0.584	0.633	0.01008
Ethanol-Water	21	363.16	0.691-1.57	-0.5	0.882	0.01189	-0.548	-0.581	0.00486
Acetone-Methanol	28	328.15	0.713-0.997	-0.684	0.124	0.00404	-0.548	-1.352	0.00453
overall average absolute deviation						0.01204			0.00510
2-Propanol_Water	21	423.15	4.706-9.035	-0.682	-0.154	0.02119	-0.563	0.583	0.02780
Ethanol-Water	17	423.15	5.511-9.730	-0.466	0.126	0.00801	-0.497	-1.55	0.01127
Methanol-Water	21	413.15	3.571-10.67	-0.333	-0.076	0.00863	-0.555	-0.337	0.01128
Methanol-Acetone	12	422.6	11.06-13.48	-0.921	0.124	0.00548	-0.688	0.146	0.00562
overall average absolute deviation						0.01167			0.01521
Acetone-Hexane	21	318.15	0.444-0.844	-0.698	0.652	0.02105	-0.655	0.784	0.02394
Acetone-Heptane	21	338.15	0.574-1.353	-0.688	0.095	0.02596	-0.59	0.42	0.03142
Ethanol-Hexane	21	333.15	0.462-1.07	-0.665	0.028	0.00331	-0.54	0.614	0.00187
Ethanol-Heptane	21	348.15	0.475-1.175	-0.651	0.582	0.01829	-0.52	0.674	0.00629
overall average absolute deviation						0.01715			0.01588
Methanol-Ethane	5	298.15	4.741-38.85	-0.252	-0.957	0.02908	-0.289	-1.7	0.03954
Acetone-Ethane	8	298.15	2.14-50.90	-0.743	0.483	0.06004	-0.623	-0.623	0.01674
Methanol-Butane	27	368.51	8.614-14.219	-0.73	0.675	0.04586	-0.54	-0.54	0.00332
2-Propanol_Butane	23	364.51	8.364-12.674	-0.38	0.04	0.00875	-0.581	-0.581	0.00472
overall average absolute deviation						0.03278			0.00841
Ethane-Propane	4	260.95	6.805-17.01	-0.967	-0.138	0.00427	-1.25	-0.157	0.00372
Ethane-Butane	11	363.40	15.23-52.56	-0.586	0.001	0.01706	-1.47	0.076	0.02106
Propane-Butane	8	363.38	13.63-33.68	-1.55	-0.29	0.00365	-1.12	-0.016	0.00647
Ethane-Hexane	7	298.15	5.012-35.03	-0.988	-0.52	0.03600	-1.12	-0.64	0.04791
overall average absolute deviation						0.01620			0.02112

Table 4: Variable 'C' values with Quadratic mixing rule used in HVOS with the share of UNIQUAC and Wilson model for all groups

Abbreviations

EOS　　= Equation of State

PR　　 = Peng Robinson

PRSV　= Peng Robinson Stryjek Vera

VLE　　= Vapor Liquid Equilibrium

WS　　 = Wong Sandlar

HVOS = Huron Vidal Orbey Sandlar

Notations

a　　　=　Equation of state attraction term parameter

b　　　=　Equation of state covolume term parameter

G_E^∞　　=　Exess Gibbs free energy at infinite dilution (J mol $^{-1}$)

h_{ij}　　=　Covolume term adjustable parameter

K_{ij}　　=　Equation of state interaction parameter

T_r　　=　reduced temperature

ω　　=　acentric factor

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ربط التوازن الطوري للبخار مع السائل للانظمة غير المثالية بأستخدام قواعد خلط عند ضغط لا متناه

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الخلاصة:

اختيرت قيم توازن البخار مع السائل تحت درجة حرارة ثابتة لخمسة أنظمة و هي الأول (قطبي-قطبي) تحت ضغط منخفض, الثاني (قطبي-قطبي) تحت ضغط عالي, الثالث (قطبي-لا قطبي) تحت ضغط منخفض, الرابع (قطبي-لا قطبي) تحت ضغط عالي, الخامس (لا قطبي- لا قطبي) تحت ضغط عالي. كل نظام من هذه الأنظمة يحتوي على أربعة أمزجة ثنائية مع 334 نقطة توازن كلية.باستخدام معادلة الحالة PRSV مع قواعد الخلط WS, HVOS عند ضغط لا متناه و قواعد الخلط هذه مشتقة من معادلة Gibbs للطاقة الحرة عند التخفيف العالي الذي يتبنى نموذجي UNIQUAC و Wilson. قواعد الخلط هذه لها فوائد كثيرة في القدرة على التعامل مع جميع الأنظمة المختلفة و بدقة عالية. مع ملاحظة أن قاعدة الخلط WS تحوي على متغير توليفي واحد بينما قاعدة الخلط HVOS لا تحوي على أي متغير توليفي.العديد من التعديلات أجريت على قواعد الخلط وكانت أفضل النتائج لهذه التعديلات في حساب توازن البخار مع السائل و لجميع الأنظمة استحصلت عند تطوير قاعدة الخلط HVOS مع متغير توليفي واحد مع إيجاد قيمة جديدة لثابت ضمن هذه القاعدة.