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ONE-FLUID MIXING RULES FOR CUBIC EQUATIONS OF STATE: I. SOLUBILITY OF PURE SOLIDS IN SUPERCRITICAL FLUIDS

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Abstract—Three cubic equations of state are carefully examined to evaluate their capability for correlating the supercritical solubility data of solid solutes in compressed gases. The overall average absolute deviatons between experimental and predicted values for 35 binary systems are 17.33% (Redlich-Kwong), 22.92% (Soave), and 22.93% (Peng-Robinson) using one binary parameter and 12.55% (Redlich-Kwong), 15.57% (Soave), and 13.71% (Peng-Robinson) using two binary parameters.

INTRODUCTION

The potential application of supercritical fluid extration in chemical separation processes has been of considerable research interest for the past decade. The fundamentals of supercritical fluid extraction technology and a number of potential applications for this technology are described in several recent review papers [1, 2, 3].

For rational process design of supercritical fluid extraction it would be highly desirable to have the appropriate estimation method of solid-solute solubility in a supercritical solvent. In this study, the applicable cubic equations of state using one-fluid mixing rules are evaluated regarding their ability to quantitatively describe experimental solubility data.

EQUATIONS OF STATE EXAMINED

It has long been realized from the extensive research on equations of state that the van der Waals equation of state is not accurate enough for the prediction of properties of compressed gases and liquids [4]. This deficiency of the van der Waals equation of state has initiated a great deal of research on the development of other equations of state. From the large number of equations of state that have been appeared in the literature, only a few of them have been found to be promising for the estimation of supercritical solubility. One of the most successful of these was that proposed by Redlich and Kwong [5]. Originally the parameters a and b appearing in the Redlich-Kwong equation were taken to be independent of temperature, but subsequent work has shown that at least one of these parameters should be allowed to be temperature-dependent if sufficient accuracy is to be attained for high-pressure phase equilibrium calculations.

The Redlich-Kwong equation of state in which the parameter a is given as a function of temperature by Soave's correlation [6] is often called as the Soave-Redlich-Kwong equation. However, the Soave equation predicts poor liquid densities in the single phase regions and a variety of alternative equations have been proposed to overcome this difficulty. The Peng and Robinsoin equation [7] is typical of these and widely used for thermodynamic property calculations. Three equations of state adopted in this study are summarized as follows;

Redlich-Kwong (RK):

$$P=\frac{RT}{v-b}-\frac{a(T)}{v(v+b)} \tag{1}$$

or

$$Z^3-Z^2+(A-B-B^2)Z-AB=0 \tag{2}$$

where

$$a(T)=0.42747\frac{R^2T_c^2}{P_c}\left(\frac{T_c}{T}\right)^{1/2}$$

$$b=0.08664\,RT_c/P_c$$

$$A=\frac{aP}{(RT)^2}$$

$$B=\frac{bP}{RT}$$

Soave (SRK):

$$P=\frac{RT}{v-b}-\frac{a(T)}{v(v+b)} \tag{3}$$

or

$$Z^3-Z^2+(A-B-B^2)Z-AB=0 \tag{4}$$

where

$$a(T)=0.42747\frac{R^2T_c^2}{P_c}\alpha(T)$$

$$b=0.08664\,RT_c/P_c$$

$$\alpha(T)=[1+m(1-T_r^{0.5})]^2$$

$$m=0.480+1.574\,\omega-0.176\,\omega^2$$

$$A=\frac{aP}{(RT)^2}$$

$$B=\frac{bP}{RT}$$

Peng and Robinson (PR):

$$P=\frac{RT}{v-b}-\frac{a(T)}{v(v+b)+b(v-b)} \tag{5}$$

or

$$Z^3-(1-B)Z^2+(A-2B-3B^2)Z-(AB-B^2-B^3)=0 \tag{6}$$

where

$$a(T)=0.45724\frac{R^2T_c^2}{P_c}\alpha(T)$$

$$b=0.07780\frac{RT_c}{P_c}$$

$$\alpha(T)=[1+\kappa(1-T_r^{0.5})]^2$$

$$\kappa=0.37464+1.54226\,\omega-0.26992\,\omega^2$$

$$A=\frac{aP}{(RT)^2}$$

$$B=\frac{bP}{RT}$$

The classical van der Waals one-fluid mixing rules have been adopted to extend these equations to mixtures as follows:

$$\theta_m=\sum_i\sum_j y_i y_j \theta_{ij} \tag{7}$$

When θ may be either, a or b, and the cross parameter θ_{ij} is given by

$$a_{ij}=(a_{ii}a_{jj})^{0.5}(1-k_{ij}) \tag{8}$$

and

$$b_{ij}=\begin{cases}(b_{ii}+b_{jj})/2 & \text{(one binary parameter)}\\ \dfrac{(b_{ii}+b_{jj})}{2}(1-l_{ij}) & \text{(two binary parameters)}\end{cases} \tag{9}$$

In the present study, the three equations of state were carefully examined with two different types of mixing rules in b_{ij}.

CALCULATION OF SUPERCRITICAL SOLUBILITY

The solubility of a solid solute 2 in a supercritical solvent 1 is given by

$$y_2=\frac{P_2^o\phi_2^o\exp[v_2^s(p-p_2^o)]}{\phi_2 P} \tag{10}$$

where P is the total pressure, P_2^o is the sublimation pressure of the pure solid, v_2^s is the molar volume of the solid, ϕ_2^o is the fugacity coefficient of the saturated pure vapor of the solid solute which is very close to unity in view of the small vapor pressures and ϕ_2 is the fugacity coefficient of the solid in the fluid phase. The most important variable ϕ_2 is given by

$$RT\ln\phi_2=\int_v^\infty\left[\left(\frac{\partial P}{\partial n_2}\right)_{T,v,n_1}-\frac{RT}{V}\right]dV-RT\ln Z \tag{11}$$

where $Z=Pv/RT$.

The basic physical properties of the 5 supercritical

Table 1. Physical properties of the supercritical solvents.

Compd	MW	T_c, °K	P_c, atm	v_c, cm^3/mol	Z_c	ω
Carbon dioxide	44.01	304.19	72.85	94.04	0.274	0.225
Ethane	30.07	305.50	48.50	141.72	0.274	0.098
Ethylene	28.05	282.40	49.70	129.00	0.227	0.085
Fluoroform	70.01	299.25	48.85	133.33	0.265	0.275
Chlorotrifluoro-methane	104.46	302.00	38.70	180.00	0.282	0.180

Table 2. Physical properties of the solutes.

Compd	Formula	MW	v_s	T_c	P_c	v_c	ω	Antoine constants		
			cm^3/mol	°K	atm	cm^3/mol		A	B	C
Benzoic acid	$C_7H_6O_2$	122.13	96.5	752	45.0	341.0	0.620	9.408	4618.1	0
1,4-Naphthoquinone	$C_{10}H_6O_2$	158.16	111.20	792*	40.7*	257.0*	0.575	9.735	4739.4	0
Naphthalene	$C_{10}H_8$	128.19	125.03	748.4	40.0	410.0	0.302	7.2144	2926.6	-35.8
1,10-Decanediol	$C_{10}H_{22}O_2$	174.29	158.4	720.4*	23.39*		1.325	12.234	5043.1	-52.914
Biphenyl	$C_{12}H_{10}$	154.21	131.0	789	38	502.	0.364	9.4068	4262	0
2,3-Dimethylnaphthalene	$C_{12}H_{12}$	156.23	154.7	785	31.748	522	0.42403	9.0646	4302.5	0
2,6-Dimethylnaphthalene	$C_{12}H_{12}$	156.23	154.7	777	31.796	516	0.42013	9.4286	4419.5	0
Hexamethylbenzene	$C_{12}H_{18}$	162.28	152.7	752*	23.5*	659*	0.498	8.1336	3855	0
Acridine	$C_{13}H_9N$	179.22	178.3	883	31.5	399	0.498	8.721	4740.1	0
Fluorene	$C_{13}H_{10}$	166.23	139.3	821	29.5	590.0	0.407	9.2046	4561.8	0
Phenanthrene	$C_{14}H_{10}$	178.24	167.6	890	32.5	644	0.429	9.6310	4873.4	0
Anthracene	$C_{14}H_{10}$	178.24	142.6	883	32.64	554	0.455	7.1464	4397.6	0
Triphenylmethane	$C_{19}H_{16}$	244.34	240.9	863*	22.1*	785*	0.576	9.7858	5228	0

*Estimated by Lydersen's method [Ref. 8]

solvents are presented in Table 1. However, the experimental values of critical constants for some solid solutes are not reported in the literature. In these solutes, the Lydersen's method [8] was used to estimate critical constants. The physical properties of the 13 solid solutes are presented in Table 2 along with the Antoine constants. Antoine vapor pressure equation used has the form of

$$\ln P_2^o[\text{bar}] = A - B/(T[K]) + C) \tag{12}$$

A nonlinear regression method coupled with polynomial roots searching method has been applied to determine the values of k_{ij} (one binary parameter) and k_{ij} and l_{ij} (two binary parameters) of three equations of state for each solute-solvent system from experimental solubility data of 35 binary systems. The objective function

$$F = \sum_{i=1}^{N} [(y_{2i}^{cal} - y_{2i}^{exp})/y_{2i}^{exp}]^2 \tag{13}$$

has been minimized in searching for the binary parameters. Here, N stands for the number of experimental data points. The quality of the calculated supercritical solubility is expressed in terms of an average absolute deviation (AAD) defined as

$$\text{AAD}(\%) = (100/N) \sum_{i=1}^{N} |(y_{2i}^{cal} - y_{2i}^{exp})/y_{2i}^{exp}| \tag{14}$$

The objective function used in eq. (13) can avoid the bias that would be produced when the calculated values are either very large or very small when compared to data.

RESULTS AND DISCUSSION

The resulting binary parameters and AAD (%) for 35 binary systems are presented in Table 3 (one binary parameter) and Table 4 (two binary parameters) along with experimental temperature and pressure ranges. The original Redlich-Kwong equation of state gives the best overall description of supercritical solubility with the overall average absolute deviations of 17.33% (one binary parameter) and 12.55% (two binary parameters), while the resulting overall deviations are 22.92% (one binary parameter) and 15.57% (two binary parameters) for the Soave equation and 22.93% (one binary parameter) and 13.71% (two binary parameters) for the Peng-Robinson equation. In Figure 1, the experimental solubility data of naphthalene in supercritical fluoroform is plotted against pressure along with the calculated values with one binary parameter (dashed line) and two binary parameters (solid line). This mixture is chosen for illustration owing to the pure component properties being known, and the pressure range of the data being quite large. Similar patterns are also shown in Figure 2 and 3 for comparison.

The following conclusions can be drawn with great generality from the results reported herein:

(1) Among the equations of state treated in this study, the original Redlich-Kwong equation with the simplest form gives the best results in correlating the solubilities of solids in supercritical fluids, i.e., the solid-gas equilibria, while the Peng-Robinson equation has been commonly used in predicting the vapor-

Table 3. Binary parameters and AAD (%) errors resulting from the three equations of state (one parameter).

System	T, °K	P, atm	No Data	RK1		SRK1		PR1		Data Source
				k_{12}	AAD(%)	k_{12}	AAD(%)	k_{12}	AAD(%)	
Carbon Dioxide										
Benzoic acid	308-343	99-359	39	-0.17554	14.12	0.00994	25.75	0.00883	25.84	9
1,4-Naphthoquinone	318-343	101-364	18	-0.12174	10.49	0.04104	29.83	0.03989	30.42	9
Naphthalene	308-328	77-319	40	0.03504	9.50	0.09735	16.32	0.09435	17.20	10
1,10-Decanediol	318-328	131-303	15	-0.18178	8.99	0.16709	6.88	0.14329	7.33	11
Biphenyl	308-330	104-484	42	-0.03568	26.62	0.07957	9.07	0.7898	13.13	12
2,3-Dimethylnaphthalene	308-328	97-276	15	-0.00625	8.57	0.10351	9.36	0.09901	11.25	13
2,6-Dimethylnaphthalene	308-328	94-276	15	-0.00531	6.25	0.10203	9.21	0.09784	10.14	13
Hexamethylbenzene	308-308	148-345	3	-0.03188	30.73	0.10670	29.29	0.09555	22.16	14
Acridine	308-343	101-359	28	-0.00628	13.41	0.11893	18.63	0.11390	16.64	9
Phenanthrene	318-338	118-276	15	0.02127	6.99	0.11980	13.90	0.11516	14.91	13
Ethane										
Benzoic acid	308-343	54-358	30	-0.20895	17.68	-0.01207	23.96	-0.00964	23.54	9
1,4-Naphthoquinone	308-343	64-364	28	-0.05970	16.97	0.10047	22.35	0.10091	24.24	9
Naphthalene	308-328	50-359	41	-0.04841	18.32	0.04034	18.36	0.04240	20.14	9
Biphenyl	308-318	69-277	10	-0.10813	12.00	0.00630	17.43	0.00719	19.40	9
Acridine	308-343	60-359	32	-0.05362	36.95	0.08295	40.96	0.08251	40.74	9
Phenanthrene	318-328	70-350	12	-0.04793	5.86	0.06599	9.78	0.06643	13.38	9
Ethylene										
Benzoic acid	318-338	118-276	15	-0.26974	9.02	-0.07407	16.71	-0.06793	17.10	13
Naphthalene	298-323	55-164	19	0.07210	12.41	-0.00137	19.64	0.00096	19.21	16
2,3-Dimethylnaphthalene	308-328	76-276	18	-0.11285	19.45	0.01363	12.43	0.01680	11.06	13
2,6-Dimethylnaphthalene	308-328	77-276	18	-0.10625	14.52	0.01318	9.40	0.01684	7.62	13
Fluorene	298-343	69-477	24	-0.11363	21.32	-0.00105	19.62	0.00509	16.72	16
Phenanthrene	318-338	118-276	15	-0.07636	12.36	0.03446	12.88	0.03758	12.75	16
Triphenylmethane	298-318	83-327	27	-0.14192	15.01	0.04102	14.43	0.03899	12.86	16
Anthracene	323-358	103-474	30	-0.07147	18.65	0.04286	24.05	0.05092	21.16	16
Fluoroform										
Benzoic acid	318-328	64-336	10	-0.17926	27.40	-0.00804	44.93	-0.00414	46.52	9
1,4-naphthoquinone	318-328	66-356	12	-0.18921	38.60	-0.02413	62.28	-0.02067	65.65	9
Naphthalene	308-328	59-346	18	0.02969	15.38	0.08624	28.05	0.08944	30.39	9
Acridine	318-328	64-328	12	-0.11355	46.45	0.01121	75.92	0.01312	80.09	9
Phenanthrene	318-328	79-359	8	0.01878	4.17	0.11075	24.26	0.11185	28.58	9
Anthracene	328-343	90-295	6	0.04946	33.19	0.13860	19.42	0.14009	18.80	9
Chlorotrifluoromethane										
Benzoic acid	318-328	59-353	13	-0.16339	11.22	0.01494	20.04	0.01844	22.73	9
1,4-Naphthoquinone	318-328	56-364	12	-0.05160	19.71	0.10008	29.21	0.10247	32.35	9
Naphthalene	308-328	49-355	21	0.02250	12.38	0.08515	18.64	0.09021	21.79	9
Acridine	318-328	66-336	10	-0.01573	23.10	0.10969	33.19	0.11088	37.81	9
Phenanthrene	318-328	74-297	8	0.01201	9.00	0.11205	15.74	0.11362	20.19	9

Table 4. Binary parameters and AAD(%) errors resulting from the three equations of sate (two parameters).

System	RK2			SRK2			PR2		
	k_{12}	l_{12}	AAD (%)	k_{12}	l_{12}	AAD (%)	k_{12}	l_{12}	AAD (%)
Carbon Dioxide									
Benzoic acid	-0.18073	-0.01106	13.97	-0.06910	-0.20344	20.29	-0.08199	0.22735	17.75
1,4-Naphthoquinone	-0.14493	-0.04803	11.11	-0.06174	-0.25418	15.74	-0.07325	-0.27337	12.22
Naphthalene	0.05791	0.04599	7.61	0.04731	-0.10812	7.80	0.03669	-0.12177	6.56
1,10-Decanediol	-0.12870	0.09032	2.89	0.15299	-0.03480	6.75	0.11422	-0.06818	5.58
Biphenyl	0.06099	0.14211	15.73	0.06612	-0.02164	8.47	0.05283	-0.04207	9.71
2,3-Dimethylnaphthalene	0.01398	0.03861	8.92	0.06242	-0.08859	6.69	0.04883	-0.10552	8.34
2,6-Dimethylnaphthalene	0.01513	0.03920	5.48	0.06425	-0.08178	7.12	0.05069	-0.09950	4.88
Hexamethylbenzene	0.08937	0.19211	5.32	0.20568	0.18124	5.68	0.17689	0.14437	5.03
Acridine	0.03483	0.08548	7.74	0.09587	-0.05578	17.70	0.07994	-0.07978	13.59
Phenanthrene	0.02517	0.00830	6.90	0.05104	-0.16698	8.43	0.03643	-0.18570	7.48
Ethane									
Benzoic acid	-0.24459	-0.07779	18.47	-0.06413	-0.13651	23.03	-0.07756	-0.17471	21.69
1,4-Naphthoquinone	-0.12292	-0.14021	12.19	0.02721	-0.19246	17.34	0.01047	-0.23323	14.55
Naphthalene	-0.02575	0.03806	18.77	-0.00350	-0.07880	12.40	-0.00903	-0.09203	12.54
Biphenyl	-0.10683	0.00234	12.01	-0.04472	-0.10118	9.21	-0.05525	-0.12214	9.19
Acridine	-0.14313	-0.19869	36.12	-0.01588	-0.25354	40.57	-0.03542	-0.29612	36.09
Phenanthrene	-0.04218	0.01223	5.43	0.04211	-0.05715	6.88	0.02687	-0.09308	6.02
Ethylene									
Benzoic acid	-0.31745	-0.10914	6.59	-0.16682	-0.25599	10.08	-0.17406	-0.28792	8.53
Naphthalene	-0.12547	-0.12099	12.36	-0.09901	-0.23828	13.02	-0.10017	-0.24068	11.22
2,3-Dimethylnaphthalene	-0.04930	0.12019	13.19	0.00112	-0.02655	13.00	0.00010	-0.03512	11.23
2,6-Dimethylnaphthalene	-0.06492	0.08151	10.38	-0.00516	-0.04065	10.41	-0.00706	-0.05236	8.47
Fluorene	-0.08025	0.06189	18.47	-0.01291	-0.02448	19.95	-0.02213	-0.05598	15.67
Phenanthrene	-0.07468	0.00371	12.15	-0.01396	-0.12065	12.87	-0.02205	-0.14624	12.02
Triphenylmethane	-0.10585	0.06357	13.74	0.02903	-0.02514	14.10	0.01039	-0.05907	11.58
Anthracene	-0.07712	0.00069	18.63	0.00364	-0.09029	24.23	-0.00132	-0.11997	20.56
Fluoroform									
Benzoic acid	-0.31601	-0.30961	8.86	-0.20564	-0.54031	18.99	-0.22069	-0.58142	16.51
1,4-naphthoquinone	-0.33574	-0.34085	24.54	-0.24083	-0.57961	36.64	-0.25989	-0.62938	32.80
Naphthalene	-0.03748	-0.14065	6.31	-0.03173	-0.26554	13.65	-0.04895	-0.30799	10.59
Acridine	-0.27454	-0.36488	38.78	-0.20934	-0.58094	51.54	-0.28219	-0.63398	46.24
Phenanthrene	0.01299	-0.01264	3.85	0.04526	-0.16187	11.76	0.02597	-0.20911	9.37
Anthracene	0.15053	0.22935	18.13	0.15440	0.04152	19.46	0.14325	0.00820	18.81
Chlorotrifluoromethane									
Benzoic acid	-0.20359	-0.09099	7.00	-0.05485	-0.19019	8.79	-0.07112	-0.24066	8.03
1,4-Naphthoquinone	-0.12915	-0.17374	12.50	0.00018	-0.26587	16.12	-0.01964	-0.32090	14.75
Naphthalene	-0.03643	-0.11959	4.76	0.00070	-0.18394	8.26	-0.01631	-0.23098	6.26
Acridine	-0.08757	-0.16090	14.67	0.01784	-0.23862	20.52	-0.00615	-0.29968	18.84
Phenanthrene	-0.01955	-0.07153	5.65	0.05740	-0.14020	7.50	0.03691	-0.19386	7.06

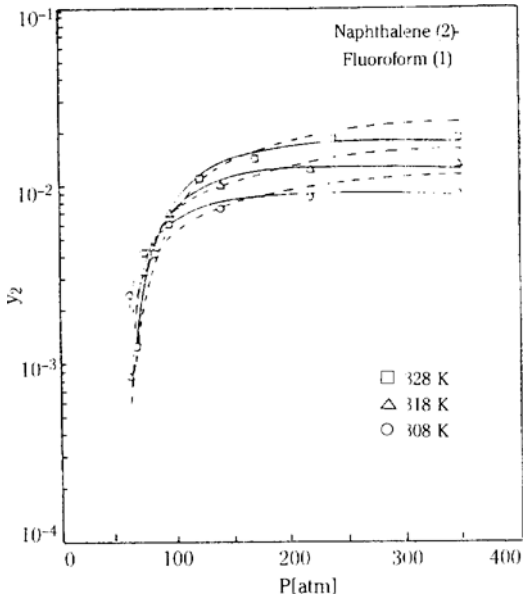

Fig. 1. Solubility of naphthalene in fluoroform:
symbols, experimental; ----, RK (one binary parameter); ——, RK (two binary parameters).

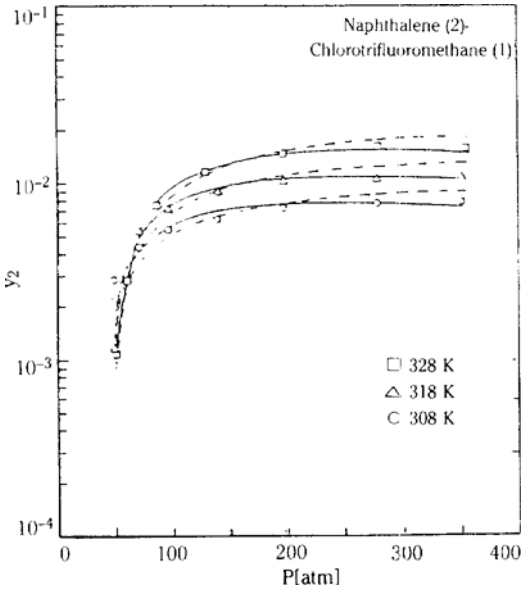

Fig. 2. Solubility of naphthalene in chlorotrifluoromethane:
symbols, experimental; ----, RK (one binary parameter); ——, RK (two binary parameters).

liquid equilibria for many types of multicomponent systemes.

(2) As expected, the introduction of a second binary parameter, l_{ij}, greatly improves the accuracy of predicted solubility values for most of the systems.

(3) In view of conclusions (1) and (2), the Redlich-Kwong equation with two binary parameters is the most attractive for the best fit of experimental solubility data of heavy solid solutes in supercritical fluids.

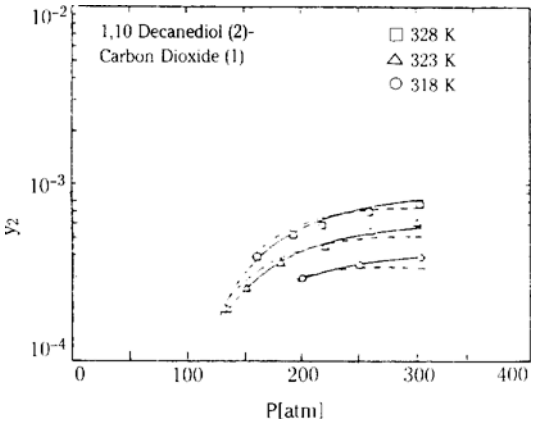

Fig. 3. Solubility of 1,10-decanediol in carbon dioxide:
symbols, experimental; ----, RK (one binary parameter); ——, RK (two binary parameters).

ACKNOWLEDGEMENT

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NOMENCLATURE

A, B	:	variable defined in eqs. (2), (4) and (6)
a, b	:	parameter defined in eqs. (1), (3) and (5)
F	:	objective function defined in eq. (13)
k_{ij}	:	binary interaction parameter associated with a
l_{ij}	:	binary interaction parameter associated with b
m	:	parameter in the soave equation of state
N	:	number of data points
P	:	total pressure
P_2^o	:	sublimation pressure of the solute
R	:	gas constant
T	:	temperature
v	:	molar volume
V	:	total volume
y	:	mole fraction
Z	:	compressibility factor
α	:	variable in eqs. (3) and (5)
κ	:	parameter in the Peng-Robinson equation of state

θ_{ij} : parameter that is to be mixed
ϕ : fugacity coefficient

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