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SIMULTANEOUS CORRELATION OF EXCESS GIBBS ENERGY AND EXCESS ENTHALPY DATA USING THE EXTENDED UNIQUAC MODEL

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ABSTRACT

Isothermal excess Gibbs energy and excess enthalpy data for 29 binary non-ideal systems have been well reproduced by means of the extended UNIQUAC model with temperature-dependent parameters. The temperature dependence of the energy parameters is given by a quadratic function of temperature. Calculated results show that the extended UNIQUAC model works better than the UNIQUAC model.

INTRODUCTION

The temperature dependence of the original UNIQUAC model [1] was investigated in the separate or simultaneous correlation of vapour–liquid equilibrium and excess enthalpy data for the hexane–methanol system usin temperature-dependent parameters [2]. Anderson and Prausnitz [3] introduced new values of surface parameters for alcohol and water used in the residual part of the original UNIQUAC model in order to improve flexibility in the representation of the composition dependence of the excess Gibbs energy. Using this modification of the UNIQUAC model with temperature-dependent parameters Demirel and Gecegörmez [4] correlated simultaneously excess Gibbs energy and excess enthalpy-data for 24 binary systems. Another modification of the original UNIQUAC model, known as extended UNIQUAC, was presented by one of the present authors [5].

In this paper, we present calculated results obtained in the simultaneous correlation of excess Gibbs energy and excess enthalpy data for 29 binary systems, based on the extended UNIQUAC model with temperature-depen-

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dent parameters and show that the extended UNIQUAC model gives smaller deviations between calculated and experimental values for most systems than those obtained by Demirel and Gecegörmez [4].

SOLUTION MODEL

The extended UNIQUAC model represents the excess Gibbs energy as the sum of two terms; combinatorial and residual ones g^E_{comb} and g^E_{res}.

$$g^E = g^E_{\mathrm{comb}} + g^E_{\mathrm{res}} \tag{1}$$

The modified form of the combinatorial part [6] is given by

$$g^E_{\mathrm{comb}}/RT = x_1 \ln(\Phi'_1/x_1) + x_2 \ln(\Phi'_2/x_2) + (z/2)[q_1 x_1 \ln(\Theta_1/\Phi_1) + q_2 x_2 \ln(\Theta_2/\Phi_2)] \tag{2}$$

where z is the coordination number, here set as 10, Φ', Φ and Θ are expressed in terms of the structural parameters r and q, which depend on molecular size and surface.

$$\begin{aligned} \Phi'_1 &= x_1 r_1^{3/4}/(x_1 r_1^{3/4} + x_2 r_2^{3/4}) \\ \Phi'_2 &= x_2 r_2^{3/4}/(x_1 r_1^{3/4} + x_2 r_2^{3/4}) \end{aligned} \tag{3}$$

$$\begin{aligned} \Phi_1 &= x_1 r_1/(x_1 r_1 + x_2 r_2) \\ \Phi_2 &= x_2 r_2/(x_1 r_1 + x_2 r_2) \end{aligned} \tag{4}$$

$$\begin{aligned} \Theta_1 &= x_1 q_1/(x_1 q_1 + x_2 q_2) \\ \Theta_2 &= x_2 q_2/(x_1 q_1 + x_2 q_2) \end{aligned} \tag{5}$$

The residual term is expressed by

$$g^E_{\mathrm{res}}/RT = -q'_1 x_1 \ln(\Theta_1 + \Theta_2 \tau_{21}) - q'_2 x_2 \ln(\Theta_2 + \Theta_1 \tau_{12}) \tag{6}$$

The parameter q' was introduced to correct the surface of interaction and is smaller than the geometrical molecular surface q. The binary adjustable parameters τ_{21} and τ_{12} are given by

$$\tau_{21} = \exp(-a_{21}/T) \qquad \tau_{12} = \exp(-a_{12}/T) \tag{7}$$

The excess enthalpy h^E is given by applying the Gibbs–Helmholtz equation to eqn. (1).

$$\begin{aligned} h^E &= \left[\frac{\partial(g^E/T)}{\partial(1/T)}\right]_{P,x} \\ &= R\left[\frac{x_1 q'_1 \Theta_2 \tau_{21}(a_{21} - T \cdot \mathrm{d}a_{21}/\mathrm{d}T)}{\Theta_1 + \Theta_2 \tau_{21}} + \frac{x_2 q'_2 \Theta_1 \tau_{12}(a_{12} - T \cdot \mathrm{d}a_{12}/\mathrm{d}T)}{\Theta_2 + \Theta_1 \tau_{12}}\right] \end{aligned} \tag{8}$$

TABLE 1

Molecular structure constants and Antoine equation constants for pure components

Compound	Molecular structure constants			Antoine constants [a]		
	r	q	q'	A	B	C
Acetonitrile	1.8701	1.7240	$q^{0.1}$	7.33986	1482.29	250.523
Benzene	3.1878	2.4000	$q^{0.1}$	6.87987	1196.76	219.161
1-Butanol	3.4543	3.0520	0.88	7.83800	1558.19	196.881
Cyclohexane	4.0464	3.2400	$q^{0.1}$	6.85146	1206.47	223.136
1,4-Dioxane	3.1854	2.6400	$q^{0.1}$	7.43155	1554.68	240.337
Ethanol	2.1055	1.9720	0.92	8.11220	1592.86	226.184
Ethylacetate	3.4786	3.1160	$q^{0.1}$	7.10179	1244.95	217.881
Ethylformate	2.8042	2.5760	$q^{0.1}$	7.00902	1123.94	218.247
n-Heptane	5.1742	4.3960	$q^{0.1}$	6.89386	1264.37	216.640
Methanol	1.4311	1.4320	0.95	8.08097	1582.27	239.726
Methylacetate	2.8042	2.5760	$q^{0.1}$	7.06524	1157.63	219.726
1-Propanol	2.7799	2.5120	0.89	7.74416	1437.69	198.463
2-Propanol	2.7791	2.5080	0.89	8.87829	2010.33	252.636
Toluene	3.9228	2.9680	$q^{0.1}$	6.95087	1342.31	219.187

[a] $\log P\ (\text{mm Hg}) = A - B/(C + t\,^\circ\text{C})$.

We assume that the temperature dependences of the energy parameters a_{12} and a_{21} are expressed by a quadratic function of temperature [7]

$$a_{21} = A_{21} + B_{21}T + C_{21}T^2 \quad a_{12} = A_{12} + B_{12}T + C_{12}T^2 \tag{9}$$

For the estimation of parameters the following objective function was minimized using the simplex method of Nelder and Mead [8].

$$F = \frac{1}{\left(\sum Nn + \sum WMm\right)} \left\{ \sum^{N} \sum^{n} \left[100\left(g^E_{\text{exp}} - g^E_{\text{calc}}\right)/g^E_{\text{exp}}\right]^2 + \sum^{M} W \sum^{m} \left[100\left(h^E_{\text{exp}} - h^E_{\text{calc}}\right)/h^E_{\text{exp}}\right]^2 \right\} \tag{10}$$

where N and M represent the numbers of specified data sets for g^E and h^E, n and m are the experimental points of each data set, and W is a weighting factor set as 1 except for some alcohol–hydrocarbon systems where W is taken as 5. The temperature-dependent parameters were obtained for 29 systems, for which experimental vapour–liquid equilibrium and h^E data were selected from the Dortmund Data Bank where the h^E data sets used are available for more than two temperatures. Vapour-phase non-ideality was taken into account in the calculation of g^E from P–x–y data. Second virial coefficients were estimated using Tsonopoulos's correlation [9]. Table 1 shows values of the structural parameters r, q and q', and Antoine constants used in this work. All these values except for q' and other related properties were taken from the Dortmund Data Bank. Values of q' were assigned as proposed in a previous paper [5].

TABLE 2

Simultaneous correlation of g^E and h^E data using the extended UNIQUAC equation with temperature-dependent parameters

No.	System (1–2)	$T(g^E)$ (°C)	No. of data points	Ref.	$T(h^E)$ (°C)	No. of data points	Ref.	Percentage deviations				Parameters		
								g^E		h^E		A_{12} A_{21}	B_{12} B_{21}	C_{12} C_{21}
								Extended UNIQUAC	UNIQUAC	Extended UNIQUAC	UNIQUAC			
1	Methylacetate–	30	10	10	25	13	10	4.06	20.05	2.14	5.22	476.00	−2.5693	0.0046
	benzene	40	7		35	6		7.83	11.66	1.11	6.58	550.40	−2.8994	0.0031
		50	11					5.78	14.50					
2	Methylacetate–	35	8	10	25	11	10	1.96	1.98	0.78	4.75	1892.78	−7.9123	0.0097
	cyclohexane	40	7		35	11		2.55	3.21	0.94	3.82	1670.18	−4.1599	0.0022
					45	9				1.97	4.36			
3	Methanol–	11	25	12	11	1.45	1.23	3.88	4.53	366.70	−1.7227	0.0000		
	ethylacetate				35	12				2.96	5.22	1182.37	−0.6814	0.0000
4	Ethanol–	55	10	11	25	12	11	1.58	2.61	3.11	4.06	501.77	−1.2057	0.0000
	ethylacetate				35	16				3.94	4.04	1534.40	−2.6188	0.0000
5	2-Propanol–	55	10	11	25	13	11	3.75	22.76	2.23	3.25	900.57	−2.6358	0.0025
	ethylacetate				35	18				2.27	4.59	1609.05	−2.9432	−0.0028
6	1-Propanol–	55	11	11	25	11	11	4.54	6.63	2.60	3.36	640.79	−1.2203	0.0002
	ethylacetate				35	20				1.14	2.13	1749.91	−3.9396	−0.0001
					45	9				1.28	2.42			
7	Ethylformate–	45	10	12	25	9	12	1.66	1.68	2.38	10.42	544.15	2.5103	−0.0045
	methanol				35	11				3.83	4.71	−364.68	3.3034	−0.0068
					45	10				1.99	7.82			
8	Ethylformate–	45	11	12	25	9	12	1.53	2.58	1.78	10.54	1203.79	−1.5092	−0.0005
	ethanol				35	13				3.77	4.59	−509.79	6.1256	−0.0115
					45	11				1.70	7.85			
9	Ethylformate–	50	8	12	25	9	12	4.31	5.24	2.66	10.09	1057.46	−0.8209	−0.0041
	1-propanol				35	13				2.81	3.11	883.49	−1.9333	0.0017
					45	11				1.33	8.42			

10	Ethylformate– 2-propanol	45	10	12	25	13	12	4.30	4.48	1.99	8.09	1643.86	−4.5664	0.0003
					35	12				1.84	1.43	732.30	0.1757	−0.0009
					45	11				1.82	8.46			
11	Methylacetate– methanol	35	12	13	25	16	13	4.02	4.94	1.79	3.58	1264.52	−1.4120	−0.0009
		45	13		35	16		3.18	4.07	1.12	1.25	77.32	0.1694	−0.0008
					45	10				1.48	4.02			
12	Methylacetate– ethanol	35	10	13	25	12	13	2.80	9.13	0.74	6.54	1665.93	−3.6562	0.0000
		45	13		35	12		4.98	12.9	1.37	2.55	505.46	−0.5440	0.0000
					45	8				2.10	6.26			
13	Acetonitrile– benzene	45	8	14	45	13	14	0.78	8.87	1.48	2.11	642.78	−2.1421	0.0000
												−187.02	2.4439	0.0000
14	Benzene– n-heptane	45	11	14	45	14	14	1.94	8.96	0.48	0.92	140.55	0.2728	0.0000
												550.58	−1.5135	0.0000
15	Acetonitrile– n-heptane	45	5	14	45	10	14	7.07	7.31	2.19	2.28	2339.02	−5.2098	0.0000
												2772.58	−4.1622	0.0000
16	Ethanol– toluene	35	10	15	25	22	16	0.90		4.90		−361.59	3.4347	−0.0059
		45	13	17	35	21		2.36	2.41	3.45	10.43	3679.65	−6.3200	−0.0011
		55	10	15	45	24		1.99		2.38	6.2			
					60	17	18			1.78	8.2			
17	2-Propanol– n-heptane	45	13	17	30	23	19	4.12	3.16	8.86	11.95	−389.71	5.9264	−0.0110
		60	13		45	21		4.37	2.95	5.74	9.14	5504.39	−13.9138	0.0082
					60	22				5.31	13.86			
18	Ethanol– cyclohexane	50	5	20	6.7	25	21	5.47		3.58		708.11	−1.7271	0.0018
					10	29				3.98		−2190.70	30.7960	−0.0562
					15	29				3.96				
					20	29				3.51				
					25	28				3.45				
					35	24				3.00				
					45	28				3.51				
19	1-Propanol– cyclohexane	25	10	22	15	14	23	4.02		4.62		−1310.24	11.3511	−0.0197
		55	17	24	25	14		2.40		4.38		4394.90	−12.1486	0.0130
		65	14		35	14		2.63		6.03				

TABLE 2 (continued)

No.	System (1–2)	$T(g^E)$ (°C)	No. of data points	Ref.	$T(h^E)$ (°C)	No. of data points	Ref.	Percentage deviations				Parameters		
								g^E		h^E		A_{12} A_{21}	B_{12} B_{21}	C_{12} C_{21}
								Extended UNIQUAC	UNIQUAC	Extended UNIQUAC	UNIQUAC			
20	2-Propanol–	40	4	25	20	18	26	3.62		6.21		−347.64	4.9795	−0.0095
	cyclohexane	55	4		25	18		0.79		6.71		4013.42	−6.7299	−0.0011
		69	4		30	18		1.52		6.37				
					50	18				3.85				
21	Methanol–	45	8	27	25	19	16	1.78		3.26		−137.18	1.6962	−0.0034
	benzene	55	8		35	22		2.51		3.35		3655.54	−6.2237	0.0008
					45	23				2.34				
22	Ethanol–	45	12	28	25	20	16	1.58		4.64		−216.07	2.5229	0.0041
	benzene				35	24				3.73		3670.22	−7.2273	0.0000
					45	25								
23	1-Propanol–	45	11	29	15	23	30	2.23		3.33		−635.26	6.1030	−0.0103
	benzene				20	23				3.28		3954.95	−12.0891	0.0090
					25	23				3.36				
					30	23				2.84				
					35	23				2.98				
					40	23				2.68				
					45	23				2.08				
					50	23				1.96				

24	2-Propanol–	45	11	31	25	24	16	2.72	3.65		538.55	−0.2666	−0.0015
	benzene				35	25			2.52		3474.07	−7.4151	0.0003
					45	23			1.81				
25	1-Butanol–	45	9	29	15	22	30	2.88	4.67		−247.89	3.4054	−0.0052
	benzene				20	22			3.53		3822.00	−10.7400	0.0043
					25	22			3.06				
					30	22			2.61				
					35	22			2.18				
					40	22			2.17				
					45	22			2.06				
					50	22			2.10				
26	Methanol–	52.89	16	32	25	14	33	3.16	1.79		344.21	−0.4233	0.0001
	acetonitrile	60.31	15		35	14		2.70	1.87		1286.18	−2.4383	−0.0001
27	Ethanol–	40	14	34	25	14	33	1.62	0.61		757.28	−0.4548	0.0000
	acetonitrile				35	14			1.03		1732.52	−4.4667	0.0000
28	1-propanol–	55	8	35	25	22	36	1.88	2.42		1688.45	−2.9122	0.0016
	acetonitrile	60.1	17	37	25	24	37	2.36	2.59		1734.37	−4.3198	−0.0012
		80.1	16	35	35	22		2.70	1.46				
					45	22				3.39			
29	Ethanol–	50	18	38	25	15	39	0.26 [a]	1.78		−1407.68	11.5000	−0.0197
	1,4-dioxane				50	26	40		0.87		886.80	−0.0306	−0.0046

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[a] Deviation in pressure.

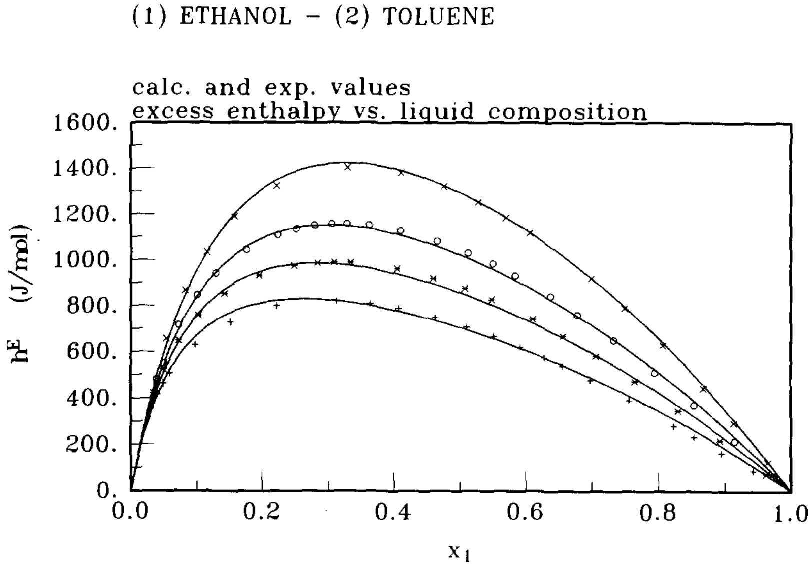

Fig. 1. Representation of excess enthalpy data for ethanol (1)–toluene (2): experimental, +, 25°; *, 35°; o, 45° (16); ×, 60°C (18); calculated, ——.

The absolute relative deviations of calculated results from experimental values at each isothermal condition and the estimated parameters are given in Table 2, together with those of Demirel and Gecegörmez [4].

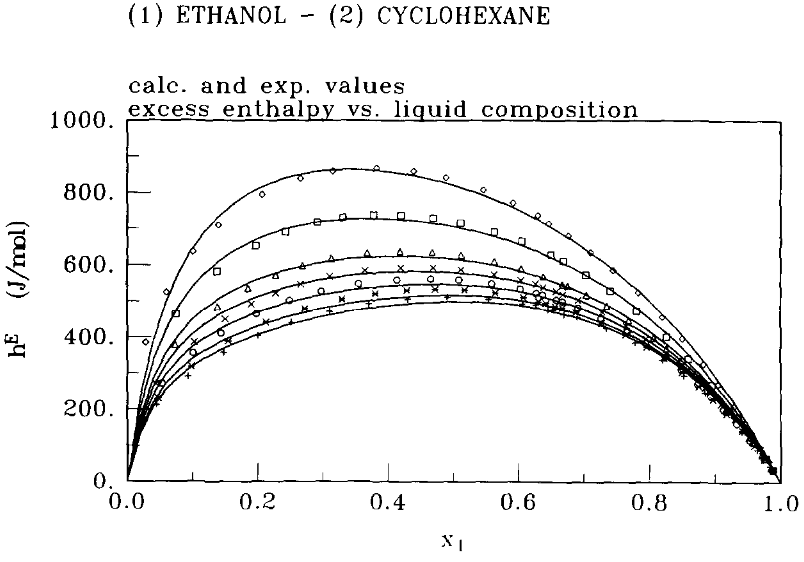

Fig. 2. Representation of excess enthalpy data for ethanol (1)–cyclohexane (2): experimental, +, 6.7°; * 10°; o, 15°; ×, 20°; △, 25°; □, 35°; ◇, 45°C (20); calculated, ——.

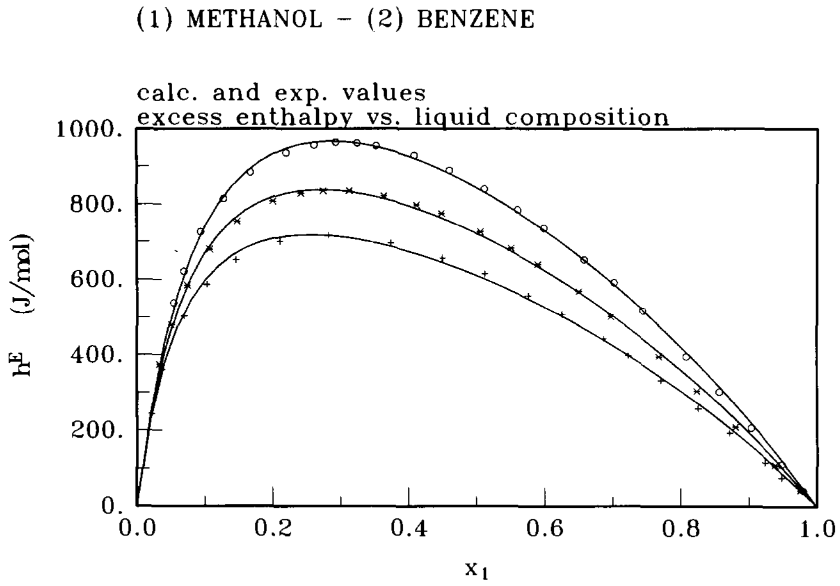

Fig. 3. Representation of excess enthalpy data for methanol (1)–benzene (2): experimental, +, 25°; *, 35°; o, 45° (66); calculated, ———.

Except for the deviations of g^E for the methanol–ethyl acetate and 2-propanol–n-heptane systems, the extended UNIQUAC model gives smaller deviations than the UNIQUAC model. A significant improvement was

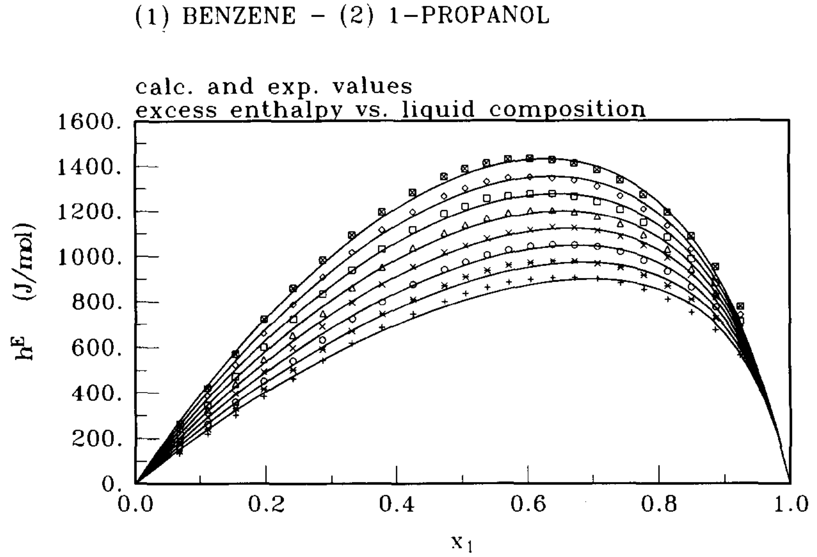

Fig. 4. Representation of excess enthalpy data for benzene (1)–1-propanol (2): experimental, +, 15°; *, 20°; o, 25°; ×, 30°; △, 35°; □, 40°; ◇, 45°; ⊠, 50 °C (29); calculated, ———.

obtained in h^E data correlations. Figures 1–4 illustrate typical examples to show the good performance of the extended UNIQUAC model in data reduction.

For the 1-propanol–benzene and 1-butanol–benzene systems the h^E data of Chao and Dai [30] were measured at eight different temperatures between 15 °C and 50 °C and those of Mrazek and Van Ness [16] were obtained at 25 °C, 35 °C and 45 °C. The smaller deviations were obtained from the h^E data of Chao and Dai and not the data of Mrazek and Van Ness. Table 2 shows the results of the former for these two systems.

We conclude that the extended UNIQUAC model has a better ability than the UNIQUAC in simultaneously correlating the g^E and h^E data for the non-ideal systems studied in this work.

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LIST OF SYMBOLS

a_{ij}	binary interaction parameter related to τ_{ij}
A_{ij}, B_{ij}, C_{ij}	coefficients related to a_{ij}
F	objective function
g^E	excess molar Gibbs energy
h^E	excess molar enthalpy
r_i	molecular size parameter for pure component i
q_i	molecular area parameter for pure component i
q_i'	molecular interaction factor for pure component i
P	pressure
R	gas constant
T	absolute temperature
x_i	liquid-phase mole fraction of component i
y_i	vapour-phase mole fraction of component i
W	weighting factor
z	lattice coordination number taken as 10

Greek letters

Δ	difference between calculated and experimental values
Θ_i	area fraction of component i

Φ_i	segment fraction of component i
Φ'_i	modified segment fraction of component i
τ_{ij}	binary parameter as defined by $\exp(-a_{ij}/T)$

Subscripts

calc	calculated
comb	combinatorial
exp	experimental
i, j	components
res	residual

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